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Impedance spectroscopy and NMR studies of fast ion conducting chalcogenide glasses

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Impedance spectroscopy and NMR studies of fast ion conducting chalcogenide glasses

Patel, Hitendra Kumar, Ph.D.
Iowa State University, 1993
Impedance spectroscopy and NMR studies of fast ion conducting chalcogenide glasses

by

Hitendra Kumar Patel

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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CHAPTER 1. INTRODUCTION

The discovery of fast ion conduction in oxide glasses by Otto in 1960 [1] and the energy crisis of the early 1970s stimulated much interest in using glasses as solid state electrolytes in advanced battery systems. A considerable research effort led to the synthesis of glasses with room temperature d.c. conductivities as high as $10^{-2}$ ($\Omega$ cm)$^{-1}$. Much of the success in choosing the chemical compositions, leading to glasses with high d.c. conductivities, may be attributed to the predictive nature of the Anderson-Stuart (structural) model [2] and the Ravine-Souquet weak electrolyte (thermodynamic) model [3]. The microscopic mechanisms responsible for ion conduction in glass, however, are still not well understood due to the difficulty in independently determining the carrier concentration and mobility. Further comparisons of experimental data to predictions of the d.c. conductivity models are necessary before either model is widely accepted, modified or even replaced by newer models.

Less attention has been given to understanding the a.c. conductivity, $\sigma(\omega)$, although most d.c. conductivity data are obtained from a complex plane analysis of frequency dependent impedance measurements. The frequency dependence of the real part of the complex conductivity for ion conducting glasses is similar to that observed for most disordered materials and exhibits the "universal dielectric response", first reported by Jonscher [4,5]. This spectrum, shown in Figure 1.1, exhibits three features: (1) a frequency independent conductivity ("d.c. plateau") observed at low frequencies and/or highest temperatures, (2) an increase in conductivity at higher frequencies and/or lower temperatures, and (3) a temperature independent resonant absorption peak at very high frequencies (Far-IR). The three regions are briefly described below and the conductivity mechanisms thought to be operating in each region are described in more detail in the next chapter.
Figure 1.1: Universal frequency response of conductivity in all disordered materials. Features defined in the three regions are (1) frequency independent conductivity ("d.c. plateau") observed at low frequencies and/or highest temperatures, (2) an increase in conductivity at higher frequencies and/or lower temperatures, and (3) a temperature independent resonant absorption peak at very high (Far-IR).

The value of the conductivity in the frequency independent region is defined as the ionic conductivity. Values for the d.c. conductivity from wide temperature conductivity isotherms are plotted against temperature to determine the temperature dependence of the conductivity.

The conductivity dispersion in region 2 is observed for all glasses. In 1957, Stevels described this feature qualitatively using a random potential energy model [6]. In the early 1970's, Macedo et al. [7] were first to suggest that the conductivity dispersion was a consequence of the conductivity relaxation in the time domain. They introduced the concept of the electrical modulus and modeled the conductivity dispersion/relaxation using a single relaxation
time exponential correlation function (Debye). This model showed that the relaxation function was non-exponential and they improved upon their model by using a distribution of conductivity relaxation times [7]. Later, Moynihan et al. [8] showed that the stretched exponential function, better known as the Koulausch-Williams-Watts (KWW) function [9-11], was a better and simpler choice for a correlation function to describe the conductivity relaxation. An alternative approach to describing the conductivity dispersion was introduced by Jonscher [4,5] and further developed by Almond and West [12-16] using a power law formalism and this method is discussed in some detail in the next chapter.

Although the conductivity dispersion phenomenon is well described, the microscopic a.c. conductivity mechanism in the glass remains unclear. It is well accepted, however, that the non-exponential correlation function results from relaxation processes occurring either in parallel, having a distribution of relaxation times, or in series, where relaxation processes interact with each other and constrain subsequent events.

Many microscopic models to describe the parallel and/or series relaxations have been offered. Glarum [17] proposed a defect diffusion model in analogy to ion motion in extremely defective crystals. Ngai [18,19] attributed the stretched exponential relaxation to ion-ion interaction and described the phenomena using a coupling model. In similar spirit, a jump relaxation model by Funke [20] emphasized the effect of mutual coulomb interactions slowing the relaxation. Dyre [21,22] offered a simple hopping model using the random free energy barrier model solved in the continuous time random walk (CTRW) approximation. Other models of ion relaxation, including the diffusion controlled relaxation model of Elliott and Owens [23,24] are based on entirely different physics. The common problem with these elaborate models is that they are difficult to test by experiment.

A complete model for ionic conductivity in glasses, however, does not exist. The main reasons for this are that published conductivity data are usually presented in formalisms inconvenient for analysis by many of the models [23]. In other cases, the conductivity data are measured over limited temperature and frequency ranges, and comparison to the temperature
and frequency limit predictions of many models are therefore not possible [22]. Furthermore, the purpose of most ion conductivity studies of glasses has been to produce highly conductive glasses. Such glasses typically have high concentrations of alkali ions, a condition where little compositional dependence to the conductivity is observed. Few conductivity studies have been performed over wide composition ranges. A study of this nature should reveal more information about the conductivity mechanism and test the predictions of conductivity models in the ultra-low and high alkali ion composition limits. In summary, the understanding of a.c conduction is still in its infancy, and a study of ionic conductivity over the widest composition, frequency and temperature range is necessary to critically test the veracity of specific conductivity models and to elucidate the a.c. conductivity mechanism.

Electrical impedance studies reveal macroscopic properties of glass and these results are often used to infer the microscopic nature of the conductivity mechanism. Nuclear magnetic resonance (NMR) techniques, with their inherent sensitivity to the microscopic structure and dynamics of glasses, are being increasingly used as an alternative to impedance measurements to study the dynamics of ionic conduction [25-30]. The relationships between the two techniques, however, have not been completely resolved and need further investigation.

NMR measurements of ion nuclear spin lattice relaxation (NSLR) times $T_1$ are typically performed at fixed frequency and variable temperature while conductivity measurements are performed at fixed temperature and variable frequency. The reported activation energy for d.c conductivity is always greater than the reported activation energy for the ion NSLR $T_1$ [25,30]. The reason why these values are different may be because the ion conductivity is measured at frequencies less than one MHz, while $T_1$ is measured at frequencies greater than one MHz [25,26]. Furthermore, the activation energy for d.c conductivity is always determined from data in the frequency-independent region while a frequency independent region is seldom observed for $T_1$, and so activation energies for this characteristic are often reported from the frequency-dependent region. It is only for the most highly conducting glasses at very high temperature that a frequency independent $T_1$ is observed. To correctly compare the
activation energies for ion dynamics, both experiments should be performed over the same temperature and frequency range.

As with ionic conductivity, non-exponential relaxation is also observed in the NSLR $T_1$ experiment. Even though the conductivity and NSLR experiments probe different correlation functions for different dynamic variables, some similarity between the two functions must, nevertheless exist, because, in both cases the same ions contribute to relaxation. Further experimental development aimed at acquiring data over the same temperature and frequency ranges coupled with comparisons of the activation energies and the correlation functions should make clear the relationship between the two experiments.

The lack of high frequency ($\nu > 1$ MHz) impedance workstations in many research groups around the world is responsible for the paucity of conductivity data suitable for comparison with NMR data. For many research groups, only the d.c. conductivity parameters are considered important, and low-frequency workstations are sufficient to obtain these data. The main reason for the lack of high frequency conductivity data, however, is that high frequency measurements over a wide range of temperatures are difficult to make, and commercial impedance workstations with this capacity are not available. Workstations have to be especially designed and constructed for such measurements and only a few prototypes capable of performing this task have been reported [31-33].

1.1. Objective of the Dissertation

The goal of this research is to bridge gaps in and elucidate the fundamental understanding of ion conductivity mechanisms in glasses. To achieve this goal, ion conductivity and NSLR $T_1$ will be measured over the widest possible glass composition, frequency and temperature ranges. The core of this project is to relate the compositional, frequency and temperature dependence to the conductivity and to determine relationships between NSLR and conductivity. In particular, the following questions will be addressed:
• Do the d.c. conductivity data for glasses support current models of the d.c. conductivity?

• How is high frequency conductivity related to temperature, frequency and glass composition?

• What is the fundamental frequency beyond which the KWW fit to the conductivity is no longer applicable, and what microscopic mechanism(s) contribute to this failure?

• What is the fundamental frequency limit beyond which the KWW fit to the $T_1$ is no longer applicable and what microscopic mechanism(s) contribute to this failure?

• Do conductivity measurements made at fixed frequencies and variable temperature yield activation energies which agree with those for $T_1$ made at the same fixed NMR frequency?

• What are the composition effects on these measurements, and are there any structural parameters which may be related to the conductivity and NMR relaxation?

• Do conductivity measurements for the alkali thioborate glass system exhibit similar trends to those reported for in the oxides?

1.2. Outline of the Dissertation

The general concepts of ionic conductivity and $T_1$ have been introduced above. The background necessary to the performance of this study and the accompanying literature review are presented in Chapter 2. d.c. and a.c. conductivity mechanisms and models are reviewed in the first two sections. A description of the NSLR $T_1$ and the relationships between NMR and conductivity are established in the third section. The chapter concludes with a brief discussion of what constitutes an ideal glass system for this study.

The experimental procedures are explained in Chapter 3. To make this study feasible, two computer-automated impedance workstations were designed, constructed and programmed to make electrical measurements over wide frequency and temperature range. Since
a major component of the project was the development of these workstations, a detailed description is given. The NSLR experiment is next explained. This is followed by a discussion of the novel techniques developed to synthesize the highly-reactive glasses used for this study. The chapter concludes with a description of sample handling and preparation for electrical and NMR characterization.

The experimental results of this dissertation are reported in Chapter 4. Wide-range temperature and frequency conductivity data over the widest possible composition range for glasses in three glass forming families are reported. The glass compositions studied in the above experiments were selected to yield the most crucial and relevant information on the properties of interest in the study.

Chapter 5 contains a thorough discussion of the results and observations on the compositional dependence of the conductivity. The hypotheses and questions posed in this study are tested and correlations and departures of the results from those predicted by existing theories are indicated.

The results of the NSLR and conductivity for various FIC lithium glasses are analyzed and discussed in Chapter 6. The relationships between the NSLR and conductivity are tested and correlations and departures of results from the theory are indicated.

Chapter 7 was added to this work based on ideas developed in the course of writing this dissertation and is considered one of the more significant contributions to this field of research. The author has come to the realization that certain assumptions made in order to test some of the hypotheses were flawed from the outset. In particular, the widely-accepted interpretation of results by fitting the Kohlrausch-Williams-Watts (KWW) stretched exponential function to the electrical modulus formalism is questioned and examined in some detail. Although some of the work reported in this dissertation is analyzed using the KWW function and the electrical modulus, which the author now suspects may be a flawed approach, pursuing this research strategy was necessary to help clarify misconceptions about the conductivity dispersion and to account for the failure of the KWW function at high frequencies. For this
reason, the analysis and discussion using the original interpretation is included in Chapters 5 and 6. Analysis and discussion using an alternative interpretation are given in Chapter 7.

Conclusions of this broad and, in light of Chapter 7, somewhat controversial study are presented in the Chapter 8. The results and relationships established are summarized. This chapter concludes by proposing future work that would be a natural extension of this study.
CHAPTER 2. BACKGROUND

The d.c. and a.c. conductivity of fast-ion-conducting glasses have been extensively studied and discussed. In this chapter, some of the prevailing theoretical and phenomenological models used to describe ion conductivity in each of the three frequency regions shown in Figure 1.1 is reviewed. This is followed by a discussion of NSLR in glasses and the relationship between ionic conductivity and NSLR. The chapter concludes with a discussion of glass systems that would be ideal for this work and experiments to test the many hypothesizes.

2.1. d.c. Conductivity (σ_{d.c.})

The conductivity in the frequency-independent plateau (Region 1) is due to long range ion motion and is defined as the d.c. conductivity, \( \sigma_{d.c.} \). The d.c. conductivity for materials with only one carrier is given by

\[
\sigma_{d.c.} = (Ze)n\mu
\]

(2.1)

where \( Ze \) is the charge of the carrier, \( n \) is the concentration of mobile carriers and \( \mu \) is the carrier mobility [34]. The concentration of mobile ions is given by

\[
n = N_e \exp \left( \frac{\Delta G_e}{kT} \right)
\]

\[
= N_e \exp \left( \frac{\Delta S_e}{k} \exp \left( \frac{\Delta H_e}{kT} \right) \right)
\]

\[
= N_e \exp \left( \frac{-\Delta H_e}{kT} \right)
\]

(2.2)
where $\Delta G^c$ is the free-energy necessary to impart a carrier population, $\Delta S^c$ is the associated entropy, $\Delta H^c$ is the enthalpy, $k$ is the Boltzman constant, $T$ is the temperature and $N_e$ is the effective infinite-temperature ion concentration which includes the entropy term [34]. The mobility is related to the diffusivity through the Nerst-Einstein relation [34],

$$\mu = \frac{Ze}{kT} D = \frac{Ze}{kT} \gamma \lambda^2 v_H$$

$$= \frac{Ze}{kT} \gamma \lambda^2 v_0 \exp \left( -\frac{\Delta G_m}{kT} \right)$$

$$= \frac{Ze}{kT} \gamma \lambda^2 v_0 \exp \left( \frac{\Delta S_m}{kT} \right) \exp \left( -\frac{\Delta H_m}{kT} \right)$$

$$= \frac{Ze}{kT} \gamma \lambda^2 v_e \exp \left( -\frac{\Delta H_m}{kT} \right)$$  \hspace{1cm} (2.3)$$

where $\Delta G_m$ is the free energy for ion migration, $\Delta S_m$ is the associated entropy, $\Delta H_m$ is the enthalpy, $\gamma$ is a geometric factor for ion hopping, $\lambda$ is the average jump distance between mobile ion sites, $v_H$ is the actual ion jump frequency, $v_0$ is the jump attempt frequency of the ion (approximated by the mobile ion IR resonance frequency) and $v_e$ is the effective jump attempt frequency including the entropy term. From the first law of thermodynamics under conditions of constant specimen volume and temperature, the enthalpy and energy state functions are equal. For this reason, many authors replace $\Delta H$ in the above carrier concentration and rate equations with $\Delta E$, and this is also done in this study [8,12-16,25]. From the above derivation, the actual ion jump frequency $v_H$ is given by

$$v_H = v_e \exp \left( \frac{\Delta E_m}{kT} \right).$$  \hspace{1cm} (2.4)$$

Finally, substituting Eqs. (2.2) and (2.3) into Eq. (2.1) yields:

$$\sigma_{d.c.} = \frac{N_e (Ze)^2 \gamma \lambda^2 v_e}{kT} \exp \left( \frac{\Delta E_c + \Delta E_m}{kT} \right).$$  \hspace{1cm} (2.5)$$
This compares well with the experimental results obtained in this laboratory (an example shown in Figure 2.1) and by others [7-16,18-30], which is analytically described by:

\[
\sigma_{d.c.} = \sigma_e \exp \left( -\frac{\Delta E_{act}}{kT} \right)
\]  

(2.6)

where \( \Delta E_{act} \) is the experimentally determined activation energy from the slope of the \( \log(\sigma_{d.c.}T) \) vs. \( 1/T \) plot and \( \sigma_e \) is the infinite temperature limit of the dc conductivity.

Unfortunately, this treatment does not allow separate values for the individual contribution of the creation \( (\Delta E_c) \) or migration \( (\Delta E_m) \) energy terms to be determined from the meas-

![Figure 2.1: Arrhenius plots of the d.c. conductivities obtained from the impedance plots of \( x\text{AgI}+(1-x)\text{AgPO}_3 \) glasses](image-url)
ured total activation energy \( \Delta E_{act} \). In addition, the individual parameters in the pre-exponential part of Eq. 2.5 cannot be separated because they are lumped into the single experimentally determined quantity \( \sigma_c \). For this reason, controversy is possible regarding the basic conduction mechanism in glass.

2.1.1. Anderson-Stuart (AS) Model

The Anderson-Stuart [2] model is a structural model which describes the energy to impart a carrier population \( \Delta E_c \) as the coulombic energy \( \Delta E_b \) binding an ion to a particular site and the migration activation energy \( \Delta E_m \) as the strain energy \( \Delta E_s \) required to dilate the glass structure to allow an ion to hop from one site to another. An atomic-level representation of this model by Martin [36] is shown in Figure 2.2. The activation energy according to the AS model is

\[
\Delta E_{act} = \Delta E_s + \Delta E_b
\]

(2.7)

where the strain energy term is given as

\[
\Delta E_s = 4 \pi G r_D (r - r_D)^2
\]

(2.8)

and the binding energy term is given as

\[
\Delta E_b = \frac{ZZ_0 \epsilon^2}{\epsilon_0} \left[ \frac{1}{r + r_o} - \frac{2}{\lambda} \right]
\]

(2.9)

In these equations, \( G \) is the shear modulus of the glass; \( r_D \), \( r \) and \( r_o \) are the interstitial window, the mobile cation and the non-bridging anion radii, respectively; \( \lambda \) is the average jump distance; \( Z \) and \( Z_0 \) are the number of charges on the mobile cation and the anion; and \( e \) is the charge on the electron.

To make the AS model more realistic, minor changes to the strain term have been proposed by McElfresh and Howitt [37]. Elliott [38] has pointed out that the AS model neglects specific polarization and repulsion terms and includes these terms in the overall coulomb po-
Figure 2.2: Representation of the energetics of cation conduction process according to the Anderson-Stuart model as interpreted by Martin and Angell [36].

Potential. Other models describing the activation energy have been suggested, but nearly all follow the general principles of the AS model.

The physical and structural parameters necessary to verify the validity of the AS model and experimental methods for measuring these parameters are:

- $\Delta E_{act}$: determined from wide temperature range ionic conductivity measurements
- $\lambda$: approximated from NMR static linewidth measurements, or density measurements
- $G$: determined from acoustic measurements
- $r_D$: the interstitial window radius determined from inert gas diffusion studies.
To test the validity of the Nerst-Einstein derivation for the pre-exponent term, the following additional parameters are needed:

- $\sigma_0$: determined from wide temperature range ionic conductivity measurements
- $\nu_0$: determined from the Far-IR ion vibrational frequency
- $\gamma$: usually taken as approximately equal to 1/6.

There are few research laboratories which have the facilities and/or equipment to determine all of these parameters independently. Collaboration with various research laboratories is necessary in order to measure these parameters, and consequently, few definitive studies confirming the validity of these models have been reported (see for example review articles by Ingram [39], Martin [40], Ravine [41] and Pradel and Ribes [42]).

2.1.2. Weak Electrolyte Theory

The addition of NaCl to water results in complete dissolution and complete ionization of Na$^+$ and Cl$^-$ ions up to the solubility limit where phase separation finally occurs. The complete dissolution and ionization of NaCl in water is a result of the high dielectric constant, $\varepsilon_r = 80$, of water. For solvents with lower dielectric constants, salts can still be dissolved, but may not completely ionize upon dissolution, due to the strong coulomb forces existing between cation and anion pairs making up the salt. Glasses are solvents with typical values for the dielectric constant between 4 and 30. The possibility exists that although alkali oxides/sulfides dissolve completely into these glasses, the cation and anion pairs may not completely ionize.

In glasses, the addition of $M_2O$ or $M_2S$ typically results in the added anions becoming part of the glass structure by covalently bonding to the glass-forming cation, while the added alkali cations reside in a local region thereby supporting charge neutrality (low energy stable ionic complexes). Most of these alkali cations are un-ionized and immobile but a small fraction may dissociate from these sites (complexes) to form ionized or dissociated "mobile" cations. It is these ions that are proposed to contribute to ion conduction. The above discus-
The formation of mobile cations, $M^+$, from associated oxide complexes in a glass is taken as analogous to the disassociation of modifier salts added to the glass [3]:

$$M_2O \leftrightarrow M^+ + OM^- \quad (2.10)$$

and

$$K = \frac{[M^+][OM^-]}{[M_2O]} \quad (2.11)$$

where $[M^+]$ is the concentration of the dissociated ions, and $K$ is the concentration independent dissociation constant. From Eq. (2.10), it can be seen that $[M^+]$ and $[OM^-]$ are equal, and the concentration of the free dissociated ions is therefore given by:

$$[M^+] = K^{\frac{1}{2}}[M_2O]^{\frac{1}{2}} = K^{\frac{1}{2}}a_{M_2O}. \quad (2.12)$$

where $a$, the thermodynamic activity, is equated to the $M_2O$ concentration. This equality is expected to be valid for dilute solutions (Henry's Law [35]). The ionic conductivity is proportional to the concentration of mobile ions, so that

$$\sigma \propto [M^+] = K^{\frac{1}{2}}a^{\frac{1}{2}} \quad (2.13)$$

Although this process does not provide any description of the physical state of the species, $M^+$ may be regarded as dissociated mobile alkali ions, $M_2O$ as trapped entities and $OM^-$ as vacancies in the glass network. Ravine and Souquet performed both ionic conductivity and concentration cell emf measurements for various sodium and potassium silicate glasses. They plotted the conductivity ratio vs. activity ratio for various pairs of glasses and showed that the slope was 1/2 for this logarithmic plot. This result is shown in Figure 2.3 lends credence to a weak electrolyte nature for these glasses and strongly suggests that the dominating effect on
the ionic conductivity is the concentration of charged carriers. The rate determining step for conduction is the creation of charge carriers and is a strong function of the coulomb force between the added anion and cation. It should also be pointed out that the ion mobility is almost constant or varies only slightly for different compositions in the same glass family.

Comparing the weak electrolyte model to the Anderson-Stuart model shows that the coulomb term in AS may be equated to the energy needed to form the dissociated pair and the strain/migration term plays a small role in the overall conductivity mechanism.

Figure 2.3: Conductivity ratio vs. activity ratio for various pairs of alkali oxide glasses. The line through the points has slope 1/2 [3]
2.2. a.c. Conductivity

In the early 1950's, the potential application of glasses in the electronic industry for large transmitting valves, x-ray tubes and similar products fostered much research aimed at understanding the temperature and frequency dependence of the dielectric properties of glasses [21]. The first systematic impedance spectroscopy study of a.c. conductivity and conductivity dispersion was carried out on oxide glasses about 35 years ago by Stevels [6]. Since then different approaches to studying the same phenomena emerged each using different terminologies and methods of presenting data. The three prevalent methodologies for analyzing glass electrical properties have focused on the relative dielectric constant, the electrical modulus and the conductivity. Though a correct analysis using each of these techniques should yield the same conclusions, it is often the case that features apparent in one formalism are suppressed in another. The conversion between forms is mathematically simple, and, in order to obtain the most complete picture analysis should be performed using more than one of these formalisms.

A review of impedance spectroscopy, complex numbers, phasors, and relationships between the various formalisms has previously been given by the author [102]. In the present work, the a.c. electrical phenomena are analyzed using the conductivity and the electrical modulus formalisms, which are discussed in the next two sections. The first part is a description of the Almond-West model, which relates the d.c. conductivity to the a.c. conductivity, and the second part is a discussion of conductivity relaxation in terms of the electrical modulus and the conductivity.

2.2.1. Almond-West (AW) Formalism

Jonscher [4-5] proposed the following empirical relationship for the dispersion in the imaginary part of the a.c. complex dielectric constant (dielectric loss):

\[
\varepsilon''(\omega) \propto \left(\frac{\omega}{\omega_p}\right)^m + \left(\frac{\omega}{\omega_p}\right)^{m-1} \tag{2.14}
\]
where \( \omega_p = 2 \pi \nu_p \) is the dielectric loss peak frequency and \( m \) and \( n \) are parameters which describe the slope on the high and low sides, respectively, of the dielectric loss peak. Similarly, Jonscher showed that a power law relationship \((\omega', \ 0 < s \leq 1)\) could be used to described the dispersion in the real part of the conductivity \( \sigma'(\omega) \). Almond and West [12-16] accounted for the conductivity in both the frequency-independent and dependent region by combining the d.c. conductivity with Jonscher's 'universal' power law behavior:

\[
\sigma'(\omega) = \sigma_{d.c.} + A\omega^s
\]  

(2.15)

where \( s \) describes the frequency dependence of the conductivity and \( A \) is a temperature dependent parameter. They related the real part of the complex conductivity to the dielectric loss through

\[
\sigma'(\omega) = \omega \varepsilon''(\omega).
\]  

(2.16)

Substituting Eq. (2.14) into Eq. (2.16), Almond and West obtained:

\[
\sigma'(\omega) \propto \omega \left[ \left( \frac{\omega}{\omega_p} \right)^m + \left( \frac{\omega}{\omega_p} \right)^{-1} \right].
\]  

(2.17)

By assuming a single proportionality constant \( K \) in both the conductivity and the dielectric loss (Eq. (21.4) and (2.17)), equating the dielectric loss frequency \( \omega_p \) to the ion hopping frequency, \( \omega_p = 2 \pi \nu_p \), and letting \( m = -1 \) and \( n = s \) they obtained:

\[
\sigma'(\omega) = K\omega \left[ \left( \frac{\omega}{\omega_H} \right)^{-1} + \left( \frac{\omega}{\omega_H} \right)^{s-1} \right]
\]  

\[
= K\omega_H + K\omega_H^{i-s} \omega^s
\]  

(2.18)

By comparing the Eq. (2.18) with Eq. (2.15), they concluded that the d.c. conductivity may be described by the ion hopping frequency:
\[ \sigma_{d.c.} = K \omega_H \]  \hspace{1cm} (2.19)

Comparison of the above equation to Eqs. (2.4) and (2.5), shows that \( K \) is composed of the carrier concentration, the ion jump distance, the geometric term, the ion charge and the Boltzmann constant. Furthermore, the a.c. and d.c. conductivities in Eq. (2.15) may be related to each other through Eqs. (2.18) and (2.19) by

\[ \sigma_{d.c.} = A \omega_H^b \]  \hspace{1cm} (2.20)

After simplifying Eq. (2.18) and writing it in terms of \( \sigma_{d.c.} \) the a.c. conductivity may be written as:

\[ \sigma' (\omega) = \sigma_{d.c.} + \sigma_{d.c.} \left( \frac{\omega}{\omega_H} \right)^b \]

\[ = \sigma_{d.c.} \left( 1 + \left( \frac{\omega}{\omega_H} \right)^b \right) \]  \hspace{1cm} (2.21a)

or, in terms of \( \nu \):

\[ \sigma'(\nu) = \sigma_{d.c.} \left( 1 + \left( \frac{\nu}{\nu_H} \right)^b \right) \]  \hspace{1cm} (2.21b)

The hopping frequency \( \nu_H \) is obtained from a.c. conductivity when

\[ \sigma'(\nu_H) = 2\sigma_{d.c.} \]  \hspace{1cm} (2.22)

Finally, substituting Eqs. (2.4) and (2.5) into Eq. (2.21b), the bulk a.c. conductivity is written in terms of physical parameters and as function of frequency and temperature:

\[ \sigma'(\nu, T) = \frac{N(Ze)^2 \gamma \lambda^2 v_e}{kT} \exp \left( \frac{\Delta E_c + \Delta E_m}{kT} \right) \left( 1 + \left( \frac{\nu}{v_e \exp \left( \frac{\Delta E_m}{kT} \right)} \right)^b \right) \] (2.23)
Table 2.1: Summary of activation energies for terms in the Almond-West model

<table>
<thead>
<tr>
<th>Term</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_s$</td>
<td>$\Delta E_c$</td>
</tr>
<tr>
<td>$\nu_H$</td>
<td>$\Delta E_m$</td>
</tr>
<tr>
<td>$\sigma_{d.c.}$</td>
<td>$\Delta E_c + \Delta E_m$</td>
</tr>
<tr>
<td>$A$</td>
<td>$\Delta E_c + (1-s)\Delta E_m$</td>
</tr>
</tbody>
</table>

From Eqs. (2.21) and (2.23) it is seen that the activation energies for $\nu_H$, $\sigma_{d.c.}$, and $A$ are all thermally activated with a different activation energy as shown in Figure (2.4). These results are summarized in Table 2.1.

The activation energies for $\sigma_{d.c.}$ and $\nu_H$ can be measured and calculated. If they are equal in magnitude then the result implies that $\Delta E_c \approx 0$. If this is the case, then the charge carrier concentration is temperature independent, hence the concentration of mobile ions is constant. Such a result would support the statement that glasses are strong electrolytes. However, if the activation energies are different, then the concentration of charge carriers is thermally activated and would lend support to the weak electrolyte theory [3].

Numerical fits to measured conductivity data using the AW model are shown in Figure (2.5). The AW model describes the data very well, but because the model is based on phenomenology, results obtained by this technique should be analyzed very carefully and conclusions drawn with caution. Getting the frequency at which the a.c. conductivity is twice the d.c. conductivity is equal to the ion hopping frequency (Eq. (2.22)) is questionable. It is plausible, however, to think that the ion hopping frequency characterizes the transition from long-range (d.c.) to short range motion. This formalism has been used by many groups [43-52] and, to date, no proof has been offered to refute the AW technique. However, criticisms have been reported and are discussed next.
Figure 2.4 Arrhenius plots of the conductivity and hopping rate, $\omega_H$, according to the Almond-West Model. (a) typical conductivity data, (b) expected slopes for $\sigma T$ and $A T$ when the carrier concentration is temperature independent ($\Delta E_c = 0$), (c) estimation of ion hopping rate by inspection of conductivity data, (d) slope of hopping rate is equal to the slope of the conductivity for $\Delta E_c = 0$, (e) expected slope for $A T$ and $\sigma T$ when $\Delta E_c$ is not equal to zero, (f) difference in slope between the hopping frequency and the conductivity when the ion concentration is thermally activated [16]
Jain and Mundy used the above technique to determine the carrier concentration in germanate and borate glasses [53]. They found that the slope, $s$, was temperature dependent and hence questioned the validity of the AW formalism which assumes a temperature independent slope. Dyre [21,22] and Lee et al. [54-55] also reported that the value of the a.c. conductivity slope approached one with decreasing measurement temperature and/or increasing frequency. Almond and West [16] also reported this feature, and Almond [49] remarked that this is not indicative of a flaw in the model, since the condition described by Eq. (2.18) occurs where $(\nu/\nu_h) = 1$ and this number raised to any power of $s$ is still one. This implies that the condition described in Eq. (2.18) is independent of $s$ or of any temperature dependence of $s$.

Figure 2.5: Fits of the Almond-West power law function to conductivity data covering a wide range of temperature for a lithium thiosilicate glass
Other criticisms have been discussed by Elliot [24] who summarized his opinion by calling the power law equation a purely phenomenological function with no physical foundations and therefore uninteresting. Dyre [22] warns that though the power law formalism appears to do an excellent job describing the a.c. conductivity curve, it may actually be an approximate power law. He reminds that any large change in a dependent quantity over a large change in the independent quantity will appear as an approximate straight line in a log-log plot. Therefore, a straight line fit does not mean that the it is an exact power law.

Nevertheless, conductivity data, are analyzed using the AW power law equation because they give quantitative and testable results which may be related to glass composition, temperature and slope variation with frequency. Hairetdinov [56] has suggested that, for electric field frequencies greater than the ion hopping frequency, the free charge carriers may behave as dipoles with non-Debye absorption. The ion hop frequency and the slope of the conductivity dispersion are therefore directly related to conductivity relaxation. These relations are discussed in the next section.

2.2.2. Conductivity Relaxation

The change over from the frequency independent ($\sigma_{dc}$) to the frequency dependent ($\sigma(\omega)$) region signals the onset of the conductivity relaxation phenomena; the transition from long-range ion motion to short-range ion motion. The electrical modulus formalism, proposed by Macedo et al. [7], is often used to relate the conductivity dispersion to the relaxation of the mobile ions. This formalism is preferred as it is easier to relate the ion relaxation to other properties, such as the dynamic mechanical modulus, and can be written as a single function of the conductivity. The real part of the conductivity is written in terms of the complex electrical modulus, $M'(\omega) = 1/\varepsilon^*(\omega)$, as

$$\sigma'(\omega) = \omega \varepsilon_0 \varepsilon''(\omega) = \omega \varepsilon_0 \left[ \frac{M''(\omega)}{M'(\omega)^2 + M''(\omega)^2} \right]$$  \hspace{1cm} (2.24)
where $\varepsilon_0$ is the dielectric permittivity of free space, $\varepsilon''$ is the imaginary component of the complex relative permittivity $\varepsilon^*$, and $M'$ and $M''$ are the real and imaginary parts of the complex electrical modulus $M'$. The electrical modulus $M'(\omega)$ is related to the time dependent electrical stress relaxation function $\phi(t)$ by

$$M'(\omega) = \frac{1}{\varepsilon^*(\omega)} = M_\infty \left[ 1 - \int_0^\infty e^{-i\omega t} \left(-\frac{\partial \phi}{\partial t}\right) dt \right]$$

(2.25)

where $M_\infty = 1/\varepsilon_\infty$ and $\varepsilon_\infty$ is the high frequency limit of the real part of the dielectric constant [7,8,57]. $\phi(t)$ is the correlation function that describes the decay in time of an applied electric field in a homogeneous conducting dielectric. Integrating by parts yields

$$M'(\omega) = M_\infty \left\{ 1 + \left[ e^{-i\omega t} \phi(t) \right]_0^\infty + i\omega \int_0^\infty e^{-i\omega t} \phi(t) dt \right\}.$$  

(2.26)

If the correlation function exhibits the following properties, $\phi(0) = 1$ and $\phi(t \to \infty) = 0$ then $M'$ simplifies to

$$M'(\omega) = i \omega M_\infty \int_0^\infty e^{-i\omega t} \phi(t) dt.$$  

(2.27)

Furthermore, the real $M'$ and imaginary $M''$ components of $M'$ can be easily separated using Euler's identity:

$$M'(\omega) = M_\infty \omega \int_0^\infty \sin(\omega t) \phi(t) dt$$  

(2.28a)

$$M''(\omega) = M_\infty \omega \int_0^\infty \cos(\omega t) \phi(t) dt.$$  

(2.28b)

Finally, the real part of the complex conductivity (Eq. 2.24) may be written in terms of the complex modulus (Eq. 2.28) as

$$\sigma'(\omega) = \frac{\varepsilon_0 \varepsilon_\infty \int_0^\infty \cos(\omega t) \phi(t) dt}{\left[ \int_0^\infty \sin(\omega t) \phi(t) dt \right]^2 + \left[ \int_0^\infty \cos(\omega t) \phi(t) dt \right]^2}.$$  

(2.29)
The conductivity spectrum for a parallel R-C circuit is similar to that observed for ion conducting glasses minus the conductivity dispersion. The electrical stress relaxation function describing the conductivity spectrum for the R-C circuit is the Debye exponential function

$$f(t) = e^{-\frac{t}{\tau}}$$  \hspace{1cm} (2.30)$$

with a single relaxation time $\tau$. The analytical solution for the electrical modulus using this relaxation function which is fitted to experimental data for a parallel R-C circuit in Figure (2.6),
\[ M^*(\omega) = M_0 \left[ \frac{(\omega \tau)^2}{1 + (\omega \tau)^2} + i \frac{\omega \tau}{1 + (\omega \tau)^2} \right]. \tag{2.31} \]

\( M'(\omega) \) increases with frequency from zero to a maximum asymptotic value of \( \varepsilon_j/C \). The frequency when \( M' \) is half the maximum value is the relaxation frequency (\( \tau^{-1} = 1/RC \)). The \( M'' \) peak value is half of the maximum of \( M' \) and the full width of the \( M'' \) peak at half its maximum value (FWHM) is 1.144 decades.

Electrical modulus data for a \( \text{Li}_2\text{S} + \text{SiS}_2 \) FIC glass are compared with those for a parallel RC circuit in Figure 2.7. The curves for the glass are similar to those observed for the parallel R-C circuit with the following differences: the frequency dispersion from the minimum to the

![Figure 2.7: Example of the frequency response of the electrical modulus for a typical disordered material - lithium thiosilicate glass](image)
maximum value for $M'$ occurs over a wider frequency range, the $M''$ peak is much broader, and the maximum value for $M''$ is much less than half of the maximum of $M'$. To facilitate the analytical discussion of the electrical modulus in glasses, it is helpful to first generate a qualitative interpretation of the electrical modulus.

The physical interpretation of the electrical modulus is similar to that of the mechanical modulus. Any change in the spectrum for $M'$ indicates a change in the stiffness of the material and the frequency region where this occurs is emphasized by a "loss" peak in $M''$. The low-frequency limit for $M'$ is zero and represents a lack of restoring force for the electric-field-induced mobile ions. These mobile ions are fully able to decay the applied electric field stress. This result is analogous to the mechanical modulus for viscous flow, where there is a lack of restoring force at low frequency under the influence of a steady shear force. As frequency increases, each ion moves a shorter and shorter distance (the glass becomes less fluid) as it changes direction to keep up with the alternating field. Finally, at high frequency, the electric field changes so rapidly that ions "rattle" only within the confines of their potential energy wells. Once the ions are confined and no longer contribute to relaxing the electric field stress, $M'$ approaches a maximum asymptotic value. The glass for all practical purposes has become "stiffer" because the mobile ions have been frozen into the structure of the glass.

The $M''$ spectrum is asymmetric approximately and is centered in the dispersion frequency region of $M'$. The peak frequency corresponds to the average electrical field relaxation time, $\tau'$. For frequencies to the left of the $M''$ peak ($\omega\tau << 1$), most ions are mobile over long distances and are easily able to decay the applied electric field stress. For higher frequencies (to the right side of $M''$ peak), $\omega\tau >> 1$, most ions are spatially confined to their potential wells and are unable to decay the applied electric field stress due to the rapidly changing field. With this phenomenological discussion on ion dynamics, the question of the broadening of the electrical modulus in glasses and the mathematics of the electrical modulus is now readressed.
Macedo et al. [7] attributed the broadening in the modulus spectra for glasses to non-exponential relaxation of the electric field. Following Williams and Watt's [9-11] usage of the Kohlrausch decay function, Moynihan et al. [8] recognized that the stretched exponential (KWW) function (see Figure (2.8)),

$$ f(t) = e^{-\left(\frac{t}{\tau}\right)^\beta} \quad 0 \leq \beta \leq 1 \quad (2.32) $$

Figure 2.8: Time domain response of the KWW function for different values of $\beta$. Notice the increase in the decay at short times and the stretched in the time decay for decreasing $\beta$ values.
was a good choice for the correlation (stress relaxation) function to describe the electrical modulus spectra. In the above function, \( \beta \) is a measure of the degree of non-exponentiality and \( \tau \) is the average relaxation time given by

\[
\tau = \tau_0 \exp \left( \frac{\Delta E}{kT} \right)
\]  

(2.33)

where \( \Delta E \) is the ion hop activation energy and \( \tau_0 \) is the relaxation time prefactor. For fixed temperatures, the KWW function (Eq. (2.28)) exhibits a rapid decay at short times and a stretched out decay at long times as shown in Figure (2.8). This treatment gives a good description of the conductivity dispersion in ion-conducting glasses and other systems and has been well documented, especially by Ngai and co-workers [58-64].

Analytical solutions for the electrical modulus using the KWW function exist for \( \beta = 0, 0.5 \) and 1, but for other \( \beta \) values, numerical analyses are necessary. Moynihan et al. [8] solved this problem by approximating the above decay function by an integrable expression of the form:

\[
f(t) = e^{-\left(\frac{t}{\tau}\right)\beta} = \sum_{i=1}^{n} g_i e^{-\frac{t}{\tau_i}}
\]

(2.34)

where \( g_i \) is the probability that alkali ions have a relaxation time \( \tau_i \). Approximately 17 terms of the series are linear least-squares fit to the KWW function for \( \beta \) in the range \( 0.3 < \beta < 0.95 \) to insure convergence of the integrals. This exponential series is easily transformed to the frequency domain using Eq. (2.27). Tables for these fitting are available from Moynihan.

The series of discrete terms suggests a distribution of discrete relaxation times for the alkali ions in a glass. Replacing the summation with an integral would imply a continuous distribution of relaxation times. This distribution in the relaxation times, as was pointed out in the introduction, may be due to parallel conduction processes acting independently of each
other or to strongly coupled serial processes constraining the relaxation of each ions. The exact nature of this process is unclear, however.

Conductivity data have been modeled in the electrical modulus formalism with great success for frequencies less than one decade above the average relaxation frequency [8,57-68] and an example is shown in Figure (2.9). The limiting behavior for the KWW function (Eq. (2.28)) in the conductivity function (Eq. (2.25)) and for the Almond-West (AW) power law function are given in Table (2.2). The limiting results for these two functions are in

![Figure 2.9: Conductivity and modulus data plotted against frequency normalized by \( M'' \) peak frequency. KWW fit of electrical modulus deviates from measured values at highest frequency](image)

0.005Na\(_2\)S + 0.995B\(_2\)S\(_3\)
agreement. They yield constant values for the conductivity in the region where $\omega \tau \ll 1$ and frequency dependent values in the region where $\omega \tau \gg 1$. The slope of the conductivity curve $s$ is related to $\beta$ by:

$$s = 1 - \beta.$$  \hfill (2.35)

Jonscher [4], Angell [70], Dyre [21,22], Lee et al. [54,55] and others believe that for all glasses, the conductivity slope will increase from zero in Region 1 ($\omega \tau \ll 1$) to a final value of one in Region 2 ($\omega \tau \gg 1$) at lowest temperature and/or highest frequency. This suggests that the degree of non-exponential behavior $\beta \rightarrow 1$ increases with frequency while in the case of the KWW fits to the electrical modulus the degree of non-exponential behavior is constant. The disagreement between the predictions of the slopes using the two treatments suggests that there must be a fundamental frequency above which the KWW function may not be valid. The initial increase in conductivity is due to relaxation processes, but the further increase at higher frequencies, not predicted by the KWW function, may be due to new loss mechanisms occurring at higher frequencies.

Table 2.2 Limiting behavior of the KWW function in the electrical modulus formalism and the Almond-West model

<table>
<thead>
<tr>
<th>Range</th>
<th>KWW</th>
<th>Almond-West</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega \tau \ll 1$</td>
<td>$\sigma(\omega) = \frac{\varepsilon_0 \varepsilon_\infty}{\omega} \int_0^\infty \phi(t) , dt &lt; \tau &gt;$</td>
<td>$\sigma(\omega) \equiv \sigma_{d.c.}$</td>
</tr>
<tr>
<td>$\omega \tau \gg 1$</td>
<td>$\sigma(\omega) \propto \tau^{-\beta} \omega^{1-\beta}$</td>
<td>$\sigma(\omega) \propto A\omega^s$</td>
</tr>
</tbody>
</table>
2.2.3. Compositional Contributions Non-Exponentiality

Many researchers have reported for various glass systems the compositional contributions to the non-exponential conductivity relaxation [7,8,57-69]. β values for all these glasses are far less than one and are weakly compositionally dependent. However, Ngai et al. [62] report from their work on alkali-germanate and alumino-germanate glasses and Simmons et al. [69] report from their work on alkali silicates, that exponential relaxation (β = 1) may be achieved by reducing the cation concentration to below 1%. Ngai [58] in his coupling model uses the anticorrelation parameter, \( n = 1 - \beta \), to show the extent of non-exponentiality. He explains the approach to single relaxation (β = 1) may be associated with a decrease in the cation-cation interactions characterized essentially by independent cation jumps relaxing in analogy to Debye dipoles.

![Figure 2.10: Plot of alkali-alkali separation distance versus composition [65](image)](image)
Martin [65] tested the above hypothesis by calculating the average cation-cation separation distances (α) from the density and composition for various sodium-modified oxide glasses and plotting α against Na₂O mole fraction, see Figure (2.10). This figure shows that α exhibits its greatest compositional dependence for x < 0.2 and thereafter α decreases slowly with composition. Furthermore, Martin created a master plot of β against cation-cation separation distance for a whole series of glasses and this is reproduced in Figure (2.11). The data show that for α less than 10 Å, all glasses exhibit β = 0.5, while for large α, (alkali-metal dilute glass), β increases to unity implying a decrease in cation-cation coupling. The compositional variation of β between the two extremes remains an open question. A study bridging the gap between the extremely low-alkali exponential region and the high alkali non-exponential region for any one complete glass system has never been performed. Such a study would show a systematic approach to exponential behavior with increasing cation-cation separation dis-
tance ($\alpha$) and corroborate the hypothesis that the non-exponential conductivity relaxation is an effect of ion-ion interaction.

As expected from the electrical modulus formalism, if the conductivity dispersion is an effect of conductivity relaxation then the slope of the conductivity curve should show a strong compositional dependence in the ultra-low ion concentration region. In fact, for glasses exhibiting near exponential conductivity relaxations ($\beta \to 1$), the conductivity slope should be close to zero, $s = 1 - \beta$. The same wide composition study as proposed above should reveal that the conductivity slope does indeed go to zero for ultra-low ion concentration glasses where ion-ion interaction has been eliminated. However, as mentioned before, it has been widely reported [4,21,22,54,55] that the slope of the conductivity at lowest temperature and/or highest frequency is one. If this is the case, then the departure from the slope predicted by the KWW function would suggest additional conductivity relaxation mechanisms. A wide composition conductivity study and analysis using the KWW function in the electrical modulus and the slope determined through the Almond-West formalism should reveal more details of the ion conduction process.

The $\beta$ parameter in the KWW function is assumed to be temperature and frequency independent and the temperature and frequency dependence of the conductivity relaxation is accounted through the relaxation time, Eq. (2.33). Experimental results have shown that the $\beta$ is in general temperature independent though in some cases it may increase slightly with temperature [26,33,57,71,72].

Mechanical and electrical relaxation due to mobile ions have been studied by Borgesson et al. [74]. Mechanical stresses can be relaxed by the localized displacements of ions. In FIC glasses, since there are many ions, a substantial mechanical response is expected. Borgesson et al. measured the mechanical response of a FIC glass over a wide frequency (11 Hz - 19 GHz) and wide temperature range, and fit the response to the KWW function (see Figure (2.12)).
In contrast to the fixed $\beta$ observed in the electrical modulus, the $\beta$ in these experiments was shown to be frequency-dependent. For low frequencies, the modulus peak is broad, but narrows at higher frequencies. In fact, $\beta$ for highest frequency (19 GHz) is unity implying a single relaxation time. This result implies that there is a wide distribution of relaxation times at low frequency for ion hops which converge to a single relaxation time at higher frequencies. The activation energies for these parallel dynamic processes are close in value to each other that the difference in their values is only apparent over the widest frequency and temperature range. Similar behavior in the electrical modulus may have not been reported to date since most laboratories are not able to perform electrical measurements above one MHz which is the region where peak narrowing is expected to occur. The deviation of the KWW fit at high frequencies may well be an artefact of this phenomena. Reasons for the narrowing of the

![Figure 2.12](image-url)  

Figure 2.12: Mechanical modulus data, collected over a wide frequency and temperature, show narrowing of peaks with increasing frequency. The peak values are normalized to one. The solid lines represent KWW fits where $\beta$ increases from 0.29 at $f \sim 100$ Hz to 1.0 at $f \sim 19$ GHz [74]
modulus peak are not clear. To the author's knowledge, no study to date to investigate the narrowing of the electrical modulus spectra as a function of frequency has been done.

Few measurements of ionic conductivity using frequencies greater than 10 MHz have been reported [29,31-33]. In order to fully examine the frequency dependence of the conductivity, higher frequency measurements are necessary where the contribution to the conductivity due to long-range ion motion are non-existent while the short-range ion motion becomes important. The data bridging Regions 2 and 3, from 1 MHz to 10 GHz, are still lacking and if the goal is to determine a unified conductivity model that describes all three regions of the conductivity spectrum, then it is crucial to determine how the conductivity data varies with frequency ($\partial \log(\sigma)/\partial \log(v)$) on its approach to IR frequencies.

2.3. Far-IR and IR Absorption

The absorption peaks in the Far-IR and IR regions are attributed to the ions oscillating anharmonically about fixed quasi-lattice positions [70]. The change of speed and intensity of an electromagnetic wave through a material are contained in the complex index of refraction $n^*$ which is related to the complex relative permittivity by

$$n^* = \sqrt{\varepsilon^*}$$ (2.36)

Taking $n^* = n - ik$, where $n$ is the refractive index and $k$ the absorption index, the following relations are obtained:

$$\varepsilon' = n^2 - k^2 \quad ; \quad \varepsilon'' = 2nk$$ (2.37)

The relationship between the absorption and the real part of the complex conductivity is given by

$$\sigma'(\omega) = \omega \varepsilon_0 \varepsilon''(\omega) = 2 \omega \varepsilon_0 n(\omega) k(\omega).$$ (2.38)
The absorption coefficient $\alpha$ is defined as [73]

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda} = \frac{2\omega k(\omega)}{c}$$  \hspace{1cm} (2.39)

and substituting Eq. (2.39) into Eq. (2.38) yields:

$$\sigma(\omega) = \varepsilon_0 c \alpha(\omega) n(\omega)$$  \hspace{1cm} (2.40)

where $c$ is the speed of light. The refractive and absorption index in the Far-IR and IR can be easily measured with modern spectrometers. The resonance Far-IR peaks will give the limiting high frequency conductivity on its approach from low frequency to the IR frequency.

2.4. Nuclear Spin Lattice Relaxation (NSLR)

In analogy to the quantum spin of electrons, nuclei may have a net spin $I$ [75-77]. The nuclear magnetic dipole moment for such a nuclei is given by

$$\mu = \gamma h I$$  \hspace{1cm} (2.41)

where $\gamma$ is the magnetogyrlic constant, $h$ is Planks constant and the values of $I$ govern magnetic spin quantum $m$ which can take values ranging from $-I$ to $I$. $\gamma$ is different for each nucleus and can be expressed by the Bohr nuclear magneton $\mu_n$ as

$$\gamma = \frac{g}{h} \left( \frac{eh}{2m_p} \right) = \frac{g \mu_n}{h}$$  \hspace{1cm} (2.42)

where $g$ is the nuclear $g$-factor and $e$ is the charge and $m_p$ is the mass of the proton. The energy of interaction (called the Zeeman energy) for this magnetic dipole in a magnetic field $\mathbf{B} = B_o \mathbf{z}$ is

$$E = -\mu \cdot B = -\gamma h I \cdot B = -\gamma h I z B_o$$  \hspace{1cm} (2.43)
If a material has a nuclear spin of $\frac{1}{2}$ then the energy will split into two Zeeman levels corresponding to $m = \frac{1}{2}$ and $-\frac{1}{2}$ as shown in Figure 2.13.

If energy, $\hbar \omega_L$, equal to the energy splitting is supplied to the material then a nuclei in the lower energy state will absorb the energy and be excited to the higher state. The absorption spectrum for this nucleus will therefore exhibit a single absorption at $\omega_L$, the Larmor frequency. Classically, $\omega_L$ is the frequency of precession of a magnetic dipole moment about a magnetic field $B$. The difference between the two energy levels using Eq. (2.43) and setting the result equal to $\hbar \omega_L$ yields the following result:

$$\omega_L = \gamma B_0 .$$

(2.44)

For a magnetic field in the Tesla range, the energy to induce a transition corresponds to the energy of a radio frequency (RF) electromagnetic wave. By increasing the magnetic field, the Zeeman energy splitting may be increased to increase the Larmour frequency.

The equilibrium population distribution of a system of nuclear spins which are distributed among a set of Zeeman energy levels is governed by a Boltzman distribution. Therefore, the population in lower energy states is larger than that in higher energy states. However,
when a sample is initially placed in a magnetic field, the population of nuclear spins in each Zeeman energy level is the same. After some time, the spins distribute themselves until they are in their equilibrium distribution given by the Boltzmann's distribution and contribute to a net magnetization $\mathcal{M}$. The net magnetization $\mathcal{M}$ is the sum $\sum \mu_i$ over all the nuclei in the sample. The rate of magnetization decay is given by

$$\frac{\partial \mathcal{M}(t)}{\partial t} = \frac{M_0 - \mathcal{M}(t)}{T_1}$$

where $M_0$ is the equilibrium magnetization and $T_1$ is called the longitudinal relaxation time or the nuclear spin lattice relaxation (NSLR) time. Integrating Eq. (2.45) with the initial condition $\mathcal{M}(0) = 0$ gives the result:

$$\mathcal{M}(t) = M_0 \left[ 1 - e^{-\frac{t}{T_1}} \right].$$

In order for a spin system to relax, after the spins have been excited to a higher energy state, its Zeeman levels must couple with the energy modes within the surrounding lattice. A typical mechanism for relaxation in an insulator is the inelastic scattering of a phonon while in a metal it is due to inelastic scattering of conduction electrons. Generally, the nuclei may interact with each other through dipole-dipole coupling or interact with the magnetic moments of electrons of other ions within the solid. Whenever any of these processes are modulated in time, transitions between Zeeman levels occur. If there are many modes within a material with frequency $\omega_\text{L}$ available, then the relaxation rate is fast and $T_1$ is short. If there are few modes with frequency $\omega_\text{L}$ then the relaxation rate is slow and $T_1$ is long.

Dynamic processes such as ionic motion (diffusion) give rise to fluctuating magnetic and electric fields at nuclear sites. In FIC glasses, the ion diffusion process is the dominant mode for nuclear spin relaxation. A hypothetical mode of relaxation in FIC glass may be the transfer of nuclei spin energy to translation, rotational or vibrational energy of a passing nuclei.
The NSLR rate in a spin system relaxing due to time varying interactions arising from random ionic motion was first determined by Bloembergen et al. \[78\] to be:

\[
R_1 \equiv \frac{1}{T_1} = C \left[ J(\omega_L) + 4J(2\omega_L) \right] \tag{2.47}
\]

where \( C \) is a temperature independent constant. \( J(\omega) \), the spectral density,

\[
J(\omega_L) = \text{Re} \left[ \int_{-\infty}^{\infty} \phi(t) \exp(-i\omega t) dt \right] \tag{2.48}
\]

is the Fourier transform of the correlation function \( \phi(t) \) which describes the fluctuation in the magnetic field due to ion motion.

Bloembergen, Pound and Purcell (BPP) applied the Debye exponential relaxation function (Eq. 2.30) as the correlation function \[78\]. This function assumes a single relaxation time \( \tau_s \) (the average time for ions to hop between sites), and works well for many systems, especially liquids. The NSLR rate, using the Debye exponential function in Eq. (2.48) and then inputting \( J(\omega) \) into Eq. (2.47), has the following form:

\[
\frac{1}{T_1} = C \left[ \frac{\tau_c}{1 + (\omega_L \tau_c)^2} + \frac{4\tau_c}{1 + 4(\omega_L \tau_c)^2} \right] \tag{2.49}
\]

where \( \tau_c \) is the correlation time and \( \omega_L \) is the Larmour frequency. Since ionic motion is thermally activated, the correlation time is also thermally activated and given by:

\[
\tau_c = \tau_0 \exp \left[ \frac{\Delta E_{\text{NMR}}}{kT} \right] \tag{2.50}
\]

where \( \Delta E_{\text{NMR}} \) is the activation energy for ion hopping and \( \tau_0 \) is the prefactor.

The frequency dependence of the NSLR time at constant temperature is determined by measuring \( T_1 \) over a wide range of magnetic fields, hence a wide range of frequencies (see Eq. 44). The splitting of the Zeeman levels is a linear function of the external field yielding
Figure 2.14: The (a) frequency and (b) temperature response for the calculated NSLR $T_1$ using an exponential function for the correlation time and the following parameters: $\Delta E_{MGR} = 37.4 \text{ kJ/mole}$, $\tau_c = 4.5 \times 10^{-14} \text{ s}$ and $C = 3.8 \times 10^9 \text{ s}^{-2}$
the resonance condition, $\omega_L = \gamma H$. The behavior expected for the simple BPP model is illustrated in Figure 2.14(a) for the choice of parameter as obtained for the FIC Li$_2$S + SiS$_2$ [79] ($\Delta E_{\text{NMR}} = 37.4$ kJ/mole, $\tau_0 = 4.5 \times 10^{-14}$ s and $C = 3.8 \times 10^{-9}$ s$^{-2}$).

At low frequencies ($\omega \tau_0 \ll 1$), $T_f$ is frequency independent and is proportional to $\tau^{-1}$. As the frequency approaches the condition where $\omega \tau_0 \sim 1$, the NSLR time begins to decrease. At higher frequencies ($\omega \tau_0 > 1$), $T_f$ increases with the square of the frequency, $T_f \propto \tau_0 \omega^2$. The Zeeman energy splitting is large and less lattice modes are available at that frequency. The spins remain in the high energy state for a longer period. This type of experiment where the Larmour frequency is continuously varied from a low to high value, however, is not performed because of the difficulty in varying the magnetic field and in measuring the net magnetization of weak fields at low frequencies. Typically, the magnetic field is fixed and the temperature of the sample is varied.

The temperature dependence of the NSLR time is contained in Eq. (2.47). Figure (2.14(b)) shows an Arrhenius plot of $1/T_f$ calculated for a series of frequencies (magnetic fields). Many features of the BPP theory are seen in this figure. At high temperatures, $T_f$ is frequency independent because $\tau$ becomes small and the $\omega$ dependence falls out of Eq. (2.46). The slope of the data to the left of the maxima (high temperature region) is proportional to $\Delta E_{\text{NMR}}$. Using Eq. (2.46) and Eq. (2.47), it can be shown that the $1/T_f$ maximum occurs when $\omega_L \tau_0 \sim 0.64$. The value for $\tau_0$, the prefactor in Eq. (2.47), is easily determined from the values of $\Delta E_{\text{NMR}}$ and $\omega_L$. Eq. (2.46) also shows that the slope of the low temperature side of the curve is the same as that on the high temperature side except for a sign change. This is the key difference between the experimental data which follows the BPP theory and that which does not.

2.5. Relationships Between NSLR And Ionic Conductivity

Instead of plotting the $T_f$ on a log scale, as in Figure 2.14(b), Figure 2.15 shows a linear plot of $T_f$ against the inverse temperature. The plot shows a strong similarity in shape to
Figure 2.15: Linear plot of $1/T_1$ against inverse temperature showing the striking similarity to the electrical modulus spectrum.

the frequency plot of the imaginary part of the complex electrical modulus (see Figures 2.6 and 2.7). The difference, however, is that the $T_1$ data is obtained by fixing the frequency and varying the temperature while $M''$ data is obtained by fixing the temperature and varying the frequency. In analogy to the imaginary part of the complex electrical modulus, the high temperature/low frequency region corresponds to $\omega L \tau_c < 1$. In this range, the time scale to relax the high energy nuclei spins to lower energy with magnetic fluctuations caused by ion motion is much less than the period associated with the energy of the Zeeman splitting. In this
region, the relaxation time is frequency independent and may be related to the conductivity in Region 1 ($\sigma_{dc}$).

The low temperature/high frequency region corresponds to $\omega_L \tau_c >> 1$. Longer NSLR times are observed at low temperatures since fewer magnetic fluctuations occur due to the decreased mobility of the thermally activated ions. At high frequencies, the energy splitting is large and only the most thermally active ions are able to cause magnetic fluctuations to couple with spins. The time scale for the relaxation is far greater than the time scale of the experiment. The ion dynamics in this region are frequency dependent and may be compared to the conductivity data in Region 2, $\sigma_{ac}$.

Recognizing that it is ion motion that causes local charge density fluctuations in the NMR experiment and the dissipation of the electric field stress in the conductivity experiment, then, there must exist some relationship between the NSLR and the conductivity relaxation. To investigate these relationships, we first need to address the choice of the correlation function in glassy systems.

Figure 2.16: Temperature dependence of the NSLR $T_1$ for a FIC Li$_2$S + SiS$_2$ glass. Data for both the frequency dependent as well as the frequency dependent region is observed for this highly conductive glass [27]
Most NSLR $T_i$ measurements in glasses are restricted to the frequency dependent region. Only for those glasses with high glass transition temperatures, $T_g$, and/or extremely high conductivities is it possible to make $T_i$ measurements in the frequency independent region ($\omega_\tau >> 1$). Figure 2.16 shows the temperature dependence of the NSLR $T_i$ for a FIC Li$_2$S + SiS$_2$ glass reported by Pradel et al. [27]. Data for both the frequency dependent as well as the frequency dependent region is observed for this highly conductive glass. If a lower Larmor frequency had been used, then the $1/T_i$ peak would be seen at lower temperatures (right side) and more data on the frequency independent side would be observed. The opposite would be true if the Larmor frequency had been higher. The peak would move to a higher temperature and only for the highest temperatures would data for the frequency independent region be observed. The above discussion is the predicted behavior according to the BPP model and was shown in Figure 2.14(b).

The general appearance of the shape of the curve show a striking similarity to the curves predicted by the BPP theory (see Figure 2.14(b)). The BPP theory, however, fails at low temperatures. This has been known for many years [79-81]. The absolute values of the slope on each side of the maxima are different, hence the peak is asymmetric. This failure in the BPP model is due to the usage of exponential function for the correlation function $\phi(t)$ which assumes a single relaxation time. In glasses, ionic motion is generally complicated due to a distribution of ion sites, activation energies, correlation times and/or possibly ion-ion interaction. For these reasons, non-exponential relaxation is expected.

In general, a distribution $g(t)$ of correlation times are used to describe the expression for the reciprocal of the NSLR time [25,75]:

$$R_i = \frac{1}{T_i} = C \left[ \int_{-\infty}^{\infty} \frac{\tau g(\tau)}{1 + (\omega \tau)^2} d\tau + 4 \int_{-\infty}^{\infty} \frac{\tau g(\tau)}{1 + (\omega \tau)^2} d\tau \right]$$

(2.48)

where

$$\int_0^\infty g(\tau) d\tau = 1$$

(2.49)
The NSLR $R_x$ collapses to the BPP expression (Eq. 46) when $g(\tau) = \delta(\tau - \tau_c)$.

The Cole-Davidson (CD) distribution [82] is another example of a function that describes the non-exponential character. It gives an analytical solution for the NSLR time and has been applied with some degree of success for lithium conductive glasses [27,75,83,84] and is given below:

\[
g(x) = \begin{cases} 
\sin(\alpha\pi)\left(\frac{x}{x^*}\right)^\alpha & \tau < \tau^* \\
0 & \tau \geq \tau^*
\end{cases}
\]

(2.50)

where $\tau^*$ is the longest correlation time and $\alpha$ is the width parameter having values in the range $0 < \alpha < 1$. Gobel et al. [83] solved the integral for the CD distribution and obtained:

\[
\frac{1}{T_1} = C \left[ \frac{x^* \sin(\alpha \arctan(\omega_0 \tau^*))}{\omega_0 x^* \left(1 + (\omega_0 \tau^*)^2\right)^{\frac{3}{2}}} + \frac{2x^* \sin(\alpha \arctan(\omega_0 \tau^*))}{\omega_0 x^* \left(1 + 4(\omega_0 \tau^*)^2\right)^{\frac{3}{2}}} \right]
\]

(2.51)

As in the case of non-exponential relaxation in conductivity the popular choice for the correlation function in the NSLR $T_x$ has been the KWW function, Eq. (2.28). The stretched exponential function describes a distribution of relaxation times as shown above in Eq. (2.30). The KWW function also collapses to the BPP expression (Eq. 46) when $\beta = 1$. This function, however, leads to the problem that

\[
J(\omega) = \text{Re} \int_{-\infty}^{\infty} e^{-\left(\frac{t}{T}\right)^\beta} e^{-i\omega t} dt = 2 \int_{0}^{\infty} \cos(\omega t) e^{-\left(\frac{t}{T}\right)^\beta} dt
\]

(2.52)

has no known analytical solution except for the case where $\beta = 0$ or 1. This problem can be resolved using the series expansion method described for the conductivity relaxation [8] or by using numerical integration [85].
The first KWW fit to NSLR $T_1$ data in FIC glasses was reported by Martin [25] and later by Trunnel et al. [30,86] who applied the technique described by Dishon et al. [85]. Trunnel et al.'s $^{7}$Li NSLR rate ($R_T = 1/T_1$) data for a $\text{B}_2\text{O}_3 + 0.7\text{Li}_2\text{O} + 0.6\text{LiCl}$ FIC glass at different resonance frequencies are shown in Figure 2.17. The lines through the data in the figure are the KWW curve fits ($\beta = 0.35$). The KWW fit are quite good at high temperatures and/or low frequencies ($\omega\tau << 1$). In the frequency dependent region ($\omega\tau >> 1$), the fit fails and deviates most for lowest temperatures and highest frequencies. The deviation at low temperatures have previously been reported in lithium-based FIC glasses [87] and may be due to additional relaxation processes at low temperatures.

The success of the KWW fit in the conductivity relaxation and the NSLR in the frequency independent region and its failure at high frequency and low temperature suggests

![Figure 2.17: $^{7}$Li nuclear spin lattice relaxation rate ($R_T = 1/T_1$) data at different resonance frequencies for a $\text{B}_2\text{O}_3 + 0.7\text{Li}_2\text{O} + 0.6\text{LiCl}$ glass. The lines through the data are the KWW curve fits ($\beta = 0.35$) [86].]
similar ion dynamic mechanisms are contributing to the dissipation driven conductivity relaxation and fluctuation driven NSLR. The $\beta$ and $\tau_c$ parameters determined for the same glass from NMR and conductivity experiments are, however, different and this suggests a different time dependence for the two correlation functions \[26,30,86\]. The difference in the $\beta$ values is explained by noting that the correlation function (KWW) in Eq. (2.25) refers to the relaxation of the electric field stress which is a macroscopic quantity while that in Eq. (2.44) for the NSLR probes the local microscopic domain. The reason for the observed non-exponential behavior in both measurements, however, is unknown but has often been attributed to correlations between ion jumps. In this explanation, successive ion jumps are expected to affect in different ways the local NMR correlation function than that in the conductivity correlation function. If a theory can be developed to relate the value of $\beta$ to microscopic parameters then the difference between the two $\beta$ values for the different measurements should be useful in understanding the dynamics of ion motion.

In conductivity, a structural relationship between the ion-ion separation distance and $\beta$ has been hypothesized \[65\]. Similarly, $T_i$, compositional studies in the ultra-low alkali glasses should be performed to test the same hypothesis that the correlation function will exhibit an approach to single relaxation behavior for decreasing alkali concentration or largest ion-ion separation distances. The Arrhenius plots of $1/T_i$ should approach the prediction of the BPP for glasses with largest ion-ion separation. Comparison between the electrical and NMR results should help clarify the nature of the cooperative processes existing in the ion hop mechanism.

The activation energy for $T_i$ in glasses is generally determined from the right (low temperature) side of the $1/T_i$ maximum \[88\]. The assumption being that the slope on both sides of the peak is the same as predicted by the BPP theory. This measured activation energy value is systematically less than the value for the d.c. conductivity activation energy, even though both processes are assumed to be thermally activated due to ion hopping \[25,26\]. In the previous discussion, it was mentioned that in glasses the correlation function is not a single
exponential function. For this reason, the $T_1$ peak is asymmetric and the activation energy determined from the opposite slopes of the $T_1$ curve are different. Angell and Martin [26] and Martin [25] hypothesized that the discrepancy between the two activation energies is attributed to the difference in the probe frequency of the two experiments. NMR measurements are always made at frequencies above 1 MHz; for most glasses these corresponds to the frequency-dependent conductivity, Region 2, whereas d.c. ionic conductivities are always measured in Region 1 as a frequency-independent quantity.

For highly conductive glasses, however, the "d.c. plateau" may be extended into the NMR frequency range by increasing the temperature. Glasses with this property should exhibit a $1/T_1$ maximum and the frequency independent region, especially for low Larmor frequencies and high temperatures. This would allow direct comparison between the temperature dependence of the frequency independent (d.c.) conductivity and the frequency independent NSLR $T_1$.

The obvious extension of the comparison of the frequency-independent activation energies is to compare the activation energies for both conductivity and NSLR processes taken from the frequency-independent region at the same frequency. This comparison relies upon the assumption that the frequency dependence of the two measurements is the same, which in turn assumes that both processes depend upon the same relaxation function describing the frequency dependence. For the KWW correlation function in the case that $\beta$ is the same for the conductivity and $T_1$, a similar value for the activation energy is expected for isofrequency measurements. Trunnel [30,86] has shown, however, that $\beta$ is different for the two experiments in FIC borate glasses. This series of experiments would be very interesting and contribute to the understanding of ion dynamics in glass and the relationship between electrical conductivity and NSLR. The expected relationships between conductivity and NSLR and those predicted by KWW stretched exponential function are summarized in the Table 2.3.

If fixed frequency and wide temperature measurements in the same range for both conductivity and $T_1$ are performed, then direct comparison between the relaxation function for the
conductivity and $T_1$ is possible by converting the conductivity data to a $T_1$ form and plotting the NSLR and the conductivity $T_1$ data on the same plot. The relationship between conductivity and $T_1$ using the electrical modulus has been shown by Ngai et al. [64] to be:

$$J(\omega) = \left( \frac{2}{\omega} \right) \left( \frac{M''(\omega)}{M_\infty} \right).$$

(2.54)

The general relationship between the NSLR and the conductivity is therefore:

$$R_1 = \frac{1}{T_1} = \frac{2C}{M_\infty \omega_L} \left[ M''(\omega_L) + 4 M''(2\omega_L) \right].$$

(2.55)

Similarity between the relaxation rates as a function of temperature and frequency would indicate identical relaxation processes and activation energies. Data of this type has never been collected and the proposed plot would be decisive proof of the relationships between the two experiments.

<table>
<thead>
<tr>
<th>Range</th>
<th>$R_1 = 1/T_1$</th>
<th>$\sigma(\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega L \tau_c \ll 1$</td>
<td>$R_1 \propto \tau_c^*$</td>
<td>$\sigma(\omega) = \sigma_{dc} \propto (\tau_c)^{-1}$</td>
</tr>
<tr>
<td>$\omega L \tau_c \gg 1$</td>
<td>$R_1 \propto \omega_L^{(1+\beta)}(\tau_c^*)^{-\beta}$</td>
<td>$\sigma(\omega) \propto \omega_L^{(1-\beta)}(\tau_c^*)^{-\beta}$</td>
</tr>
<tr>
<td>$\omega L \tau_c \approx 1$</td>
<td>$(R_1)<em>{max} \propto \exp\left(\frac{E</em>{NMR}^*}{kT}\right)$</td>
<td></td>
</tr>
</tbody>
</table>
2.6. Selection of Fast Ion Conducting Glass Systems

An optimize FIC glass system to investigate ion dynamics should not only have a high ionic conductivity, but also a glass forming range encompassing wide variations in alkali content. Only in highly conductive glasses is it possible to observe the frequency-independent $T_i$ over a wide temperature range. Furthermore, extremely low alkali content (ppm levels) would be an interesting regime of the glass forming region to study conduction and $T_i$ relaxation phenomenon. The ion-ion interaction which may be responsible for the non-Debye conductivity relaxation could be well tracked with the ion-ion separation distance in a glass. The compositional effects on the d.c. conductivity, the conductivity activation energy, and the degree of non-Debye behavior over a wide glass forming region would yield further information about the ion environments present in the glass.

An example of such a glass system is the chalcogenide series $xNa_2S + (1-x)B_2S_3$ for which Levasseur et al. [90] have shown room temperature conductivities of greater than $10^{-6}(\Omega cm)^{-1}$ for glasses formed in the range $0.1 < xNa_2S < 0.3$. Bloyer [91] and Martin and Bloyer [92,93] have shown through IR studies of these glasses that there exists a homogeneous glass forming region $0 < xNa_2S < 0.25$. Susman et al. [94] reported sodium glasses for $x = 0.5$ and 0.6. Recently, Cho [95] and Cho and Martin [96] have shown that there also exists a high alkali glass forming region in the range $0.5 < xNa_2S < 0.8$.

A similar wide compositional range has been reported by Cho [95] for the $K_2S + B_2S_3$ glass system. Glasses in the $Li_2S + B_2S_3$ system have been extensively studied [90,95-99] and its glass forming region has been well defined. The glass forming regions for these sulfide glasses and their oxide analogues are shown in Figure 2.18. Parallel compositional studies to the sodium glass system should lend support to the universality of the trends observed in the sodium system.
Figure 2.18: The glass forming regions for sulfide glasses and oxide analogues for lithium, sodium and potassium modifiers [94]

Pradel and Ribes have shown [27,28,42] that in the Li$_2$S + SiS$_2$ system the 1/$T$ maximum and the frequency independent region can be observed at high temperatures and low frequencies. Since the $^7$Li NMR signal is strong, the glass is a fast ion conductor and the glass forming region has been well defined, it is apparent that glasses in this family are extremely attractive for a parallel study of ionic conductivity and NSLR.

A study of the ionic conductivity in these glasses would yield significant information about the conductivity mechanisms and processes in NSLR. The difficulty in preparing contaminant-free sulfide glasses has been the biggest barrier against a more complete study.
For that reason, only a few cases comparing the oxide and sulfide glasses have been reported [97-100].

2.7. Proposed Plan Of Study

Throughout the discussion in the last six sections, the gaps in the fundamental understanding of the ionic conduction phenomenon in glasses have been described. The research goal here is to elucidate many of the questions posed in the previous sections. A summary of these questions are listed below:

- Does the d.c. conductivity data for alkali thioborate glasses support current models of the d.c. conductivity?
- How is high frequency conductivity related to temperature, frequency and glass composition?
- What is the fundamental frequency beyond which the KWW fit to the conductivity is no longer applicable, and what microscopic mechanism(s) contribute to this failure?
- What is the fundamental frequency limit beyond which the KWW fit to the $T_1$ is no longer applicable and what microscopic mechanism(s) contribute to this failure?
- Do conductivity measurements made at fixed frequencies and variable temperature yield activation energies which agree with those for $T_1$ made at the same fixed NMR frequency?
- What are the composition effects on these measurements, and are there any structural parameters which may be related to the conductivity and NMR relaxation?
- Do conductivity measurements for the alkali thiaborate glass system follow similar trends to those reported for in the oxides?
The questions posed need to be answered in order to understand the d.c. conductivity, the a.c. conductivity frequency dependence and the correlation between \( \sigma \) and the NSLR \( T_r \).

The following experiments are proposed to answer some if not all of these questions:

- **Development of a wide temperature (100 - 500 K) and wide frequency (1 Hz - 1 GHz)** impedance spectroscopy workstation to perform this study.

- **Wide compositional study of the conductivity over wide temperature and frequency ranges for the following glass systems:**
  
  (1) \( xNa_2S + (1-x)B_2S_3 \)
  
  (2) \( xK_2S + (1-x)B_2S_3 \)
  
  (3) \( xLi_2S + (1-x)B_2S_3 \)
  
  (4) \( xLi_2S + (1-x)SiS_2 \)

- **Wide temperature (100 - 500 K) and wide frequency (4 MHz - 100 MHz) measurements of the nuclear spin lattice relaxation time for glasses in the above system.**

This proposed wide composition conductivity study should clearly exhibit the conductivity behavior in regions 1 and 2. Data in the Region 1 will be used to verify or modify previously reported d.c. conductivity models. The end goal will be a model that relates structural parameters of the glass to the d.c. conductivity variables over the complete glass forming range.

The high frequency (1 MHz - 1 GHz) and the wide temperature study of ionic conductivity in glass over a wide composition range will be the first ever report of such a study. The slope of the \( \log(\sigma) - \log(\omega) \) curve at high frequencies will be of most interest in verifying the many predictions of the different relaxation models.

Conductivity measurements will be made over the entire glass forming region. Lower and lower alkali content glasses will be prepared until conductivity measurements are no longer possible. The decoupling between the alkali ions in the conductivity mechanism with increasing separation distance (decreasing alkali content glass) will be an interesting region to
study the ion relaxation processes. The other interesting region of study is the $0.5 < x < 0.8$ composition range, where a maximum in the conductivity is predicted as in the oxide analogue [100] or as in its lithium counterpart [96] where both the conductivity and the activation energy increase.

The following experiments are proposed to test the hypothesis that the activation energy for NSLR and conductivity will have the same value if both the probe frequency and the relaxation correlation function are the same for both processes. a.c. conductivity will be measured over the same frequency and temperature range as the NSLR experiment. The activation energy for the two processes in the frequency independent region will be compared. The conductivity relaxation occurs in the frequency dependent region and the activation energy for the two processes at the same frequency will be measured. Similarity in these results would indicate that like relaxation processes are occurring, as hypothesized, and allow the use of the same correlation function to describe the conductivity and the NSLR time. Nonlinear least-square fitting of $T_c$ and $\sigma(\omega)$ measurements to the KWW stretched exponential correlation function will be performed to describe the frequency dependence. The KWW function will be modified or a new correlation function will be proposed to describe the region where the KWW fit fails.
CHAPTER 3. EXPERIMENTAL METHODS

To answer many of the questions posed in the previous chapter, a wide compositional ionic conductivity study over wide temperature and frequency ranges for glasses in the akalithioborate and thiosilicate systems has been proposed. In addition, a comparison of conductivity and NSLR data over the same frequency and temperature range has been suggested. The development of instrumentation and facilities to perform the electrical measurements and the synthesis of these glasses are discussed in this chapter. The design, construction, software programming and characterization of the impedance spectroscopy workstations are covered in the first two sections. The last section describes the preparation technique to synthesize the glasses and sample preparation for the conductivity and NSLR characterization experiments.

3.1. Low Frequency (1 Hz - 1 MHz) Impedance Spectroscopy Workstation

A computer automated impedance spectroscopy workstation (see Figure 3.1) was developed by the author as part of his M.S. thesis has been described in detail in Ref. [103]. High quality measurement capability in the temperature range of 100 K to 500 K and a frequency range of 0.1 Hz to 1 MHz was reported for this workstation. The Solartron 1260 Impedance Gain-Phase Analyzer made by Schlumberger Instruments¹ used in this workstation, however, has an upper probe frequency limit of 32 MHz. Data were not collected or reported in this upper frequency range because measurements in this region were dramatically influenced by the electrical leads, lead lengths and the electrode setup of the conductivity cell. In anticipation of high frequency (1 MHz - 1 GHz) conductivity measurements, it was crucial to show that measurements using the two bridges in the region of frequency overlap gave similar re-

¹ Schlumberger Instruments, Victoria Road, Farnborough, Hampshire, England GU147PW
Figure 3.1: Block diagram of low frequency impedance spectroscopy workstation
sults. This rigorous test would indicate the accuracy and reliability of data comparison between data collected using the two bridges and the validity of measurements in their respective measuring frequency ranges.

If one decade (1MHz - 10 MHz) could be added to the measuring capability of the low frequency impedance workstation, then a whole decade of overlap between the two instruments would be available and be more than sufficient for comparison. To obtain quality data, flaws in the original conductivity cell design had to be identified and improvements incorporated. This is the topic of discussion for the first section. The improvement in the conductivity measurements after implementing changes are shown in the second section.

3.1.1 Problems in the Original Design

The original conductivity cell design was intended for use at an elevated temperatures above 600 K. This requirement set limitations in the cell design and contributed to errors in making good measurements at high frequencies. Identifying these limitations and understanding how they contribute to errors are the key topics discussed in this section. The schematic for the cell is given in Figures 3.2 and 3.3.

The electrode system of the sample holder necessitated the use of both rigid and flexible cables. Commercially manufactured, high temperature, flexible coaxial cables were not available and had to be designed by the author. To maintain a characteristic impedance \( Z_0 \) of 50 \( \Omega \) to match the source impedance of the analyzer, a fixed geometry between the inner and outer conductor, and the insulator has to be preserved over the entire length of the cable. Mismatches contribute to reflections and phase changes. This geometry is defined by the equation given below:

\[
Z_0 = 60 \sqrt{\frac{\mu_r \varepsilon_r}{\varepsilon_r}} \ln \left( \frac{b}{a} \right)
\]  

(3.1)
where $\mu_r$ is the relative magnetic permeability and $\varepsilon_r$ is the relative dielectric constant of the insulating medium separating the inner conductor of radius $a$ and the outer conductor of radius $b$ in a coaxial cable (for derivation see next section).

In the original design, a high temperature, 50 $\Omega$ characteristic impedance, rigid cable was designed. A platinum wire used as the inner conductor ($a = 0.5$ mm) was fed through a rigid, electrically insulating, silica tube ($a = 0.5$ mm, $b = 3$ mm, $\varepsilon_r = 3.81$) which was wrapped with a flexible copper wire mesh sleeve acting as the outer conductor. The flexible copper sleeve

![Diagram of the low frequency conductivity cell - original design](image)

**Figure 3.2**: Low frequency conductivity cell - original design
fits loosely and any physical contact changes the overall geometry of the cable. This effect results in a change in the characteristic impedance and could affect conductivity measurements, especially at high frequencies.

The top electrode in the conductivity cell is movable (see Figures 3.2 and 3.3) and for that reason the coaxial cable was designed to be flexible as well as to be able to withstand high

---

**Figure 3.3:** Electrode and cable connections for conductivity cell - original design
temperature. This cable was designed with platinum wire as the central conductor, alumina beads \((4.55 \leq \varepsilon_r \leq 8.4)\) as the flexible insulator and an outer conductor similar to the one used in the rigid cable assembly. The inconsistency in geometry due to the added flexibility of the cable and the variation in the permittivity of alumina may result in a length dependent characteristic impedance and errors in measurement especially in the high frequency region.

Another possible site where impedance mismatch occurs is where the homebuilt cables connect to the hermetic BNC connectors in the conductivity cell. If this connection point were modified or eliminated and cables with 50 \(\Omega\) characteristic impedance were used, then any errors in measurements could be attributed to the electrodes or the analyzer.

The cell is connected to the instrument with flexible, low temperature coaxial cables terminated on both ends with BNC connectors. This eases the processes of connecting the vertically standing conductivity cell. The connection points may also have some impedance mismatches. Decreasing the number of insertion points should decrease the number of potential impedance mismatches and therefore reflections.

The electrodes to hold the sample in the conductivity cell are also not symmetric. This means that the path length of the measurement signals is not the same and contributes to some shift in the phase, especially at shortest wavelengths (highest frequencies).

Lastly, the distance between the instrument and the sample is approximately 50 cm. Any decrease in length (decrease in line inductance) will improve the quality of the collected data.

Many flaws in the original design have been pointed out. To defend the original design, however, effects of lead lengths, impedance mismatches and path length do not contribute significantly at low frequencies and only at the highest frequencies are these effects problematic. For that reason, measurements using this cell design were of acceptable quality for the intended use.
3.1.2. Conductivity Cell Improvements

The upper temperature limit for making useful electrical measurements of glass is set by the glass transition temperature, \( T_g \). Most measurements are made approximately at \( T < T_g - 50 \). Above this temperature, glasses soften and their geometry changes making it difficult to accurately extract material properties. In the case of sulfide glasses, \( T_g - 50 \) is below 573 K for most compositions [95]. Most sulfide glasses could be examined using a conductivity cell with a temperature range of 100 to 510 K. Setting the upper temperature limit to 510 K allows the use of certain commercially available semi-rigid coaxial cables.

The problems with the cell have been defined in the last section. The following modifications to the cell should extend measurements capability in the 1 - 10 MHz region:

(a) Rigid cable should be used with a 50 \( \Omega \) characteristic impedance.

(b) A high degree of symmetry should be used in cell design. Alternatively stated, the distance between the positive and negative terminals to their connection point on the analyzer should be kept the same.

(c) The length between the sample fixtures and the analyzer should be decreased.

(d) All impedance mismatches should be minimized or eliminated.

Commercially available semi-rigid coaxial 50 Ohm cables\(^2\) made of copper wire as the inner conductor, Teflon as the insulation material and stainless steel as the outer conductor should be used. These cables have an upper temperature limit use of 230 °C. These cables should be directly connected to the impedance analyzer and, using a Swagelok feed-through, passed hermetically through the walls of the conductivity cell to connect to the sample fixtures. This design would have a 50 \( \Omega \) characteristic impedance all the way from the instrument to the sample electrodes.

\(^2\) Micro-Coax Components, Inc., Box E, Collegeville, PA 19426.
To increase the symmetry, the sample holder (fixtures) should be rotated 90°. This is a minor modification and would ensure that the length of the signal path through the connecting cables were all the same.

The rigidity of the cables force a modification to the method of connecting the cell to the analyzer. The instrument's test port and the cell connectors are perpendicular to each other. 90° bends in the cables or a horizontal loading scheme would alleviate this problem. The horizontal technique is preferred because it offers a decrease in the total lead length distance.

The design, development and testing of this work was done in collaboration with Joseph Kincs and details of this work will be reported in his M.S. Thesis [104]. Figure 3.4 shows a schematic of the new conductivity cell with the BNC connectors, cables, cable feed-throughs and the sample electrode fixtures. The only mismatch in the electrical connections between the instrument and the sample occur at points where the cables connect to the electrode fixtures. This discontinuity is anticipated to affect measurements greater than 10 MHz.

3.1.3. Characterization of the Optimized Conductivity Cell

The degree of extraneous contributions to electrical measurements due to the conductivity cell and leads were determined using the following experiment. Impedance measurements of (a) a 150 KΩ resistor in parallel to a 15 pF capacitor and (b) a 22 MΩ resistor in parallel to another 15 pF capacitor were carried out using the following configurations:

1. **Setup 1**: Measurements made using the Solartron 12601 Component Module connected directly to the Solartron 1260.

2. **Setup 2**: Measurements made using the Solartron 12601 Component Module connected to the Solartron 1260 with 30 cm long coaxial cables.

3. **Setup 3**: Measurements made using the Solartron 12603 Component Module connected to the Solartron 1260 (90 cm long coaxial cables).

4. **Setup 4**: Measurements made with original conductivity cell with pseudo-rigid cables.
Figure 3.4: Low frequency conductivity cell - new improved design [104]
5. **Setup 5**: Measurements made with improved designed conductivity cell.

Setup 1 is considered ideal and measurements for all other setups are compared to it. In setup 4, the cables in the original cell were replaced by rigid 50 Ω coaxial cables. A 15 pF capacitor was selected to simulate a glassy dielectric constant of 18 and the value for the resistors were selected to observe resonance behavior over two very different frequency regions.

Previously, measurements made by the Solartron 1260 using different lead lengths showed dramatic deviations and discontinuities in the data as shown in Figure 3.5. The solution to this problem is described below.

The 1260 applies a sinusoidal voltage wave of fixed magnitude and measures the vector current which varies with the magnitude of the impedance. There are 6 analyzers in the 1260,

![Graph showing electrical modulus data](image)

**Figure 3.5:** Electrical modulus data showing measurement errors are dramatically increased with increasing lead lengths and this effect can be reduced by manipulating the selection of current analyzers in the Solartron 1260.
each optimized for a particular current magnitude range. By measuring a wide range of RC components, it was observed that the amount of measurement error could be decreased by selecting a different current analyzer then the one selected automatically by the instrument. The selection of the appropriate current analyzer was a function of both magnitude and frequency. The most dramatic improvement to the measurements was in the 100 kHz - 1 MHz frequency range where it was observed that the 60 - 600 µA range current analyzer measurements are more accurate for currents between 10 - 60 µA than those measured by the designated 6 - 60 µA range current analyzer. By switching to the higher current analyzer for lower currents, accurate and precise measurements are obtained. Other frequency and current regions where this may similar problems occurred were noted and incorporated into a software algorithm to select the best current analyzer for the particular frequency and magnitude. This algorithm is found in Appendix B. This problem has been discussed with the manufacturer.

As an example, Figure 3.5 shows electrical modulus data for a 22 MΩ resistor in parallel to a 15 pF capacitor measured by the 1260 using different setups (lead lengths). The data for setups 1 - 4 allow the 1260 to internally select the best current analyzer while for setup 4b the analyzer is selected by the user defined software algorithm. The results of setup 1 exhibit no discontinuities for M' and may be considered as an ideal measurement. Setup 3 with the longest leads shows the largest deviation and discontinuity. The same features of approximately equal magnitude are observed for setup 2 and 4 but are less than that of Setup 3. The abrupt discontinuity in the data is attributed to a change in the analyzer. The gradual deviation from the data of setup 1 is due to an ineffective current analyzer being used in that particular frequency and impedance range. Data obtained for setup 4b are almost identical to the result of setup 1. Some deviation is observed at 100 KHz but the change in the current analyzer at approximately 150 KHz drives the curve back to that of setup 1. Measurements of various RC combinations (resonance frequencies) in setup 4b give similar results and the software algorithm has been incorporated into the data collection module.
Impedance measurements in the frequency range 0.1 Hz - 1 MHz for the two RC combinations were collected for the five setups. The data for all the setups were identical for frequencies less than 100 kHz. Impedance data, as mentioned before, may be viewed in various forms. Some forms reveal features more clearly and distinctly than others. Figures 3.6 and 3.7 show the phase of the impedance for all five setups. Even with the software algorithm, it is apparent in the frequency range between 200 - 800 kHz in Figure 3.6, that the largest deviation is observed for setup 3, followed by setup 4, 2 and 5, respectively. Elimination of lead length is crucial for quality measurements. The phase data for the 100 KΩ resistor in the same frequency range shown in Figure 3.7 are quite good for all the setups. The response of the newly designed cell is near ideal in this region.

Figure 3.6  Phase response of a 22 MΩ resistor measured in parallel with a 15 pF capacitor for the five setups defined in text
High frequency data in the range 1 - 10 MHz in both figures show scatter for all the setups. Surprisingly, the first prototype design gives better results than the final design but the difference is not that striking. Observe that the data obtained for setups 2-5 for the higher resonant frequency circuit (100 kΩ) where the phase is not close to -90° follow closely the results of setup 1 up to 7 MHz. The 22 MΩ circuit deviates for frequencies greater than 5 MHz. The results for setup 4 and 5 are close to those for setup 2. It is apparent that the quality of the high frequency data improve with a decreasing resistance in the parallel RC circuits. For glasses, the measurements should improve at higher temperatures. In summary, good conductivity data can be consistently obtained up to 5 MHz and even higher frequency data are attainable for glasses by heating them and shifting the conductivity dispersion region out of the high frequency range.
The prognosticated added capability of a decade of frequency was not attained. A significant overlap of 1 MHz to 5 MHz, however, was achieved between the anticipated high frequency and low frequency workstations. Furthermore, the new design makes the conductivity cell more robust and invariant. Overall a marked improvement in the low frequency impedance spectroscopy workstation capabilities has been achieved.

3.2. High Frequency (1 MHz - 1 GHz) Impedance Spectroscopy Workstation

Reliable impedance/dielectric measurements of materials in the frequency range 0.1 Hz - 1 MHz are typically performed using steady state bridges (frequency response analysis). For higher frequencies, where sample size begins to become comparable to the signal wavelength, new techniques such as resonance [33,104] and reflectometric methods [29,31,32,105] must be used. While the application of the resonance technique is restricted to a finite number of frequencies, rapid advances in instrumentation using reflectometric techniques offer opportunity to make measurements with high resolution over a wide frequency range. The Hewlett Packard (HP) 4191A RF Impedance Analyzer\(^3\) (1 MHz - 1 GHz) is an example of an instrument that uses reflectometric techniques. In this section, the design, construction, computer automation and characterization of an impedance spectroscopy workstation using the HP4191A is discussed.

In analogy to the goals set during the development of the low frequency impedance spectroscopy workstation reported in the author's Master's thesis, this workstation is designed and built to achieve the following performance criteria: (1) it must have a frequency range of 1 MHz - 1 GHz, (2) a temperature range of 100 K - 500 K, (3) the sample under study must be protected from mechanical abuse and environmental contamination and reaction during measurement, (4) software controlled to operate the complete experiment unattended once the experimental conditions are set, (5) after measurements are made, the data must be stored in a systematic manner for later identification and retrieval, (6) software must be user-friendly during experimental setup and data analysis.

\(^3\) Hewlett Packard, 8050 Foothills Blvd., Roseville CA 95678
. Before designing any instrumentation, the fundamentals of the experimental technique must be understood. A discussion of this is given in the first section. The instrument automation of the workstation can be divided into the assembling and programming of the equipment. The assembling part includes selection of instrumentation and the design of the conductivity cell and the furnace. The programming encompasses the development of a user-friendly interface for configuring the instruments, setting up the experimental conditions, controlling the entire IS experiment and storing the impedance data.

3.2.1. Principles of Reflectance Measurements

In the low (0.1 Hz - 1 MHz) frequency region, the physical dimensions of the electric networks are much smaller than the wavelength of the measuring signal and can be considered discrete and analyzed using lumped parameters. At higher frequencies, residual impedances, phase shifts, propagation losses and other unwanted effects incident to lumped constant measuring circuit parameters cause significant, and unacceptable measurement errors (see discussion in low frequency workstation section).

Vector measurements in the RF region are much easier handled by a distributed constant measuring circuit arrangement. In the low frequency workstation, impedance is determined by taking the ratio of the measured vector voltage over the sample to the measured vector current passing through the sample. At high frequencies, the reflection and/or transmission coefficient parameter values for a transmission line terminated with a sample are measured to obtain the desired characteristics of the sample.

A review of the theory of transmission lines and terminators is given first. Next, the principles of impedance measurements using transmission lines terminated with a sample are developed. Since coaxial cables are intended for use in both the low frequency and the high frequency workstation, the design, geometry and electrical characteristics are reviewed. Lastly, the section is concluded with a discussion of the problems and limitations encountered in the reflectometric impedance measuring technique. Details of the theory and discussion
presented below are found in most electromagnetic and microwave theory textbooks [105-110].

3.2.1.1. Transmission Lines  A transmission line is a system of material boundaries forming a continuous path from one point to another with the capability of guiding electromagnetic energy along its path. It is a waveguide that transmits electrical energy from a generator to a load. In general, a transmission line is composed of two conductors separated by a dielectric material. A transmission line where no electrical losses occur is considered ideal and it is called uniform if the cross-section perpendicular to the propagation of the electromagnetic energy is the same throughout the line.

A sinusoidal wave applied to an infinitely long transmission line will propagate along the line. In a medium other than air, the velocity ($3 \times 10^8$ m/s) of the wave is decreased by a factor $1/\sqrt{e_r}$, where $e_r$ is the dielectric constant of the insulator. In addition, at any point on the line, an equal but oppositely directed current flows in the two conductors and a voltage difference exists across the line. The spatial variation in the current and the voltage cannot be determined using lumped-circuit elements. A small section of a transmission line, however, can be analyzed using a lumped circuit analogy as shown in Figure 3.8. The transmission line could then be modeled by cascading the piecewise circuit along the lines length.

![Figure 3.8: Unit-length piece of parallel wire and its equivalent lumped-circuit model](image)
The equivalent circuit for a unit length $\Delta z$ of a transmission line is shown in Figure 3.8. All wires exhibit some resistance and according to the Biot-Savart law, wires are also inductive since a magnetic field is created around a wire when a current is passed through it. All conductors can therefore be described in terms of a resistor ($R$) and inductor ($L$) in series. The separation of any two conductors a finite distance apart forms some parallel capacitance ($C$). The dielectric medium separating the two conductors may not be ideal (lossy) and contribute to some conductance ($G$). It can be imagined that a transmission line is built of an infinite number of infinitely small lengths of this type of "two port" network connected in tandem (cascaded one after the other).

For harmonic time dependence, the telegraphist's equations describing the voltage and the current as a function of location along the transmission line and time can be easily written in terms of phasors as:

$$\frac{dV(z)}{dz} = (R + j\omega L)I(z) \quad (3.2a)$$

$$\frac{dI(z)}{dz} = (G + j\omega C)V(z) \quad (3.2b)$$

where $j$ is the square-root of $-1$ and $\omega$ is the angular frequency. The two equations can be combined to yield the following second order differential equations:

$$\frac{d^2V(z)}{dz^2} = \gamma^2 V(z) \quad (3.3a)$$

$$\frac{d^2I(z)}{dz^2} = \gamma^2 I(z) \quad (3.3b)$$

where

$$\gamma = \alpha + j\beta = \sqrt{(R + j\omega L)(G + j\omega C)} \quad (m^{-1}) \quad (3.4)$$
is the propagation constant whose real and imaginary parts, $\alpha$ and $\beta$ are the attenuation constant (Nepers/m) and phase constant (rad/m) of the line, respectively. These quantities are not really constants because, in general, they depend on $\omega$. The solutions to these differential equations are:

$$V(z) = V^+(z) + V^-(z) = V_0^+ e^{\alpha z} + V_0^- e^{-\alpha z} \quad (3.5a)$$

$$I(z) = I^+(z) + I^-(z) = I_0^+ e^{\alpha z} + I_0^- e^{-\alpha z} \quad (3.5b)$$

where the plus and minus superscripts denote waves traveling in the $+z$ and $-z$ direction, respectively. The forward and backward propagating waves in Eq. (3.5a) are both solutions to Eq. (3.2). The wave amplitudes for the forward voltage and current waveforms are determined by inputting the first derivative of the voltage function and the respective current function into Eq. (3.2a) or Eq. (3.2b). The same can be done for the backward propagating wave to yield the following result:

$$\frac{V_0^+}{I_0^+} = \frac{V_0^-}{I_0^-} = \frac{R + j\omega L}{G + j\omega C} = \frac{\gamma}{\sqrt{G + j\omega C}} \quad (3.6)$$

The above equation is the ratio of the voltage to the current at any point on the transmission line and is defined as the characteristic impedance, $Z_e$. Note that this value is independent of transmission line length, and depends only on the values of $R$, $L$, $G$, and $C$. If $R$ and $G$ are negligible in size, that is there are no absorbative loss on the transmission line, and the characteristic impedance is simply given by
The characteristic impedance in such a transmission line is frequency independent. This result is very significant and its importance is revealed in the next two discussions.

3.2.1.2. Terminated Transmission Line  A finite length, \( l \), transmission line connected to a generator and terminated with a load is shown in the Figure 3.9. The net voltage across the load is \( V_L \). A forward propagating wave from the generator and a reflected wave from the load may exist at the same time due to the discontinuity in the line produced by the insertion of the load. The net voltage across the load is

\[
V_L(l) = V_0^+ e^{\gamma l} + V_0^- e^{-\gamma l}
\]  

(3.8)

and the current flow into the load is

\[
I_L(l) = I_0^+ e^{\gamma l} + I_0^- e^{-\gamma l}
\]  

(3.9)

The load impedance, \( Z_L \), is given by the phasor ratio

\[
Z_L = \frac{V_L}{I_L}
\]  

(3.10)

Figure 3.9: Transmission line terminated with a load impedance
hence, the load current may be rewritten as

\[ I_L = \frac{V_L}{Z_L} \]  \hspace{1cm} (3.11)

The right hand side of the load current in Eq. (3.9) can be written in terms of the voltage and the characteristic impedance, \( Z_o \)

\[ I^+ + I^- = \frac{V^+}{Z_o} - \frac{V^-}{Z_o} = \frac{V_L}{Z_L}. \]  \hspace{1cm} (3.12)

The \textit{reflection coefficient} is the ratio of the reflected voltage to the applied voltage and is defined by

\[ \Gamma = \frac{V^-}{V^+} = \frac{V_o e^{-\gamma l}}{V_o e^{\gamma l}} = \Gamma_0 e^{-2\gamma l}. \]  \hspace{1cm} (3.13)

By writing \( V_L \) as in Eq. (3.8) and multiply through by \( Z_o/V^+ \) in Eq. (3.12), the terms can be separated to give the following equation for the \textit{reflection coefficient}:

\[ \Gamma = \frac{Z_L - Z_o}{Z_L + Z_o} \]  \hspace{1cm} (3.14)

and the load impedance

\[ Z_L = Z_o \frac{1 + \Gamma_0 e^{-2\gamma l}}{1 - \Gamma_0 e^{-2\gamma l}}. \]  \hspace{1cm} (3.15)

From the Eq. (3.14), it is quite apparent that there is no reflection when the transmission line is terminated with a load \( Z_L \) of impedance equivalent to \( Z_o \). All the power flows into the load and the line is defined as matched to the load. It is interesting to note that a finite length transmission line with a matched load gives the same response as an infinitely long transmission line.
The theory for impedance measurements using reflectance techniques is based on the result shown in Eqs. (3.14) and (3.15). If the characteristic impedance of a transmission line is accurately and precisely known then the impedance of an unknown load material terminating that transmission line can be determined. A measurement frequency sinusoidal signal is applied to the transmission line and the vector voltage of the reflected wave is measured. The reflection coefficient is calculated from the reflected and incident vector voltage and the result input into Eq. (3.15) to give the impedance of the sample.

3.2.1.3. Problems and Limitations of the Technique  Figure 3.10 is a linear-log plot of Eq. (3.14) with a varying resistive load and a characteristic impedance of 50 Ω. The most accurate and precise measurements are made for load impedance values within an order of magnitude of the characteristic impedance. The value of the reflectance coefficient varies greatly for small changes in the impedance in this range. For impedance magnitudes less than 0.1 Ω and greater 10 KΩ, the slope of the reflection coefficient curve is small. Small errors in measuring the reflection coefficient in this region would yield large errors for the calculated load impedance. The impedance range for accurate and precise measurements is clearly defined through Figure 3.10.

Up to this point in the discussion, transmission lines were assumed to be ideal. Real components are lossy and all electromagnetic radiation attenuates as it propagates down a waveguide. The attenuation constant, α, is affected by many factors such as the following:

1. Conductor losses (skin effect)
2. Dielectric losses
3. Hysteresis losses
4. Mismatch losses
5. Losses due to radiation
The losses due to the first three items dissipate energy. Mismatches cause reflections and radiation guide the energy away from the transmission line.

Conductor losses are caused by the series resistance of the conductor. As frequency increases, the current is restricted to travel only on the surface layer of the conductor due to the skin effect. The skin depth of the conduction layer is a function of frequency and resistivity of the material and is given by

$$\delta = \frac{1}{2\pi} \sqrt{\frac{\rho}{\nu \mu_r}}$$  \hspace{1cm} (3.16)
where \( \rho \) is the specific resistivity of the conductor (\( \Omega \text{cm} \)), \( \mu \) is the relative permeability of the conductor and \( \nu \) is the operating frequency in GHz. In the microwave frequencies, the skin depth is typically a small fraction of the conductor thickness. For a frequency varying from 1 to 1000 MHz, the skin depth for gold (\( \rho = 2.44 \times 10^6 \Omega \text{cm} \)) varies from an initial value of 78 to 2.5 \( \mu \text{m} \). The decreasing cross-section for current conduction contributes to losses, but this problem can be overcome by using highly conductive materials to keep the overall resistance low. Plating the conductor approximately three to five times the skin depth for the lowest transmitting frequency will assure conduction through the highly conductive material. Surfaces of conductors should be highly polished to decrease the path length of the current. Even microscopic scratches crossing the current flow can appreciably increase the equivalent resistance of the conductor.

*Dielectric losses* are due to the lossy nature of real insulating materials. Teflon is often used and losses in the microwave range for it are typically small. Great care must be taken in selecting low loss insulators.

*Hysteresis losses* are due to magnetic properties of the conductor and are included in the skin depth equation. Typically this feature is not dominant for conductive materials such as gold, silver and copper and therefore not very consequential.

*Impedance mismatch losses* are due to reflections of the propagating wave at discontinuities in the transmission lines. This discontinuities are due to a change in cross-sectional geometry or dielectric material which changes the values of the characteristic impedance. Discontinuities on transmission lines are more problematic at higher frequencies, especially as the wavelength begin to approach the physical size of flaws. The designer has much control in minimizing these effects by designing uniform geometry waveguides.

*Radiation losses* occur due to leaks in a waveguide. The electromagnetic wave will radiate out of a hole or a crack and cause losses. For solid waveguides this is not a significant problem, but at high frequencies cables have to be double and triple shielded to alleviate losses due to radiation.
3.2.1.4. Coaxial Transmission Lines A coaxial transmission line or cable was described in the section 3.1. as consisting of a center conductor with another conductor around it. A dielectric filler material may be added between the two conductors to ensure that the cross-sectional geometry does not change. Flexible cables take advantage of this setup. Typically, the best transmission lines are those with air instead of a dielectric spacer. These transmission lines have little flexibility but offer near ideal transmission line characteristics.

For many applications, both the inner conductor and the outer conductor in a transmission line are cylindrical. This shape is commonly used because long lengths of metal and polymer tubing can be extruded with very high uniformity. Figure 3.11 shows the configuration of a coaxial cable.

Determination of the characteristic impedance of cylindrical coaxial cable with a dielectric spacer is simplified by the nature of its geometry. The inductance ($L$), resistance ($R$), capacitance ($C$) and conductance ($G$) of a unit length of cable are easily determined from sophomore level electromagnetic theory. Only the results of these derivations are given here. The unit length inductance, for a cylindrical coaxial cable is given by:

$$L = \frac{\mu_0 \mu_r}{2\pi} \ln \left( \frac{b}{a} \right) \quad \text{H/cm} \quad (3.17)$$

where $\mu_0$ is the magnetic permeability of free space, $\mu_r$ is the relative permeability, $b$ is the inner radius of the outer conductor and $a$ is the outer radius of the inner conductor. The natural log relationship is a result of the cylindrical geometry. This equation neglects current penetration into the conductor. In

$$C = \frac{2\pi \varepsilon_0 \varepsilon_r}{\ln \left( \frac{b}{a} \right)} \quad \text{F/cm} \quad (3.18)$$

$\varepsilon_0$ and $\varepsilon_r$ stand for the permittivity of free space and the dielectric constant of the insulating material, respectively. The resistance given by
Figure 3.11: Configuration of a typical flexible and rigid coaxial cable
where $\delta$ is the skin depth (see last section) and $\rho$ is the resistivity of the conductor. Substituting Eq. (3.16) into the above equation shows that the resistance is proportional to the square root of the frequency. This effect becomes significant at very high frequencies. The conductance in a coaxial line is almost negligible if the conductors are separated by air or by a pseudo-ideal dielectric material such as Teflon. The conductance is a function of the dielectric loss, $\delta$, frequency and the capacitor, $C$, in parallel to give

$$G = \omega C \tan \delta.$$  \hspace{1cm} (3.20) 

Combining these equations into Eq. (3.6) gives a fairly complicated result. If losses are small or negligible, then $R$ and $G$ are very small and the result simplifies to Eq. (3.7). Inputting Eq. (3.18) and (3.19) into Eq. (3.7) gives the characteristic impedance for a coaxial cable

$$Z_0 = \sqrt{\frac{L}{C}} = \sqrt{\frac{\mu_0 \ln \left( \frac{b}{a} \right)}{2\pi \rho_{\delta} \tan \delta}}.$$  \hspace{1cm} (3.20)

The above equation can be used to design cables/transmission lines with a specific characteristic impedance by varying the ratio of diameters of the two conductors and choosing the appropriate dielectric medium.

3.2.1.4. Summary To summarize this section on principles of measurements, the definition of transmission line was given. Theory was developed to define the line's characteristic impedance through the use of distributed piece-wise circuits. Wave propagation and reflection through a waveguide were discussed. It was pointed out that terminating a
A waveguide with a load introduces a discontinuity in the line and contributes to reflections. These reflections can be used to get information about the electrical properties of the load (see Eq. (3.14)). Limitation in the impedance measuring range was shown through Figure 3.10. Anticipating building a transmission line to make high frequency measurements, a discussion about materials and losses due to different mechanisms and transmission line geometry were discussed. With this solid background on transmission lines, the design of the high frequency impedance spectroscopy workstations is addressed next.

3.2.2. Instrumentation Hardware

A block diagram for the impedance spectroscopy workstation is shown in Figure 3.12. In order to computer automate this workstation, it was necessary to purchase an impedance analyzer, temperature reader and temperature controller that were all computer interfacable. To meet the objectives of both ease of programming and flexibility in the system, it would have been preferred that all the devices were computer interfacable through one common communication link such as the general purpose interface bus (IEEE-488 GPIB). In the present setup, however, only the HP-4191A analyzer is connected to the computer through the GPIB bus. The temperature controller is connected to the RS-232 port on the IBM-PC. Due to the rapid miniaturization of electronic devices, commercial analog-to-digital IO computer cards are available for direct installation inside computers. A signal conditioning card for temperature measurements using thermocouples is connected to an A/D converter installed in the computer. Three different software drivers had to be developed to ensure computer control of each device in this workstation. A general description of each instrument and their capabilities is given next. A complete explanation of the design, materials and implementation of the conductivity cell and the furnace is emphasized.

3.2.2.1. Computer controller The controller for the workstation is an IBM compatible 50 MHz 486 Apex PC running the Microsoft MS-DOS operating system. It has 210 megabyte hard drive, a 1.5 megabyte 3.5" floppy disk drive and 320 Kbyte floppy disk drive for data storage. The computer is connected to a Hewlett-Packard Laserjet III printer
Figure 3.12: Block diagram of high frequency impedance spectroscopy workstation
through an Ethernet card. GPIB capability is nonstandard to most IBM compatible PCs, and for this system is provided by a commercially available GPIB-IO card (CIO-PC2A) from Computer Boards, Inc.\(^4\) The card is inserted in one of the expansion slots and with the provided software drivers (CIO-PC2A-DRV) is immediately ready for use with most high level computer languages. Instructions for installation of this card and programming are found in their respective user’s manual \([111,112]\). The HP-4191A bridge \([113]\) is assigned the GP-IB address 16 and is connected to the GPIB card for instrument control and data acquisition.

A multifunction analog and digital IO card (CIO-DAS08) is also installed in one of the expansion slots in the computer \([114]\). A temperature signal conditioning card (CIO-EXP16) is connected to the A/D card and provides means for digital temperature measurements \([115]\). Both card are available from Computer Boards, Inc. More detail about the arrangement is given in the temperature reader section.

Finally, the Eurotherm 808 temperature controller is connected to the computer through the RS-232 port \([116,117]\). Special software had to be developed to provide communications between the two instruments and will be discussed in the temperature controller section.

3.2.2.2. Impedance Analyzer The Hewlett Packard 4191A RF Impedance Analyzer is used to collect impedance data in the 1 - 1000 MHz frequency range in this workstation. The instrument uses the reflectometric impedance measuring technique described in the section. It generates a voltage signal to a test port where a device under test (DUT) is connected and measures the reflected signal using a vector voltage ratio detector. A summary of the basic measurement theory described in the instruments operational manual \([113]\) is given below.

The block diagram for the HP-4191A is shown in Figure 3.13. The signal source produces a 1 - 1000 MHz sinusoidal signal from the output of a crystal oscillator using a special frequency synthesis technique. The measurement signal is applied to the input of the directional bridge unit where it is divided by a power splitter, and flows to the test channel and the reference channel. The reference channel signal provides the amplitude and phase references

\[^4\] Computer Boards, Inc., 44 Wood Avenue, Mansfield, MA 020408
Figure 3.13: HP-4191A block diagram [113]
for the test channel signal to be measured. The test channel signal is input to the RF directional bridge network to be applied to the DUT. The signal travels from the test port to the DUT and the reflected signal returns to the test port. The directional bridge yields a vector voltage output in response to the reflected wave representing the electronic characteristics of the DUT. The technique to separate the incident and reflected signal is quite elegant and is described below.

The conceptual directional bridge circuit is composed of five fixed value resistors and the DUT, as shown in Figure 3.14. All the resistor elements have the same value as the characteristic impedance (50 Ohms) of the measuring circuit. A test signal is applied with an amplitude \( V^* \) in the direction of \( I_1 \). The signal currents or voltages can be summed using Kirchoff's law to give the following equations for Figure 3.14:

\[
I_2 + I_3 = I_1 \quad \text{(3.21a)}
\]

\[
ZI_1 + ZI_2 + Z(I_2 - I_4) = V^* \quad \text{(3.21b)}
\]

\[
ZI_1 + ZI_3 + Z(I_3 - I_4) = V^* \quad \text{(3.21c)}
\]

Figure 3.14: Basic directional bridge circuit [113]
These simultaneous equations are solved for $I_4$ to yield

$$ZI_2 + ZI_4 = ZI_3$$

(3.21d)

Multiplying through by $8/V^+$ gives the value for the reflection coefficient:

$$8V^- = \left( \frac{8}{V^+} \right) \left( \frac{1}{8} \right) \left( \frac{Z - Z_x}{Z + Z_x} \right) V^+ = \Gamma$$

(3.23)

In the HP-4191A, the bridge arm for $I_4$ is replaced with an RF transformer to obtain $V$ and is shown in Figure 3.15.

![Diagram of directional bridge circuit]

Figure 3.15: Directional bridge circuit of the 4191A

The HP-16091A coaxial termination fixture is a sample holder and can be described as a near ideal, uniform transmission line of length 1.87 cm with fixtures to terminate the line with a sample. This unit can be connected to the test port of the instrument through an Amphenol
Precision Connector (APC-7). This effect of the additional wave path length of 2 x 1.87 cm is equalized by increasing the path length of the reference channel by connecting an electrical length compensator cable as shown in Figure 3.13. The path length of the compensator cable should be twice that of the signal path length between the transmission line and the test port. This makes the relative phase shift between the reference and the test channel signals small, and keeps measurements errors to a minimum. The apparent path length, \( l' = \frac{l}{\sqrt{\varepsilon_r}} \), varies according to the dielectric medium of the transmission line and it's length, \( l \), by the following equation

\[
l' = \frac{l}{\sqrt{\varepsilon_r}}.
\]  

The apparent length of the compensating cable should be twice that of the apparent length of the transmission line. The option to change the electric length cable compensator offers opportunity for heating and cooling the DUT by extending a transmission line from the test port to a safe distance from the instrument and hence decoupling it from the heat source or sink.

The reflected test signal and the reference signal are output of the RF directional bridge unit and converted 100 kHz signals. By converting all measurement frequencies to 100 kHz, state-of-the-art technology in the low frequency vector measurements, such as a precision phase detector, can be used to make high quality measurements. Additionally, the conversion to one frequency facilitates optimizing the operating performance of the actual circuits to achieve accurate vector measurements.

The vector ratio of the reference and test channel signals is detected for both the real and imaginary component vectors. This components coincide with the components of the measured vector reflection coefficient. Other measurement parameters, such as impedance, are calculated from the values determined above.

The directivity errors in the bridge circuit, undesired reflections of the measurement signal in the line between the test port and the DUT due to mismatches, inappropriate electric length compensator cable and other factors related to the inaccuracy of the measurement cir-
cuit will result in considerable errors in the measured vectors. If the errors are minor, then measurement values involving these errors are automatically corrected by determining the error vectors at the frequencies where the measurements are taken. The auto-calibration function of the HP-4191A calculates the error vectors from the measurements of three reference terminations; 0 Ω, 0 S and 50 Ω. The calibration data obtained from the reflection coefficient measurements for the reference terminations is stored in the memory of the HP-4191A and is used to correct for the measured vectors of the DUT's.

The instrument is set manually or remotely through the GPIB (IEEE-477 Standard) using a computer. Data are available through LED displays on the front side of the instrument or can be ported to a computer through the GPIB interface bus.

3.2.2.3. Furnace Temperature Controller The Eurotherm 808 temperature controller is a microprocessor-based instrument with a hardware programmable temperature range and 1 °C resolution. It allows the user option to select thermocouple type and has autotuning PID feature and a RS-232 communication link [116,117]. The instrument has been configured to have a temperature control range of ±250 °C and a Type T thermocouple as its input. The temperature is set digitally by the computer through the RS-232 port and temperature readings can be ported from the Type-T T/C back to the computer through the same link.

The temperature controller has a 0-5 V logic output which is used to control the on and off cycles of the furnace. The logic output is connected to the control side of a solid state relay (SSR240DC25) obtained from OMEGA. When the control side logic is high, the load side switches on and allows current to flow through the relay and hence the furnace and a 10 A quick blow fuse. The power supply for the furnace is completely isolated from the temperature controller. The schematic of the connections is shown in Figure 3.16. The electrical wiring of the furnace heater is given in the furnace section of the cell design.

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5 Eurotherm Corporation, 1842 Centerpoint Dr., Suite 106-S, Naperville, Illinois 60563

6 OMEGA Engineering, Inc., P. O. Box 4047, Stamford, CT 06907-0047
The temperature controller has three term control - proportional, integral and derivative (PID). The three parameters are proportional band, integral time constant and derivative time constant and can be set to give optimum control and steady-state conditions in the furnace. The controller has an auto-tuning feature which can select the optimal settings and allow as rapidly as possible the attainment of steady-state conditions and optimal control at the set point.

The temperature controller measures the temperature of the furnace through a Type-T thermocouple (T/C). Type-T T/C are best suited for subzero temperatures and can be used in oxidizing, reducing, inert or vacuum atmospheres up to 370 °C [118]. The controller has an internal cold junction point allowing it to calculate the temperature (see next section for explanation). The temperature is digitally displayed at all times. Secondary calibration all T/C's was done using a calibrated precision platinum resistance temperature detector (RTD). Details of this experiment are explained in the conductivity cell characterization section.

3.2.2.4. Temperature reader The sample temperature is measured using a Type-T T/C. A thermocouple is made of two dissimilar wires touching each other at one end. As a result of this contact, a temperature dependent voltage is produced and is called the Seeback
voltage. The method for acquiring and determining the temperature from the T/C Seeback
voltage is discussed here.

The Seeback voltage is typically very low (mV) and without amplification, differences in
voltage measurements (40 μV/°C) are not resolvable by most analog-to-digital devices. Using
an amplification gain between 100 - 800, gives a temperature resolution of 0.5 - 0.07 °C.
Most A/D converters have a measuring range of ±5 V, hence impose an upper limit on the
value for the gain. If the upper limit is not taken into account, then data clipping will occur at
highest temperatures.

As mentioned above, all dissimilar wires on contact produce a voltage. This includes the
point where the T/C lead wires connect to the measuring circuit (cold junction). This effect is
corrected for by knowing the cold junction voltage and adding its effect to the measurement.
The sum of the two voltages is input into a linearization equation to give the temperature.

The CIO-EXP16 is ideal for T/C signal conditioning. It has up to 16 multiplexed T/C in­
puts, a controllable gain amplifier and a semiconductor cold junction temperature sensor. The
selected amplified T/C signal and the cold junction voltage are ported to a A/D converter and
made available to the computer.

The A/D converter used for this purpose is the CIO-DAS08 which is a Metrabyte Das-8
close. This card is directly input in one of the slots in the computer controller. It has four
controllable digital output lines to select 1 of 16 T/C inputs and up to 8 analog single ended
input channels.

The A/D converter is configured for ±5V. An amplifier gain of 300 is set on the
CIO-EXP16 card. These two settings allow a maximum measuring range of ±400 °C and a
measuring resolution of 0.2 °C. Using hardware jumpers on the CIOEXP-16, the T/C voltage
and the cold junction compensator voltage are output to channel 0 and channel 1, respectively.
These output signals from the CIO-EXP16 are input to the CIO-DAS08 single ended inputs.
The device converts the analog signal voltage to a digital value. Computer control of this
card and data acquisition are available through software drivers provided by T-Tools\(^7\).

A software algorithm calculates the temperature by adding the two voltages and inputting the result in the following seventh order linearization equation:

\[
T = a + bV + cV^2 + dV^3 + eV^4 + fV^5 + gV^6 + hV^7
\]  

(3.25)

where

\[
\begin{align*}
a &= 1.00860910 \times 10^{-1} & e &= -9.247486589 \times 10^6 \\
b &= 2.572794369 \times 10^4 & f &= 6.97688 \times 10^{11} \\
c &= -7.673458295 \times 10^6 & g &= -2.66192 \times 10^{13} \\
d &= 7.802559581 \times 10^7 & h &= 3.94078 \times 10^{14}.
\end{align*}
\]

The data acquisition rate is very fast and a large number of temperature measurements can be measured and averaged. The software to control and acquire data is called \texttt{<ReadTemp.Pas>}. 

3.2.3. Conductivity Cell Design and Setup

The design of a conductivity cell is sample and user specific. For the purpose of this project, FIC chalcogenide glasses will be studied using this workstation. Chalcogenide glasses decompose rapidly in air and as such are stable only in an inert gas environments. Loading the conductivity cell with the glass sample has to be done in a glovebox after which it is transported to the high frequency impedance spectroscopy workstation. The conductivity cell has to accommodate these needs, as well as allow impedance measurements to be made with accuracy and precision.

The cell is designed to be (1) hermetically sealed in order to protect the glass from decomposition, (2) small enough to pass through the glovebox exchange chamber, (3) easy to handle and manipulate during operations in the glovebox, (4) able to heat up or cool down

\(^7\) Quinn-Curtis, 35 Highland Circle, Needham, MA 02194, USA.
rapidly, (5) able to withstand the temperature range of ±230 °C and (6) electronically noise-free so as to not affect impedance measurements due to unnecessary losses.

The fundamental understanding and limitations of the measurement technique and the HP-4191A are needed for the next discussion. The reader is recommended to review Section 3.2.1. on the principles of reflectance measurement and the Section 3.2.2 describing the operations of the impedance analyzer.

The first detailed description of a setup for making wide temperature radio frequency reflectivity measurements was reported in 1989 by Bohmer et al. [32]. This design is used as the prototype for developing an equivalent or better design. The Bohmer workstation meets all the requirements mentioned above except for hermeticity and ease of sample loading.

The setup developed for this project is shown in Figure 3.17. The sensitive electronics circuitry in the directional bridge near the test port of the analyzer must be maintained at a constant ambient temperature. For temperature-dependent measurements, the analyzer is thermally decoupled from the sample by extending a transmission line away from the test port. A DUT in a sample holder terminates the transmission line. The sample holder temperature is increased with electrical heaters or decreased through a coldfinger and reflection data are collected on approaching steady-state temperatures.

At extreme temperatures, heat loss to or gain from the ambient environment are maximum. This can result in instability in the temperature control. Furthermore, at cryogenic temperatures water condensation becomes a problem. Water condensing on any surface of the transmission line would change either the insulating medium or the geometry of the waveguide and introduce unaccounted reflections. Both these problems are eliminated by surrounding the setup with a vacuum chamber.

An overview of the setup in Figure 3.17 has been given. AutoCad drawings for the components designed and manufactured in this setup are found in Appendix C. Each major component in the overall design is discussed in detail below. These components are the transmission line, sample holder, vacuum chamber and the temperature control facility.
Figure 3.17: High frequency conductivity cell and temperature control setup
3.2.3.1. Transmission line  The waveguide used in this setup is a commercially available 20 cm airline (HP-11567A) from Hewlett Packard and is shown in Figure 3.18. The setup of the transmission line is similar to that of Figure 3.11. Two polymer dielectric rings (bead) near each end of the airline hold the berillium/copper alloy center conductor (o.d. = 3 mm) concentric to the outer aluminium conductor (i.d. = 7 mm). The characteristic impedance for this waveguide is 50 Ω and is calculated through Eq. (3.20) using air as the dielectric medium. Each end is terminated with a characteristic 50 Ω impedance APC-7 sexless connector. One end of the airline can be directly connected to the APC-7 connector at the test port of the HP-4191A and the other end to the sample holder.

The APC-7 stands for Amphenol Precision 7 mm 50 Ω Connectors developed by Amphenol Corporation\(^8\) and is shown in Figure 3.19. The coupling mechanism is sexless thus permits any two connectors in the 7 mm line size to be interconnected. The electrical and mechanical contact is made in an identical plane permitting accurate determination of the electrical length of a mated pair of connectors or of the total arrangement.

By replacing the low temperature dielectric spacers in the airline with Teflon and minor modifications to the geometry of the APC-7 connectors to maintain a 50 Ω characteristic impedance, the upper temperature limit of the airline may be extended to 230 °C and one end of the airline can be hermetically sealed. The spacer bead at the hot end of the airline is replaced with a Teflon spacer inserted firmly in an aluminium ring to maintain the characteristic impedance of the airline. The dimensions are given in Table 3.1.

The spacer bead at the bottom end of the airline is replaced with a Teflon spacer to provide a hermetic seal. The length of the airline is decreased by 2 mm to make space for a 1 mm thick brass washer and the 4 mm thick Teflon spacer inserted in the APC-7 connector. The opening on the airline side of the APC-7 connector is bored through to accommodate these two rings. The hole diameter of the Teflon bead is made slightly smaller than the diameter of the inner conductor to ensure a snug fit. The Teflon spacer sits between the airline and the brass

\(^8\) Amphenol Corporation, 358 Fall Ave., Wallingford, CT 06492
7mm air line

Figure 3.18: Extension of test port using a 7 mm air transmission line. The assembly diagram shows the inner (3 mm) and outer (7 mm) conductors terminated at each end with APC-7 sexless connectors [119]
Figure 3.19: Schematic showing dimensions of the precision 7 mm sexless (APC-7) connector [119]
washer. On tightening the APC-7 connector, pressure is applied on the Teflon spacer by the surface in contact with the airline and the brass washer. The Teflon deforms and fills cavities and spaces at the contact points and makes a hermetic seal. The dimensions of the two rings are given in Table 3.1 and were selected to maintain a characteristic impedance of the airline.

<table>
<thead>
<tr>
<th>Location</th>
<th>Inner (mm)</th>
<th>Outer (mm)</th>
<th>Dielectric Medium</th>
<th>Length (mm)</th>
<th>$Z_0$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Airline</td>
<td>3.042</td>
<td>7.00</td>
<td>Air</td>
<td>200.00</td>
<td>50.01</td>
</tr>
<tr>
<td>High temperature end - airline</td>
<td>1.520</td>
<td>5.10</td>
<td>Teflon</td>
<td>2.96</td>
<td>50.12</td>
</tr>
<tr>
<td>Hermetic seal end - airline</td>
<td>3.042</td>
<td>10.16</td>
<td>Teflon</td>
<td>4.00</td>
<td>49.93</td>
</tr>
<tr>
<td>Hermetic seal - cell</td>
<td>3.042</td>
<td>10.20</td>
<td>Teflon</td>
<td>4.00</td>
<td>50.09</td>
</tr>
</tbody>
</table>

To decrease heat flow through the airline, an 8 cm length of the airline (outer conductor tube) was ground down to a diameter of 8 mm. This bottleneck in the outer conductor and the 3 mm diameter inner conductor allow the heat flow through the airline of approximately one joule per hour, calculated for a temperature difference of 200 K. This slow flow rate is sufficient to thermally decouple the analyzer from the heat source or sink near the sample.

The airline is passed hermetically through the bottom of the vacuum chamber with a compression fitting. The airline is mechanically supported inside the vacuum chamber to minimize stress to the thin walls of the airline. A U shaped 33.3 cm long semi-rigid (0.141" O.D.) electrical length compensator cable with SMA connectors at each end is connected to increase the path length of the reference channel on the HP-4191A to account for the additional signal path length due to the transmission line in the measuring circuit.

3.2.3.2. Sample holder The HP-16091A test fixture provided with the HP-4191A analyzer is shown in Figure 3.21. It is a 1.87 cm transmission line and offers minimal imped-
ance mismatches from the electrode system immobilizing the sample. The geometry of the test fixture was optimized by Hewlett Packard to give high quality measurements. This test fixture was modified to meet the experimental requirements to act as the sample holder.

The base sleeve labelled (2) in Figure 3.20 is replaced with an identical sleeve (labelled hermetic bottom in Figure 3.21) but with a larger diameter and a 1.25 " groove for a Viton O-ring. The bead labelled (4) is similar to the one in the airline and is replaced with a 10.2 mm diameter Teflon ring. The thickness of the Teflon ring is slightly greater than the depth of the

Figure 3.20: Exploded view of the HP-16091A test fixture [111]
Figure 3.21: Machining schematic of components used in the high frequency conductivity cell to hermetically seal, heat and cool the cell. An exploded view of the assembled cell is also given.
groove in the hermetic bottom. The groove diameter is also increased to make a snug fit for the Teflon ring. The center electrodes (3) and (4) are replaced by two 3 mm diameter electrodes with a 0.5 mm ridge placed 1.5 mm from the end of the side where they can be threaded together. The electrodes fit tightly through the hole in the Teflon ring. On tightening the two electrodes, the ridges on each electrode apply pressure on the ring and deform the Teflon to make a hermetic seal between the ring and the center electrodes.

The ratchet fixture (10) is designed to apply pressure and make good electrical contacts with the waveguide and the sample. During heating, some glass samples broke and it was hypothesized that the ratchet fixture mobilized on one end expanded on the other end and crushed the glass. Figure 3.22 shows a spring loaded, threaded tube terminated with a piston-like brass cylinder, machined to have good thermal contact with the sleeve. The new fixture is flexible and transfers heat to the sample quickly and is easy to use in a glovebox.

Figure 3.22: Original top electrode assembly is replaced by a movable, spring loaded electrode in the HP-16091A test fixture
3.2.3.3. Hermetic Container  The modified HP-16091A test fixture fits snugly into
the cylindrical brass block labelled hermetic cap in Figure 3.21. The exploded view shows
how the base of the hermetic container sits on modified hermetic bottom of the test fixture.
Tightening the screws deforms the Viton or Teflon O-ring between the two interface and
makes an hermetic seal. The hermetic container and the test fixture constitute the con­
ductivity cell and is extremely compact with a height of 9 cm and a diameter of 4.5 cm.

3.2.3.4. High temperature facility  The hermetic container also acts as a thermal
block. Two, 4 inch, 250 watt electric cartridge heaters (CIR-1025/120) from OMEGA Engi­
neering, Inc., are inserted in 4 " deep holes spaced 180° on the top side of the hermetic con­
tainer (see Figure 3.21). The heaters are electrically wired in parallel. Heat in the hermetic
container is quickly conducted to the sample through the large contact surface area between
the hermetic container and the machined to fit test fixture. A Type-T T/C is used as the fur­
nace temperature sensor and is embedded in a 3 " hole next to one of the heaters. A stainless
steel tube sealed on one end, is hermetically passed through the center of top side of the ther­
mal block using a compression fitting. The sealed end of the tube resides in the hole of the
modified top electrode (see last section). It is anticipated that the temperature of the T/C in­
serted all the way to the end of stainless steel tube is a measure of the sample measurement.

An electrical panel (see Figure 3.21) to mount jacks for the heater power supply and
T/C's is connected on the top side of the cell. The exploded view shows how the panel is fas­
tened and thermally isolated from the heat source. The compact design of the cell makes
loading the cell very manageable and the electrical panel facilitates the connecting of the electri­
cal leads and T/C wires. The small design is easy to transport and load and extremely robust.

3.2.3.5. Low temperature facility  A liquid nitrogen dewar was specially designed
for this experiment and is shown in Figure 3.24. It is made of a stainless steel container,
wrapped with highly reflective aluminum foil and hermetically welded inside another stainless
steel container except for matching holes near the bottom of the lower half side of of each
container. Contact between the two containers occurs only at the mouth. The hole in the in­
Figure 3.23: Schematic of liquid nitrogen dewar
ner container has 1.25 " NPT female threads. A specially designed dewar cold finger adaptor made out of copper (see Figure 3.23) with 1.25 " NPT male threads, hermetically seals the inner conductor. A vacuum seal flange is welded on the outside of the the hole in the outer container. A 2 cm long cold finger (2 cm diameter copper rod) plugs directly into the dewar cold finger adaptor. The plug on the coldfinger has been designed to ensure maximum surface contact between the adaptor and the cold finger over the whole temperature range.

Another specially designed conductivity cell cold finger adapter or collar is slipped over the conductivity cell as shown in Figure 3.21. It is machined to fit over the hermetic container and bottom to a very high tolerance. The surface contact between the collar and the cell is further increased by tightening a screw which decreases the diameter of the collar. The coldfinger from the dewar, plugs into the conductivity cell cold finger adaptor. The dewar and the bottom vacuum chamber are hermetically sealed to each other through their respective flanges. The vacuum used to insulating the conductivity cell is shared with the dewar. On pulling a vacuum on the setup and filling liquid nitrogen in the dewar, heat rapidly flows out by conduction from the sample to the conductivity cell, to the cell cold finger adaptor, to the cold finger, to the dewar cold finger adapter and ends up boiling the liquid nitrogen. Up to four liters of liquid nitrogen is needed to cool the thermal mass of the dewar, the coldfinger and adpater and the conductivity cell.

The following steps were taken to improve the cryogenic capabilities of the low temperature facility. The vacuum in this setup is used to eliminate condensation and heat conduction by air between the outer container and the the inner container and to eliminate convectional currents. The long neck separating the inner container and the outer container of the dewar and the choice of material (steel) is intended to decrease heat flow from the outside container to the inner container. The reflective aluminum foil around the inner container decreases absorption by radiation. Cryogenic design fundamentals are found in references [120,121].

3.2.3.6. Vacuum Chamber The vacuum chamber is composed of three units: the bottom, top and dewar. During the heating process, only the bottom and the top are used and
are sealed to each other through a rubber "L" ring. The connection point of the dewar to the bottom chamber is sealed using a blank flange. The vacuum chamber top has a low pressure meter and a T/C pressure sensor attached to it. The assembly pulls together and seals rapidly on turning on a roughing vacuum pump. To separate the unit after an experiment, air is leaked back into the chamber through a leak valve also located on the vacuum chamber top.

3.2.4. Temperature Characterization and Control

3.2.4.1. Thermocouple Calibration Calibration of the furnace and cell Type-T thermocouples used in this experiment was done using a calibrated precision platinum resistance temperature detector (G1Pt50) supplied by OMEGA. Both uncalibrated thermocouples and the RTD were inserted in holes approximately 5 mm apart and 8 cm deep in the hermetic cap/furnace block of the conductivity cell. The brass block has a large enough thermal mass and high enough conductivity to assume limited thermal gradients between the sensors.

The temperature for the T/C's were read directly from the temperature controller and the temperature reader. The RTD was connected to a digital multimeter (Tektronix M50M20) and the measured resistance was converted to temperature using the following equation [118]

$$T_{RTD} = -243.498 + 2.306R + 0.00126532R^2 .$$  \hspace{1cm} (3.25)

For secondary calibration, the block temperature was increased by energizing the electric heaters in the block using the temperature facility described in the last section. The temperature was ramped from 30 to 200 °C in steps of 5 °C. The temperature of the sensors were recorded when ten consecutive temperature (RTD) readings spaced over ten seconds differed by no more than ±0.02 °C. The brass block was also submerged in a liquid nitrogen and an ice water bath for calibrating the thermocouples at subambient temperatures. The results of the experiments for each thermocouple are shown in Figures 3.24 and 3.25.
Figure 3.24: Calibration of Type-T sample thermocouple against OMEGA precision RTD

The calibration data may be divided into a low temperature region where only two calibration data points are available for fitting and a high temperature region where there are many data points available for fitting. The fits for the cell thermocouple are given by

\[ T = 0.992469 T_{\text{Cell}} + 1.02674 \quad T \geq 0 \]

and

\[ T = 1.01132 T_{\text{Cell}} + 1.21359 \quad T < 0. \quad (3.26) \]

and for the furnace thermocouple are given by

\[ T = 0.998211 T_{\text{Furnace}} - 0.215155 \quad T \geq 0 \]
Both thermocouples are in good agreement with the calibrated value.

To set the furnace to a desired set point temperature, the actual set point has to be modified by the following equation:

\[
Controller_{sp} = 1.00173 \text{Setpoint} + 0.221208.
\]  

(3.27)

3.2.4.2. Sample Temperature Calibration The furnace and cell thermocouples were inserted in their respective sites in the conductivity cell. The RTD was loaded to act as the
sample in the cell. A vacuum was pulled to simulate a real experiment. The conductivity cell was ramped from 20 °C to 180 °C in steps of 10 °C and the RTD temperature was used to determine steady-state temperature. On achieving steady-state, the setup was allowed to stabilize for an additional 25 minutes. The temperature-time profile of all the sensors are shown in Figure 3.26.

![Figure 3.26: Time-temperature profile of the DUT (RTD), the cell and furnace thermocouple in the conductivity cell](image)

Furnace Temperature is hottest followed by cell temperature and sample temperature.
At low temperatures, the calibrated temperature values for the cell and the furnace thermocouples are in close agreement to each other. However as temperature increases, the two measurements deviate from each other. This trend is also observed for the RTD but with a much larger deviation. In fact, when the furnace temperature is stabilized at 180 °C, the steady-state RTD temperature is 173 °C. This temperature difference is an effect of the separation distance between the sensors and the deviation increase with temperature indicates increasing heat losses to the environment due to temperature gradients.

Figure 3.27: Approach to steady-state temperature response of conductivity cell ramped from 100 °C to 120 °C
This following discussion explains how the sample temperature is determined. Figure 3.27 is a blow up of Figure 3.28 and shows both the transient and steady-state temperature response. The transient response in region one takes less than 5 minutes and steady-state (±0.1 °C/min) takes approximately 3 minutes for both the sensors in the furnace and the cell. The temperature profile for the RTD, however, is more sluggish. By waiting an additional 16 minutes, the RTD sensor temperature stabilizes with less than ±0.05 °C/min deviation. The difference between the cell and the RTD temperatures is almost a constant and is due to a steady-state heat losses. As long as the ambient temperature does not vary much, the temperature of the sample may be determined by calibrating the state cell sensor measurements to the RTD measurements at steady-state. The result of this calibration is given in the equation given below:

\[
T_{\text{sample}} = 0.9677T_{\text{cell}} + 1.0285 \quad T \geq 0.
\] (3.28)

The result in Figure 3.27 shows that the temperature of the sample is less than the desired set point temperature. The furnace needs to be heated to a higher temperature to raise the sample temperature to a defined value. The equation of the line generated by plotting the steady-state temperature readings for the sample against the furnace can be used to alleviate this problem and is given below:

\[
T_{\text{setpoint}} = 1.03T_{\text{sample}} - 1
\] (3.29)

The above equation is used to estimate the applied furnace temperature necessary to raise the sample temperature to a chosen value.

3.2.4.3. Steady-State Temperature (T \geq 0) To determine whether the sample temperature is at steady-state, the results of Figure 3.27 are used. The cell sensor approaches steady-state within 6 minutes of ramping but it is apparent that the same is not true for the sample. By waiting an additional 16 minutes, all the sensors including the sample achieve
steady-state. From this information, steady-state temperature for the sample will be determined by waiting an additional 20 minutes after the cell sensor has achieved steady-state.

3.2.4.4. Cryogenic Calibration To determine the sample temperature using the cell sensor, the RTD was loaded in the cell and sealed. The liquid nitrogen dewar, coldfinger, and

![Figure 3.28: Cooling and warming curve of conductivity cell in cryogenic experiment](image-url)

Figure 3.28: Cooling and warming curve of conductivity cell in cryogenic experiment
the collar were connected to the cell and evacuated. The dewar was filled with liquid nitrogen and all three temperature sensor measurements were recorded as the conductivity cell cooled and then warmed as the liquid nitrogen evaporated. The results are shown in Figure 3.29.

The cooling curve shows that temperature gradient in the cell between the sample and the cell and furnace sensors. The lowest temperature attainable is approximately -130 °C. The whole cell can be cooled within 90 minutes. The warming profile shows some scatter in the temperature readings of the RTD due to water condensation. The heat flow to the sensors is a function of the ambient temperature and as the cell warms the temperature gradient decreases and so does the heat flow. The RTD temperature approaches the temperature of the Type-T furnace thermocouple near room temperature.

For cryogenic measurements, the furnace thermocouple is used to predict the temperature of the sample. A straight line fit of the sample temperature versus the furnace thermocouple temperature is used to determine the sample temperature and is given below:

\[
T_{\text{sample}} = 0.972527T_{\text{cell}} - 0.43656. \tag{3.30}
\]

3.2.4.5. Steady-State Temperature (T > 0) If the dewar were permanently kept filled with liquid nitrogen, then the ambient temperature would be approximately -130 °C. Heaters could be used to heat the conductivity cell up to room temperature. The problem with this setup is that a person has to be present during the experiment to keep filling liquid nitrogen in the dewar.

An alternative possibility is to let the cooled cell warm naturally in air and make immediate measurements once the set point temperature is reached. The assumption is that the heating rate is small compared to the frequency sweep rate of the impedance experiment. The impedance measuring frequency sweep takes approximately sixty seconds during which time sample warms up by approximately by 1 °C at lowest temperatures and only by 0.1 °C as higher temperatures. This variation in temperature is tolerable for the impedance measurements.
3.2.5. Automation Software

As is the case for the low frequency impedance workstation, a designated computer coordinates and directs the entire system in performing the high frequency impedance spectroscopy experiment. It assigns tasks to and receives data from the various instruments and monitors the system's progress. Once data are acquired and processed, the computer is responsible for storing and/or displaying the results. The instructions for the program are written in Turbo Pascal\(^9\) version 5.0 and are found in Appendix B. The data-collect routines provide automated collection for the IS experiment and the data are immediately ready for analysis. A description of the software and its development in terms of controlling the system, data processing, storing data and program operation are discussed in this section.

The impedance experiment is described as a series of isothermal impedance measurements. The variables that define the impedance measuring part of the experiment are the frequency range, logarithmic or linear and display. The thermal parameters are the start temperature \(T_s\), final temperature \(T_f\) and the temperature increment \(T_{inc}\).

3.2.5.1. System control Impedance variables are output to the Solartron through a configuration file sent by the computer. The thermal variables are input through the keyboard of the computer. A flow chart of the complete data collection procedure once experimental conditions are set is shown in Figure 3.29.

The software control of this experiment using the hardware shown in Figure 3.12 is presented here. \(T_o\) is the initial sample temperature at which impedance measurements are to be made, however, the furnace set point temperature to heat the sample is calculated by using Eq. (3.29) and output to the temperature controller through the RS-232 port.

The temperature of the sample is monitored by the computer through the Type-T T/C connected to the CIO-EXP16 signal conditioning card and the CIODAS08 A/D converter.

Figure 3.29: Flow chart of software control of the impedance experiment
The sample temperature is calculated from a linearization quartic Eq. (3.25) and calibration Eqs. (3.26), (3.28) and (3.29).

The computer begins checking for steady-state once the sample temperature is within 2 °C of the target temperature. Steady-state, in this experiment is defined as 10 consecutive temperature measurements spaced out by $N$ seconds that differ by no more than 0.05 °C from the initial measurement. $N$ is one tenth of the total measurement time for the HP-4191A bridge to sweep through the frequency range. Once steady-state is achieved, the HP-4191A is prompted to make impedance measurements on the sample. In this way, the deviation of the temperature during the sweep is anticipated to be no more than ±0.05 °C.

The impedance data are displayed graphically on the CRT and the values numerically written above the graph on the CRT. The temperature is monitored throughout the impedance data collection period and the largest temperature deviation during the sweep is stored. The bridge is configured to always output the impedance data in terms of the magnitude and phase. The data are standardized in this manner to conform with the data storage scheme of the low frequency workstation and to make the data immediately available for analysis software developed by the author. The raw data are stored on the hard drive of the computer and the sample set point temperature is incremented by $T_{mc}$.

If the new set point is less than or equal to the $T_f$, then the above procedure is repeated. When the set temperature exceeds $T_f$, the experiment is complete and the furnace turned off by setting the temperature controller to -250 °C.

3.2.5.2. Data processing Data strings sent through the various communications links contain, in addition to the numerical data of interest, string information that contains the device address and the units of the quantity being measured. In order to store the numerical data, they must be first extracted from the data strings and this is accomplished as the data are received at the computer controller using standard string manipulation routines available in Turbo Pascal. The interested reader is encouraged to look directly at the code in Appendix B.
3.2.5.3. **Data Storage** A sophisticated yet simple data storage is essential for the purpose of analysis, retrieval, identification and optimizing memory use. The technique described for the low frequency IS workstation [103] has worked very well and is used in this case also.

3.2.5.4. **Program operation** This section is included to act as a user's guide to operation of the data-collection routine. Execution of the program `<HF_WkStn.EXE>` will display a software identification screen. By pressing any key, a second screen will appear prompting the user to choose one of the many options. In the following paragraphs, each of the options available to the user from the data-collection menu will be described.

**Select HP-4191A:** The first option gives the user the option to choose one of nine impedance measuring setups stored on the computer. When selecting this option, the cursor will jump to the box for that option and wait for a number to be keyed in to select a setup. All other data-collection options are performed using the selected experimental setup here.

**Configure HP-4191A Analyzer:** The second option allows the user to configure the HP-4191A bridge to the specific needs of a new experiment. Selection of this option clears the screen and displays the contents of the configuration file `<HP_SET UP.#>` where the # mark represents the number of the currently selected setup. The displayed file can be edited and additional commands can be added by complying to the format described in the HP-4191A user's manual. This new configuration can be saved and becomes the default setup.

**Null Conductivity Cell:** The third option allows calibration of the conductivity cell and the transmission line. The user is prompted to terminate the transmission line with various reference loads to characterize the waveguide. The first load is a short circuit followed by an open circuit and concluded with a 50 Ω reference. During the nulling process, the computer monitors the results and will warn the user of an ineffective null by beeping. It is crucial to perform the nulling procedure before collecting data. Most errors in the setup can be caught at this point.
Cell Temperature: The fourth option displays the temperature of the furnace and the sample. The data is displayed in real time.

Configure Temperature Controller: The fifth option is a RS-232 communication program specifically written to send commands and receive data from the Eurotherm temperature controller. This option is useful when diagnosing the performance of the RS-232 or of instruments connected to it. All commands used to configure the temperature controller are sent continuously from the computer to the controller and its response is displayed on the screen.

Impedance Measurement: The sixth option allows immediate acquisition and graphical display of impedance data over the frequency range specified by the HP 4191A setup. The purpose of this option is to allow the user immediate display of data to make sure that the sample and setup are configured correctly.

Isothermal: The seventh option selects the IS experiment described above (see Figure 3.30). A screen for entering the sample name, user identification cell constant and temperature settings appears on the screen. Entering zero for all the temperature settings allows a single frequency sweep to be made without a temperature program. Inputting \( T_o, T_f \) and \( T_{inc} \) will cause the workstation to perform as described in the last section. The input name, date and time of logging onto the collection module are stored in a user log file called <IS_WkStn.Log>. On completion of the impedance experiment the user is logged out and returned to the main data-collect menu.

Time Interval Impedance Measurement: The eighth option selects an IS experiment where isothermal sweeps are collected in time intervals over a wide period. This experiment is useful in determining the time dependent stability of a material. The temperature to test the sample stability is set using the fourth option.

GPIB Communications: The last option is a communication program for the GPIB interface where commands can be sent and received from the GPIB. This option is useful when diagnosis the performance of the GPIB or of GPIB devices connected to the interface bus.
A strong similarity exists between the software for the low frequency and high frequency workstations. The user interface for operating the workstation is similar and a person trained on one workstation should easily be able to operate the other workstation. The similarity between the data storage format makes data compatible between the two workstations. Any analysis done on data collected on one workstation should be possible for data from the other workstation.

3.2.6. Data Analysis Software

A data analysis software was developed for data collected using the low frequency IS workstation by the author [103]. It provides for easy transformation of the raw data into other electrical properties in order to enhance data interpretation and to provide insight into the electrical response of the electronic materials. Two dimensional data presentation for all impedance related functions in both the complex plane and the frequency domain is provided. The analysis package has been continuously updated with more powerful analysis capabilities. It is presently in the process of being converted into a MS-Windows compatible program to make it available to other impedance spectroscopists. The software is extremely capable, powerful, diverse, user-friendly and large. For these reasons it is only summarized here. An analysis package user's manual is being developed and will give a complete description of the package.

Some of the powerful capabilities of this software are the linear and non-linear least-squares-routines used to evaluate various conductivity parameters. The d.c. conductivity is determined by fitting a circle to data in the complex impedance plane. The activation energy and the high temperature limit value for d.c. conduction and loss peak frequency are determined by converting the raw impedance data to the Arrhenius form and fitting to a straight line. The parameters in the Almond-West formalism are calculated by a non-linear-least-squares fit to the conductivity data. All fits are internally done during the graphical analysis and the results output graphically. Other features include graphical determination of $\beta$ in the KWW formalism of the electrical modulus and conductivity using an extension of the tech-
nique described in Section 2.2.2. The modifications to the routine are described later in this section.

Some utility programs have also been developed to generate data files for alternative data formats. For example, the d.c. conductivity of a material is temperature dependent, the d.c. conductivity calculated from complex plane analysis, can be extracted from the raw data files and a new file created in which the d.c. conductivity along with its corresponding temperature are stored. The conductivity and electrical modulus are also frequency dependent and fixed frequency conductivity or electrical modulus can also be extracted and stored in the manner described above. These utilities are very useful for comparative analysis of the data and without them this work would be extremely cumbersome and almost unmanageable.

3.2.6.1. Improvements to the KWW Fit The KWW tables generated by Moynihan et al. [8] described in Section 2.2.2 are sufficient for linear-log analysis of the electrical modulus frequency spectrum, but are inadequate for analysis using log-log plots. Moynihan et al.'s fits appear choppy and discontinuous due to low resolution and fail to effectively predict the high and low frequency limits. Anticipating a wider frequency measuring range and log-log analysis of the electrical modulus frequency spectrum to relate to the log-log analysis of the conductivity data, the KKW function was expanded to 48 terms for \( \tau_i \) in the range \( 10^{-5} < \tau_i < 10^4 \) and linear-least-squares fit to the KWW function to determine \( g_i \). The linear-least-squares Turbo Pascal program to generate tables for \( g_i \) and \( \tau_i \) for \( \beta \) in the range \( 0.3 < \beta < 1 \) is found in Appendix B. The time domain result is converted to the frequency domain by inputting the values of \( g_i \) and \( \tau_i \) into the Fourier transform of the right side of Eq. (2.30) shown below:

\[
M^*(\omega) = M_o \sum_{i=1}^{48} g_i \left[ \frac{(\omega \tau_i)^2}{1 + (\omega \tau_i)^2} + i \frac{\omega \tau_i}{1 + (\omega \tau_i)^2} \right].
\]  

\hspace{1cm} (3.31)

A plot of \( g^2 \) vs. \( \tau \) is plotted for various values of \( \beta \) between 0.3 and 1 in Figure 3.30. The square of \( g \) is plotted because the fitting conduction required that \( \Sigma g_i = 1 \) and due to round off
errors in the fitting negative values for small values of $g$, were calculated. The plot is choppy due to the discrete nature of the fit especially for $\beta$ values close to one. For $\beta = 1$, $g$ is a delta function centered at $\tau = 1$. For slightly smaller $\beta$ values, the curve looks like a gaussian distribution with the peak centered approximately at $\tau = 1$. For decreasing values of $\beta$, the distribution becomes broad and is skewed to longer relaxation times. For $\beta = 0.5$, the number of processed relaxing at short time (four decades away from the peak relaxation time) is quite significant.

This above formalism is a mathematical result of fitting the KWW to a series of exponential functions with different relaxation times. Interpreting the mathematical result to imply a

![Figure 3.30: Distribution of relaxation times determined by fitting the KWW function to a summed series of single exponential functions](image)

Figure 3.30: Distribution of relaxation times determined by fitting the KWW function to a summed series of single exponential functions
broad distribution of relaxation times for conducting ions in a glassy network is an issue of
discussion and debate [8,12-16,18-24].

3.2.7. Workstation Performance

The workstation performance and typical results obtained using this workstation are
given in this section. Comparison of data for standard materials obtained using the setup sug­
gested by Hewlett-Packard and the high frequency impedance workstation are discussed first.
This is followed by showing wide temperature range impedance data for Teflon and a sulfide
glass. The measurement on the sulfide glass is also a test of the hermeticity of the setup.

3.2.7.1. Standard materials To test the effect of the transmission line and the spe­
cially designed conductivity cell on impedance measurements using the HP-4191A, data were
collected using the following four different setups:

1. **Setup 1**: The sample is loaded into the factory provided HP-16091A test fixture and
connected directly to the test port of the HP-4191A

2. **Setup 2**: The sample is loaded into the modified HP-16091A test fixture as described
in Section 3.2.3 and connected directly to the test port of the HP-4191A

3. **Setup 3**: The sample is loaded into the modified HP-16091A fixture and connected
through a factory provided transmission airline (HP-11567A) to the test port of the
HP-4191A

4. **Setup 4**: The sample is loaded into the modified HP-16091A test fixture and con­
nected through the modified transmission airline (HP-11567A) to the port of the
HP-4191A

Comparison of the data using setup 1 and 2 should show the effects of the modifications
to the original design of the HP-16091A. Comparison of the data using setup 2 to setup 3
should show the effect of including a transmission line to the setup. Finally, comparison be­
tween setup 3 and 4 should clearly show the effect of the modified airline on the measure­
ments. Measurements on two other setups, the factory provided HP-16091A connected to the unmodified and modified transmission lines, were deemed unnecessary due to the results obtained using setup 1 and 2.

Figure 3.31 shows the measurements results of a 50 Ω standard terminator for the different setups. There is no visible difference between the results of setup 1 and setup 2 suggesting that the modification in the cell does not affect measurements of the resistor close to the value of the characteristic impedance. Data from setup 3 is also identical to that of setups 1 and 2 showing that the effect of the airline is effectively negated by the addition of the com-

![Figure 3.31: Impedance measurements of a 50 Ω load terminator](image-url)
pensator cable to the path length of the reference channel. A slight deviation is observed for setup 4 at low frequencies and goes away with increasing frequency. This deviation is less then one percent from the actual value.

To further test the capability of the HP-4191A and the conductivity cell, dielectric measurements of a 3.47 mm radius and 0.397 mm thick Teflon disk electroplated with copper were performed. The relative dielectric constant for Teflon is 2.1 [122]. The results for the four setup are shown in Figure 3.32. The value for the dielectric constant for frequencies less than 60 MHz are slightly scattered (±14%) for all setups. This is due to the inability of the HP-4191A to accurately measure impedance values greater than 10 kΩ in the low frequency range. For higher frequencies the results stabilize and the measured value for the dielectric

![Figure 3.32: Dielectric measurement of Teflon](image-url)

k' = 2.1 for Teflon
constant is 2.1. Finally at highest frequencies, a slight increase in the dielectric constant value is observed for all four setups. Overall the measurements show little deviation for the four setups and show clearly the low frequency limits of HP-4191A instrument.

Impedance measurements of a 100 Ω resistor and a 5 pF capacitor in parallel was also performed. The resistance and capacitance values were selected to simulate a fast ion conducting glass. The resonance frequency for this parallel RC is 318 MHz. The results for setup 1,3 and 4 are shown in Figure 3.33. The results of setup 2 are not shown because they are found to be identical to those of setup 1. The low frequency impedance and phase for all the setups are 100 Ω and 0°, respectively. The results are consistent for increasing frequencies up to 200 MHz. Above this frequency, data for setup 3 and 4 deviation from the data of setup 1. The rate at which the phase component of the impedance decreases from 0° to -90° for the first setup is much greater that for setups 3 and 4. The apparent signal length for the

![Bode plot of magnitude and phase for a 100 Ω and 5 pF parallel RC circuit](image)

Figure 3.33: Bode plot of magnitude and phase for a 100 Ω and 5 pF parallel RC circuit
transmission line and directional bridge circuit must be shorter than the reference channel and hence causing a decrease in the phase delay. The reasons for this, however, are not entirely clear. This deviation is also present in the magnitude of the impedance, but not as apparent.

The resonance frequency was shifted to lower frequencies by replacing the capacitor with a 15 pF capacitor (see Figure 3.34). The resonance frequency for this circuit is 106 MHz. The low frequency impedance and phase data for all three setups are 100 Ω and 0°, respectively. The data are consistent to the different setups up to 300 MHz. The phase is 45° at approximately 106 MHz, agreeing with the calculated resonance frequency. For frequencies greater than 300 MHz, the phase becomes positive and the magnitude increases. This may be

Figure 3.34: Impedance of a 100 Ω resistor in parallel to a 15 pF capacitor
a result of the electrical leads of the RC components contributing to the circuit as inductors. The amount of deviation from the data of setup 1 observed in the previous circuit is not observed in this case.

To summarize this section, resistance and pure dielectric materials can be measured accurately and precisely over the whole frequency range as long as the impedance values are within the instruments measuring range. The erroneous contribution to the impedance measurements is minimal for the modified airline and test fixture.

Combination of parallel RC circuits reveal that measurements for frequencies greater than 200 MHz are questionable for all setups. One explanation for this failure at high frequencies may be due to the inductive contribution of the electrical leads of the RC components. This feature is further explored in the next section where the impedance of a fast ion conducting glass is measured over a wide temperature range.

In conclusion, the effect of modifying the transmission line and the test fixture to allow wide temperature capability and hermeticity does not significantly affect the impedance measuring capability of the HP-4191A.

3.2.7.2. Temperature controlled impedance measurements High temperature impedance measurements were performed on a Teflon capacitor loaded in the conductivity cell. The results are shown in Figure 3.35. It is quite apparent that the value of the dielectric constant is approximately 2.1 at lowest temperature over the whole frequency range and decreases slightly with increasing temperature. The dielectric constant of Teflon, however, is both temperature and frequency independent [122]. The dielectric constant calculated for Teflon placed between two parallel metal plates is given by the following equation:

\[ k = \varepsilon_r = \frac{d}{A \varepsilon_0} C \]  

(3.32)

where \( C \) is the measured capacitance, \( d \) is the distance between the parallel electrode plates, \( A \) is the surface area of the plate and \( \varepsilon_0 \) is the dielectric permittivity of free space. The linear de-
crease in the dielectric constant with temperature over the whole frequency range is a result of the change of geometry of the capacitor due to thermal expansion changes in the Teflon. The unit of the geometric constant, $K_o = d/A$, is inverse length (cm$^{-1}$). Teflon also has a positive coefficient of thermal expansion, $\alpha$. $K_o$ decreases by approximately $1/(1+\alpha\Delta T)$ with increasing temperature, hence a decrease in the calculated dielectric constant is expected. The ratio between any two temperature dielectric constant measurements can be used to approximately determine the coefficient of linear thermal expansion of Teflon.

The electrical calibration performed at room temperature on the airline and conductivity cell are valid over the whole temperature range and the influence of the thermal expansion of the metal airline is negligible, even at the highest temperatures.

Figure 3.35: Dielectric measurements of Teflon at various temperatures
Wide temperature ionic conductivity measurements using both the low frequency and the high frequency workstations were performed on a silver ion conducting glass having the following composition, 0.5Ag$_2$S + 0.5(SiS$_2$ + B$_2$S$_3$).

At high temperatures, Ag$^+$ ions are highly conductive and participate in long range conduction. Since the dominant feature is conduction, the glass acts like a resistor. As the glass cools, long range conduction decreases due to a decrease in thermal energy for ion hopping. The glassy network without the conducting ions is an insulator and acts as a dielectric material. The parallel response of the conducting ions and the dielectric glass is similar to that of a parallel RC circuit. The resonance frequency, $\omega_r$, is given by the following equation

$$\omega_r = \frac{\sigma_{dc}}{\varepsilon_0 \varepsilon_\infty}$$

and the resonance frequency temperature dependence in given through the d.c. conductivity in Eq. (2.6). Impedance measurements for frequencies less than the resonance frequency should show a constant value for the magnitude and a phase of zero implying resistive behavior. For frequency measurements greater than the resonance frequency, the phase should approach -90° and the magnitude should decrease linearly with frequency as in the case of capacitors.

The magnitude and phase data measured over a wide temperature range using the high frequency workstation are shown in Figure 3.36. The magnitude of the impedance is strongly temperature dependent and varies over three decades over a temperature range of approximately 200 °C. At highest temperatures and lowest frequencies, the magnitude and phase of the impedance are frequency independent and the phase is equal to zero. As the temperature decreases and/or the frequency increases the magnitude of the impedance is no longer constant and begins to decrease approximately linearly with frequency. In the same frequency region, the phase also decreases from 0° to -90°. When the phase is -45°, this is the resonance frequency for a parallel RC circuit but in the case of the glass, it is an approximate value for the resonance frequency as was explained in the previous chapter. The high temperature data behaves very well, while the low temperature data show some unusual behavior.
Figure 3.36: (a) Magnitude and (b) phase response of the impedance over a wide temperature range for 0.5Ag$_2$S + 0.5(SiS$_2$ + B$_2$S$_3$) fast ion conducting glass
The low temperature ($T < -50^\circ \text{C}$) data show an approximate linear dependence to the frequency, but the data coalesces to the same value at approximately 200 MHz. This behavior is extremely unusual for a temperature dependent processes. The phase shows that for the same temperature and frequency range, that it begins to increase from approximately $-90^\circ$ to a higher value for frequencies greater than 100 MHz. This result is obviously an artifact of the conductivity cell design and not a function of the glass. These additional dielectric losses may be due to intrinsic dispersion effects caused by the Teflon rings in the cell used for supporting and insulating the inner conductor and hermetically sealing the cell. This result also puts an upper limit of 200 MHz for high quality impedance measurements.

Wide temperature data collected using the low frequency bridge are shown in the conductivity formalism in Figure 3.37. The approximate same temperature data for the high frequency workstation are also plotted on this graph. The graph shows the excellent overlap of conductivity data in the 1 to 10 MHz frequency region for the two bridges. This result is exceptional. Two highly reactive sulfide glass disks with different dimensions made from the same batch were measured on two different workstations using different impedance measurement techniques and temperature control, yet, show an outstanding agreement in the frequency and temperature dependence of the conductivity data. The poor overlap for $T = 0^\circ \text{C}$ is due to differences in the actual measurement temperature due to a software algorithm error in the high frequency workstation and has been rectified.

3.2.7.3. **Summary** One of the major goals of this Ph.D. project has been accomplished. A convenient, fast, accurate and precise wide temperature (150 K - 500 K) and high frequency (1 MHz - 200 MHz) range computer automated workstation has been successfully designed, constructed, computer programmed and implemented. A specially designed conductivity cell has been made to allow ease in loading samples in the glovebox and to protect samples from mechanical and environmental abuse.

The workstation through the menu driven data-collection software allows automated calibration of the conductivity cell, easy input of operator selected experimental parameters and unattended operation of the complete experiment.
Figure 3.37: Wide temperature conductivity data collected using both impedance spectroscopy workstations for $0.5\text{Li}_2\text{S} + 0.5(\text{SiS}_2 + \text{B}_2\text{S}_3)$ glass

Data analysis is facilitated through graphical display of all the impedance related functions. Sophisticated fitting routines for various conductivity models are available and examples of analysis are found in the next two chapters. Finally, graphs can be customized on the CRT and prepared in publication-quality for presentations. In fact, all impedance-related graphs found in this dissertation were generated using the data analysis program.

Improvements in this high frequency impedance spectroscopy workstation are, nevertheless, possible. The frequency window may be widened from 200 MHz to 1000 MHz. This may be a difficult task, but the additional reflectance and losses due to the conductivity cell and the transmission line can be accounted for mathematically. Finally, higher temperature ca-
pability would be definite improvement to the workstation capabilities but the hermeticity re-
requirement may be the limiting factor.

3.3 NSLR Measurements

The NSLR measurements were performed using the NMR facility in the Solid-State
Physics department at Iowa State University in collaboration with David Torgeson and Pro-
fessor Ferdinando Borsa. The NMR samples were sealed under vacuum in quartz ampules
and supplied to the Solid-State Physics group for measurements.

$^7$Li relaxation measurements were performed at 4, 7, 12.2 and 40 MHz over a tempera-
ture range of 100 - 500 K using a phase coherent NMR spectrometer [123,124]. The sample
temperatures were varied by means of a variable temperature chamber with a vacuum jacketed
counter-flow, heat exchanger design and a three-term OMEGA CN-2012 programmable tem-
perature controller system. An NMR inversion recovery rf pulse sequence of $\pi - \pi/2$ was
used to measure $R_1$ and is described here.

A rf coil wrapped along the length of a sample tube is placed perpendicular to a strong
magnetic field. If the field is in the $z$ direction then magnetic dipoles in the sample will align
with the magnetic field and induce a net equilibrium magnetization $M_o$ in the sample. Inver-
sion-recovery consists of applying through the coil, a 180° rf pulse to the sample to invert the
samples net magnetization into the opposite direction. This magnetization will decay along
the $z$-axis back to its initial value $+M_o$ according to

$$
M(t) = M_o \left[ 1 - 2 \exp \left( \frac{t}{T_1} \right) \right]
$$

(3.34)

which is a slight modification of Eq. (2.46). The decay process is shown in Figure 3.38. Af-
ter waiting some time $t$, all magnetic moments still remaining in the $-z$ direction are rotated to
the $x$-$y$ plane with a 90° pulse. Immediately afterwards, the magnitude of the magnetization in
the x-y plane is measured through the coil as an induced voltage. The sample is then allowed to completely recover back to its equilibrium magnetization by waiting longer than five times the relaxation time. This process is repeated at even increments of time $t$ to obtain measurements of the magnetization in the -z direction as a function of time. The entire process is repeated and the results averaged until the signal to noise ratio is reasonable. The magnetization versus time data are curve fit to Eq. (3.34) to solve for $T_I$. The set point sample temperature is changed to a new value and on stabilized, $T_I$ is determined using the process described above. Wide temperature $T_I$ measurements are obtained in this manner. The experimental Larmor frequency is varied by changing the strength of the magnetic field as described by Eq. (2.44).

Figure 3.38: Magnetization versus time for inversion
An advantage of the inversion-recovery method is that the magnetization goes from $-M_s$ to $+M_s$ and therefore gives a wide range of values to evaluate $T_1$. The only problem with this technique is when $T_1$ is long, especially at low temperatures, the time for recovery of the equilibrium magnetization is very long ($< 5T_1$) and this slows down the data taking process. Other techniques such as the picket fence method can be used [30].

3.4. Glass Preparation

The techniques used to synthesize glasses are discussed in this section. The sulfide glasses used for this study are extremely hygroscopic, reactive and hard to handle, hence novel techniques have been developed to overcome these problems.

3.4.1. $\text{B}_2\text{S}_3$ Glasses

$\text{B}_2\text{S}_3$ was synthesized in the laboratory because commercially available $\text{B}_2\text{S}_3$ has low purity and has large amounts of contamination due to oxygen and water. Preparation of $\text{B}_2\text{S}_3$ was reported as early as 1858 by Sainte-Claire-Deville and Wahler [125] and it is only recently that a number of alternative techniques have been developed to prepare this compound (see reference [91-93] and references therein). The glass preparation technique used for this project was developed and optimized by Bloyer [91] and Bloyer and Martin [92,93] at Iowa State University.

The preparation technique best suited to prepare $\nu\text{-B}_2\text{S}_3$ is the direct reaction of 2:3 ratio of elemental boron and sulfur in a carburized (graphitized) silica tube at 850 °C. The preparation technique is explained below and is broken into five parts:

1. Carburizing silica tubes
2. Elemental powder
3. Batch preparation
4. Heat cycle
5. Crushing glass
The whole preparation and synthesis experiment is done using a vacuum sealed tube or in a \( O_2 \) and \( H_2O \)-free (ppm level) He glovebox. The He gas in the glovebox is circulated through Zr at 500 °C and a 0.3 nm molecular sieve at 25 °C to remove residual \( O_2 \) and \( H_2O \) contamination, respectively. An exposed element light bulb in the glovebox is used to monitor \( O_2 \) levels.

3.4.1.1. Carburizing silica tube

The silica tube is coated with carbon to prevent the reaction between the silica tube and the starting elements or end product:

\[
B_2S_3 + SiO_2 \rightarrow B_2O_3 + SiS_2
\]

The carburizing technique is described below

(a) A 30 cm long closed-end 10-mm ID x 12-mm OD silica tube is inserted 27 cm into a tube furnace at 850 °C.

(b) Nitrogen gas is bubbled in liquid acetone in a closed glass container. The acetone saturated nitrogen gas stream generated by the bubbling is delivered to the closed-end silica tube through a smaller O.D. silica tube inserted approximately 3 cm inside the larger silica tube. The consistency and amount of the flow rate is critical for achieving a uniform and durable coating. A flow rate of approximately 50 mL/min is used to get the best results. The close-ended silica tube is heated with the gas stream flowing through it for approximately five hours and then immediately taken out of the furnace. The acetone (CH\(_3\)COCH\(_3\)) cracks down to form a very hard layer of pyrolytic carbon which is deposited on the inside of the heated length of the tube.

(c) On cooling, the tube is rinsed with acetone and examined to make sure that there is adherence of the carbon to the silica tube and no pinholes. The tube is dried placed in a oven at approximately 150 °C for at least half an hour.

(d) The first 6 cm on the open side of the tube should have no carbon coating on it because sealing the tube is difficult when there is a carbon layer between the sealing surfaces.
Excess carbon near the opening of the tube is removed by heating the outside of the silica tube with an oxygen flame and blowing air inside the tube. The tube is rinsed with acetone and stored in a drying oven as before.

(e) The silica tube is connected to a rubber vacuum hose attached to a stopcock. The other side of the stopcock is connected to a roughing pump through a liquid nitrogen trap and outgassed at ~1000 °C using an oxygen torch.

(f) The stopcock is closed off and disconnected from the vacuum system. The stopcock and tube assembly are then brought into the He glovebox.

3.4.1.2. Elemental Powders To increase the reaction between boron and sulfur, extremely fine (< 1 μm particle size) 3N purity amorphous boron is used. The particle size of the sulfur is not crucial because it goes into liquid/gas form at low temperatures unlike boron. Therefore, the contact area between the fine boron particles and the liquid/gas sulfur is very high. Crystalline boron is not used because of its anticipated large lattice energy, which limits the overall reaction. Both chemicals were purchased from Cerac, Inc.¹⁰

The physical properties of these elements and their compounds are given in Table 3.2. Materials with large differences in melting points often require special techniques to prevent evaporation or volatalization of one material and allow a solid-liquid/gas state reaction. This is the case for the synthesis of B₂S₃ where there is a large temperature difference between the melting points of the two starting elements. The similarity between the boron and sulfur electronegativity suggests that the B-S bond will form stronger covalent than B-O bond.

3.4.1.3. Batch Preparation (a) The optimal batch size is 4 g for the carburized silica tube described above. For larger batch sizes, explosions have occurred during the heating process. To make a 4 g B₂S₃ batch, 0.734 g and 3.266 g of boron and sulfur are used.

¹⁰ Cerac, Inc., P. O. Box 1178, Milwaukee, WI 53201
Table 3.2. Physical properties of starting elements

<table>
<thead>
<tr>
<th>Element Compound</th>
<th>Atomic Number</th>
<th>Molecular Weight (g/cc)</th>
<th>Density (g/cc)</th>
<th>M.P. or T (°C)</th>
<th>B.P. (°C)</th>
<th>Electro-negetivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron B</td>
<td>5</td>
<td>10.81</td>
<td>2.34</td>
<td>2,300</td>
<td>2,550</td>
<td>2.04</td>
<td>[126]</td>
</tr>
<tr>
<td>Oxygen O</td>
<td>8</td>
<td>16.00</td>
<td>-</td>
<td>-218</td>
<td>-183</td>
<td>3.44</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sulfur S</td>
<td>16</td>
<td>32.06</td>
<td>2.07</td>
<td>113</td>
<td>445</td>
<td>2.58</td>
<td>&quot;</td>
</tr>
<tr>
<td>B₂O₃</td>
<td></td>
<td>69.62</td>
<td>1.81</td>
<td>260</td>
<td></td>
<td>[127]</td>
<td></td>
</tr>
<tr>
<td>B₂S₃</td>
<td></td>
<td>117.80</td>
<td>1.70</td>
<td>334</td>
<td></td>
<td>[91]</td>
<td></td>
</tr>
</tbody>
</table>

(b) The appropriate weight for each element is measured in a vitreous carbon crucible using a FX-300 precision electronic balance\(^\text{11}\) (± 0.001 g). The elements in the crucible are mixed until the yellow sulfur pieces are completely stained by the brown colored boron.

(c) Using a funnel, the powder is transferred into the carburized silica tube.

(d) The silica tube is closed off using the stopcock assembly and brought out of the glovebox for sealing.

(e) The stopcock is connected to the roughing pump through the nitrogen trap described above and the pump turned on. After a few minutes, the stopcock is opened slowly to take air out of the tube. If the valve is opened too quickly then some of the batch mixture may be carried out of the of tube by the evacuating air stream. Powders electrostatically stuck to the uncarburized walls of the tube are shaken from the wall by inserting the tube in an acoustic vibrator. After approximately five minutes of evacuating, the edge separating the carburized and clear region of the silica tube is heated carefully with an oxygen torch ( T ≥ 1500 °C). The silica tube softens and collapses inwards due to the vacuum. By spinning the tube while heating, the collapsing region is kept symmetric and the tube walls have a uniform thickness as

\(^\text{11}\) A&D Engineering, Inc., 1555 McCandless Drive, Milpitas, CA 95035
they converge towards each other to make a seal. This process requires great patience and is
difficult to master. In the worst case, only one centimeter of the inside of the the silica tube
should be bare without a carbon coating. This non-carburized surface on the silica tube is a
potential reaction site for silica, boron, sulfur and $B_2S_3$. Care must be taken during the sealing
process to decrease the amount of exposed silica.

3.4.1.4. Heat cycle  (a) Up to four sealed carburized tube can be loaded in the fur-
nace tube holder. The tube holder is a 50 cm long stainless steel rod with four small stainless
steel tubes welded in parallel and spaced 90° apart at the end of the rod. The welded tubes
have a flat bottom and are 1 cm in height and have an inner diameter of 12 mm. The silica
tubes are loaded by inserting into these stainless steel tubes and held in place by looping high
temperature T/C wire around the tubes and the rod.

(b) The tube holder is inserted with the sample end first into a pre-heated (300 °C)
Lindberg\textsuperscript{12} 524233 horizontal tube furnace. The other end of the stainless steel rod is fed
through a ball-bearing hub support system and connected to the spindle of a rotating electric
motor (1 RPM). Approximately 40 cm of the rod is in the furnace and the four tubes are
completely immersed in the most uniform heat zone of the furnace. The rotating rod is angled
downwards by 5° to keep the melt away from the exposed silica and it has been observed that
this angle is critical for complete reaction and high quality $B_2S_3$ yield.

(c) To avoid explosions of the reaction tube due to high sulfur pressures during the
ramp-up to the reaction temperature of 850 °C, the heat cycle shown in Table 3.3 is used and
programmed into the Eurotherm 818 temperature controller on the Lindberg 58125 control
console. Although the goal is to react these elements at 850 °C and the rapid approach to this
temperature would decrease the temperature cycle time, it has been observed that the final re-
sult is strongly dependent on the heat profile from 300 to 850 °C . Bypassing the dwell at
600 °C on occasion results in gross phase separation of sulfur, boron and a glassy mixture.
The reason for this phenomenon is unclear, but may be due to formation of intermediate com-

\textsuperscript{12} Lindberg/Blue M, 304 Hart Street, Watertown, WI 53094
pounds \( (B_xS_y, S_z) \) at lower temperatures which act as catalysts or mediums to drive the reaction to \( v-B_2S_3 \).

(d) The tube is removed from the furnace and held up vertically to allow the melt to flow down and consolidate at the bottom of the tube. On cooling, the tube is immediately taken into the glovebox to prevent possible exposure to air/water due to cracks in the silica tube because of thermal expansion mismatches between the \( B_2S_3 \) and the silica tube.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Ramp Rate ( (^\circ C/min) )</th>
<th>Set Point ( (^\circ C) )</th>
<th>Dwell Time ( (hrs) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>400</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>600</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>850</td>
<td>8</td>
</tr>
</tbody>
</table>

3.4.1.4. Crushing glass  (a) The lower side of the silica tube is scratched with a glass cutter and the silica tube mechanically broken. A transparent green colored \( B_2S_3 \) rod (10 mm OD x 5 cm long) should easily slide out of silica tube and show no tendency to wet the sides of the carbon-coated silica tube. All the materials in the silica tube are collected and weighed to make sure that all of the 4 g batch is retrieved. If the rod is not homogeneous then all the pieces should be crushed using a stainless steel mortar and pestle, mixed and resealed in a carburized tube and reheated as described above. Otherwise, the glass rod is crushed into a fine powder and used as a starting material for synthesizing alkali thioborate glasses.

An IR spectra of a typical \( v-B_2S_3 \) glass prepared using this technique is shown in Figure 3.39. Contamination due to oxygen, water or silicon is easily revealed using IR spectroscopy. Peaks due to water contamination (O-H an S-H) occur at \(~3500\) and \(~2550\) cm\(^{-1}\). Contamination due to oxygen results in B-O stretching modes at \(~1300\) cm\(^{-1}\). Improper carborization of the silica tube can give rise to Si-O peak at \(~1150\) cm\(^{-1}\) and a broad Si-S peak between 500 and 600 cm\(^{-1}\).
Figure 3.39: IR spectra of high purity $\nu$-B$_2$S$_3$
3.4.2. $M_2S + B_2S_3$ Glasses

The physical properties for the alkali metal (M) and their oxides and sulfides are given in Table 3.4. $xM_2S + (1-x)B_2S_3$ glasses in the range $0.05 < x$, were prepared in the $O_2$ and $H_2O$-free glovebox. 2.5 g batches of $M_2S$ (3N, Cerac) and $B_2S_3$ (see previous section) were carefully weighed out on a FX-300 precision electronic balance ($\pm 0.001$ g). The mixture was then melted in a covered vitreous carbon crucible at $\sim 800 \, ^{\circ}C$ in a Thermolyne\textsuperscript{13} model FB1315M muffle furnace for 5-10 minutes. The melt in the crucible was taken out of the furnace, stirred by shaking the crucible, visually examined to make sure the melt was clear and bubble free and on solidifying checked for weight loss. After which the crucible was put back in the furnace for one minute to remelt the glass. All melts were then quenched from 800 °C

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Molecular Weight</th>
<th>Density (g/cc)</th>
<th>M.P. or T$_g$ (°C)</th>
<th>B.P. (°C)</th>
<th>Electro-negetivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>3</td>
<td>6.94</td>
<td>0.53</td>
<td>180.5</td>
<td>1,347</td>
<td>0.98</td>
<td>[126]</td>
</tr>
<tr>
<td>Sodium</td>
<td>11</td>
<td>22.99</td>
<td>0.97</td>
<td>97.8</td>
<td>883</td>
<td>0.93</td>
<td>&quot;</td>
</tr>
<tr>
<td>Potassium</td>
<td>19</td>
<td>39.10</td>
<td>0.86</td>
<td>63.6</td>
<td>774</td>
<td>0.82</td>
<td>&quot;</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8</td>
<td>16.00</td>
<td>-</td>
<td>-218</td>
<td>-183</td>
<td>3.44</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sulfur</td>
<td>16</td>
<td>32.06</td>
<td>2.07</td>
<td>113.0</td>
<td>445</td>
<td>2.58</td>
<td>&quot;</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td></td>
<td>29.88</td>
<td>2.01</td>
<td>&gt;1700</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td></td>
<td>61.98</td>
<td>2.27</td>
<td>1275</td>
<td>1,275</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td></td>
<td>94.20</td>
<td>2.32</td>
<td>350</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>Li$_S$</td>
<td></td>
<td>45.94</td>
<td>1.66</td>
<td>900</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>Na$_2$S</td>
<td></td>
<td>78.04</td>
<td>1.86</td>
<td>1180</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>K$_2$S</td>
<td></td>
<td>110.26</td>
<td>1.81</td>
<td>840</td>
<td>-</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>B$_2$S$_3$</td>
<td></td>
<td>117.80</td>
<td>1.70</td>
<td>334</td>
<td>-</td>
<td>[91]</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{13} Barnstead |Thermolyne Corporation, 2555 Kerper Boulevard, P. O. Box 797, Denuque, IA 52004
to \((T_g - 50) \, ^\circ C\) by casting the liquid into disks in a pre-heated stainless steel mold. The mold was held at that temperature for two hours to anneal the glass and then cooled slowly to room temperature with a cooling rate of approximately 1 \(\, ^\circ C/min\).

The preparation of glasses using the above technique for compositions \(x < 0.05\) showed weight losses of the same order of magnitude as the quantity of \(M_xS\) used to prepare the 2.5 g samples. To overcome this problem, glasses were prepared by diluting a measured amount of \(x = 0.05\) glass in pure \(\nu-B_2S_3\) to make compositions in the range of \(0.01 < x < 0.05\). Further dilution of \(x = 0.01\) glass with pure \(\nu-B_2S_3\) was used to prepare glasses of even lower alkali compositions.

### 3.4.3. \(M_xS + SiS_2\) Glasses

Some of the physical properties of silicon and its oxide and sulfide are shown in Table 3.5. \(xLi_2S + (1-x)SiS_2\) glasses in the range \(0.5 < x < 0.61\), were prepared in the \(O_2\) and \(H_2O\) - free glovebox. 3 g batches of \(Li_2S\) (3N, Cerac) and \(SiS_2\) (4N Cerac) were carefully weighed out on a FX-300 precision electronic balance (± 0.001 g). The mixture was then melted in a covered vitreous carbon crucible at \(~1000 \, ^\circ C\) in a Thermolyne muffle furnace for approximately 30 minutes. The melt in the crucible was taken out of the furnace, stirred by swirling the crucible, visually examined to make sure the melt was bubble free and clear and on solidifying checked for weight loss. After which the crucible was put back in the furnace for one minute to remelt the solid. All melts were then quenched from 800 \(\, ^\circ C\) to \((T_g - 50) \, ^\circ C\) by casting the liquid into disks in a pre-heated stainless steel mold and given the same thermal history.

### 3.4.4. Sample Preparation

#### 3.4.4.1. Electrical Measurements

The top surface of the bottom plate of the stainless steel mold has cylindrical holes (1-2 mm deep) to cast glass disks of various diameters (6, 7, 8, and 20 mm). The sides of the holes are machined to have a 45\(^\circ\) slope to accommodate re-
moyal of these disks. 20 mm glass disks are used for the low frequency workstation and the 6 and 7 mm disks are used for the high frequency cell.

Two identical aluminum washers with an inner diameter less than the diameter of the glass and a outer diameter much greater than that of the glass is used as a template for sputtering gold electrodes. Three holes spaced 120° apart aligned perfectly on both washers are used to fasten the two washers to each other using nuts and bolts. The glass disk is placed centered between the two washers and held in place by tightening the nuts. Three such sets of washers exist with different inner diameters to make different size electrodes and to load different size disks.

| Element Compound | Atomic Number | Molecular Weight | Density (g/cc) | M.P. or T_s (°C) | B.P. (°C) | Electro- | Ref. |
|------------------|---------------|------------------|---------------|------------------|----------| negativity |     |
| Silicon          | 14            | 28.09            | 2.33          | 1,410            | -        | 1.90       | [126]|
| Oxygen           | 8             | 16.00            | -             | -218             | -183     | 3.44       | "    |
| Sulfur           | 16            | 32.06            | 2.07          | 113.0            | 445      | 2.58       | "    |
| SiO_2            | 60.08         | 2.20             | 1,020         | -                | [127]    |           |     |
| SiS_2            | 92.21         | 2.02             | 1,090         | 1,090            | [126]    |           |     |

The glass and washer assembly is sealed in a glass jar and transported out of the glove-box to a Fisions SC502 gold sputter coater inside a nitrogen glovebag. The glass and washer assembly are loaded in a vacuum chamber in the sputter coater and the gas evacuated. The unit applies a fix votage (V) of 1 kV and the current (I) is set 18 mA by controlling the leak rate of argon gas into the chamber. The glass sample is sputtered on both side for 10 minutes ( t = 600 s). The thickness of the deposited gold film is the product of the above

14 Fisions Instruments, P. O. Box 1409, 355 Shoreway Rd., San Carlos, CA 94070
three variables and a material dependent constant \((k = 0.17\) for gold). The thickness is given in angstroms by \(d = kVIt\) in the units defined for each variable above and is approximately 0.2 \(\mu m\). This thick sputtered gold layer is opaque, shiney and adheres very well to the glass surface. The sputtering coating time could have been decreased but was not to maintain consistency. The sample was sealed in the glass jar taken back to the glovbox and loaded in the conductivity cell.

During transporation of the glass-washer assembly in the glovebag, exposure to oxygen and water was minimized by flushing nitrogen gas over the highly reactive glass sample while opening the glass jar, loading the washer assembly in the sputter coater and resealing the sample in the glass jar. The geometric cell constant of this parallel gold plate capacitor with a lossy dielectric is the ratio of the thickness of the sample to the area of the gold electrodes.

3.4.4.2. NSLR Sample Preparation The quantity of excess glasses from the preparation of glasses for conductivity measurements can be used for NSLR measurements. One gram of glass pieces \((2 \times 2 \times 2\) mm\) is sealed in a silica tube \((10\) mm I.D.) for the NSLR experiment. For all samples prepared for NSLR measurements, conductivity measurements were also performed on the glasses made from the same batch.
CHAPTER 4: CONDUCTIVITY RESULTS

The goal of this project is to understand the compositional contribution to the ionic conductivity and the relationships between electrical transport properties and NSLR. Glasses in the alkali-thioborate and thio-silicate families were synthesized for this study using techniques described in the last chapter. Electrical measurements were performed on all glasses and NSLR measurements were also performed on three different fast lithium conducting glasses. The conductivity results of these measurements are compiled in the first section of this chapter on Tables 4.1 - 4.3 and the techniques to determine each parameter is given in the following sections. The compositional contribution to the conductivity is discussed in Chapter 5. The NSLR results are condensed on Table 6.1 and analyzed in Chapter 6.

4.1. Summary of Results

A large quantity of impedance data is collected for each glass composition because of the wide temperature and frequency measurement ranges. For this reason, the raw impedance data for each glass are not given and only the results of the impedance analyses of the data for each glass examined are given here. The conductivity parameters to characterize the impedance spectrum for each glass are grouped together by their binary glass family on Tables 4.1 - 4.3.

The conductivity spectrum of glassy ionic conductors is sufficiently characterized once the d.c. conductivity preexponent ($\sigma_0$), d.c. activation energy ($\Delta E_{\text{act}}$), the ionic ($\varepsilon_i$) and the host glass ($\varepsilon_g$) contribution to the dielectric constant, the fractional (Kohlrausch) exponent $\beta$ and the Almond-West parameters ($\nu_1$ and $s$) are known. These parameters have been described in the Background Section. The data analysis sequence to determine each parameter is described in the following sections. A wide range of compositional glasses will be used to
Table 4.1: Best fit values for conductivity parameters for $x$Na$_2$S + (1-$x$)B$_2$S$_3$ glasses determined from techniques described in Section 4.2. Calculated $\sigma_{dc}(150^\circ C)$ is also reported.

<table>
<thead>
<tr>
<th>x</th>
<th>d.c. Conductivity</th>
<th>Dielectric</th>
<th>Electrical Modulus &amp; KWW</th>
<th>Almond-West</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log $\sigma_o$</td>
<td>$\Delta E_o$</td>
<td>log$\sigma$ (150$^\circ$C)</td>
<td>$\log v_{ho}$</td>
</tr>
<tr>
<td></td>
<td>[K/Ωcm]</td>
<td>[eV]</td>
<td>[Ωcm]</td>
<td>[Hz]</td>
</tr>
<tr>
<td>0.0010</td>
<td>3.51</td>
<td>0.770</td>
<td>-8.29</td>
<td>0.48</td>
</tr>
<tr>
<td>0.0025</td>
<td>3.77</td>
<td>0.767</td>
<td>-7.99</td>
<td>1.27</td>
</tr>
<tr>
<td>0.0050</td>
<td>3.78</td>
<td>0.754</td>
<td>-7.83</td>
<td>1.36</td>
</tr>
<tr>
<td>0.0100</td>
<td>3.66</td>
<td>0.705</td>
<td>-7.37</td>
<td>3.20</td>
</tr>
<tr>
<td>0.0200</td>
<td>3.87</td>
<td>0.705</td>
<td>-7.16</td>
<td>6.22</td>
</tr>
<tr>
<td>0.0300</td>
<td>3.26</td>
<td>0.678</td>
<td>-7.44</td>
<td>10.50</td>
</tr>
<tr>
<td>0.0400</td>
<td>4.07</td>
<td>0.677</td>
<td>-6.62</td>
<td>30.00</td>
</tr>
<tr>
<td>0.0500</td>
<td>3.53</td>
<td>0.564</td>
<td>-5.82</td>
<td>-</td>
</tr>
<tr>
<td>0.0500</td>
<td>3.48</td>
<td>0.564</td>
<td>-5.87</td>
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<td>0.564</td>
<td>-5.82</td>
<td>-</td>
</tr>
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<tr>
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</tr>
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<td>5.08</td>
<td>0.439</td>
<td>-2.78</td>
<td>29.78</td>
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</table>
Table 4.2: Best fit values for conductivity parameters for $x\text{K}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses determined from techniques described in Section 4.2. Calculated $\sigma_{dc}$ at $T = 150^\circ\text{C}$ are also reported.

<table>
<thead>
<tr>
<th>$x$</th>
<th>d.c. Conductivity</th>
<th>Dielectric</th>
<th>Electrical Modulus &amp; KWW</th>
<th>Almond-West</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\log \sigma_0$</td>
<td>$\Delta E_0$</td>
<td>$\log \sigma_{(150^\circ\text{C})}$</td>
<td>$\epsilon_1$</td>
</tr>
<tr>
<td></td>
<td>[K/Ωcm]</td>
<td>[eV]</td>
<td>[Ωcm]</td>
<td>[Hz]</td>
</tr>
<tr>
<td>0.0005</td>
<td>3.93</td>
<td>0.832</td>
<td>-8.50</td>
<td>1.82</td>
</tr>
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<td>2.33</td>
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<td>0.0080</td>
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</tr>
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<td>-6.45</td>
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<td>0.704</td>
<td>-6.42</td>
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<tr>
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<td>0.704</td>
<td>-6.38</td>
<td>12.14</td>
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<tr>
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<td>4.14</td>
<td>0.665</td>
<td>-6.41</td>
<td>12.65</td>
</tr>
<tr>
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<td>4.84</td>
<td>0.671</td>
<td>-5.78</td>
<td>12.83</td>
</tr>
<tr>
<td>0.3500</td>
<td>4.36</td>
<td>0.635</td>
<td>-5.83</td>
<td>13.05</td>
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<tr>
<td>0.4000</td>
<td>5.00</td>
<td>0.645</td>
<td>-5.31</td>
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</table>
Table 4.3: Best fit values for conductivity parameters for \(x\text{Li}_2\text{S} + (1-x)\text{SiS}_2\) glasses determined from techniques described in Section 4.2. Calculated \(\sigma_{dc}(150^\circ\text{C})\) is also reported.

<table>
<thead>
<tr>
<th>(x)</th>
<th>d.c. Conductivity</th>
<th>Dielectric</th>
<th>Electrical Modulus &amp; KWW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\log \sigma_0)</td>
<td>(\Delta E_\alpha)</td>
<td>(\log \sigma(150^\circ\text{C}))</td>
</tr>
<tr>
<td>(\text{[K}/\Omega\text{cm]})</td>
<td>([\text{eV}])</td>
<td>([\Omega\text{cm]})</td>
<td>([\text{Hz}])</td>
</tr>
<tr>
<td>0.50</td>
<td>5.28</td>
<td>0.359</td>
<td>-1.62</td>
</tr>
<tr>
<td>0.56</td>
<td>5.52</td>
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<td>5.59</td>
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<tr>
<td>0.60</td>
<td>5.48</td>
<td>0.344</td>
<td>-1.24</td>
</tr>
</tbody>
</table>
elucidate these methods to show both the universality of the analyses techniques and to show samples of different glass composition data and the various impedance formalisms. All the graphs for each glass composition in the various formalisms could have been included here making this chapter very large and tedious, instead sample graphs are provided to represent the gross features of typical glass data and the finite differences are tabulated. For the interested reader, graphs of some of these glasses have been compiled in Appendix D.

The range of compositions studied for glasses in the thio-borate and thio-silicate glass family is indicative of the glass forming region where approximately 2 mm thick homogeneous glass disks can be cast. Attempts were made to make glasses near the edge of the glass forming region by rapid quenching and changing thermal histories, but in most cases, these samples crystallized or were fragile and broke.

4.2. Conductivity Parameters

4.2.1. d.c. conductivity parameters

Numeric values for the d.c. activation energy ($\Delta E_{ac}$), the d.c. conductivity prefactor ($\sigma_0$) and the room temperature d.c. conductivity ($\sigma_{293}$) are resolved using complex plane analysis of wide temperature and frequency range isothermal impedance data. Figures 4.1(a) and 4.1(b) show the complex impedance plot for a ultra-low sodium thioborate glasses and for a highly modified lithium thiosilicate glass. The semicircle represents the bulk impedance response of the glass while the data to the right of the semi-circle is due to the blocking electrodes on the sample. The line through the data is the expected response for a parallel resistor-capacitor circuit.

Glasses are lossy materials where both conduction and polarization of species occur. This behavior can be modeled by a parallel resistor-capacitor circuit where the ohmic losses are due to a single component resistor and the polarization is due to a capacitor. The semicircle produced by a RC circuit has a diameter R and the center located at (R/2,0) in the x-y
Figure 4.1: (a) Complex impedance plane plot for 0.0025Na$_2$S + 0.9975B$_2$S$_3$ glass at 146 °C and (b) 0.56Li$_2$S + 0.44SiS$_2$ glass at -110°C
The frequency is a parameter in this plot and increases from right to left in the direction of the arrow. The magnitude of the resistance of the resistor may be determined by the intersection of the impedance arc at the low frequency (right) side of the semicircle with the x-axis. As frequency increases, the magnitude of the imaginary impedance goes through a maximum value at the relaxation frequency of the circuit. Once the relaxation frequency and the resistance is known, the capacitance can be determined using the relaxation frequency equation for a parallel RC circuit ($\omega = 1/RC$). At high frequencies, both the real and imaginary parts go to zero.

The center of the circle defined by the glass data, however, is below the axis for both glasses, especially for the case of the highly concentrated lithium glass. Arcs of this type are called depressed semi-circles and arise because of conductivity or dielectric relaxation of ions in the glass or because of overlapping arcs due to the presence of other relaxations such as grain boundaries, contact polarization and surface adlayers. A least-squares routine for the equation of a circle is used to locate the center of the depressed arc marked by a cross in both figures) and the x-axis intercept of the fit yields the resistance of the glass. The inverse of this value and dividing by the cell geometry gives the value for the d.c. ionic conductivity.

The dramatic change in resistivity with temperature for both glasses is shown in Figure 4.2. The depressed arcs decrease in radius as the temperature increases which implies an increase in conductivity. To match the impedance of the two glasses, the ultra-low sodium composition glass had to be heated to an elevated temperature (146 °C) and the highly modified lithium glass had to cooled (-110 °C) to make the ions less thermally activated.

Wide temperature d.c. conductivity values determined from the complex plane are multiplied by the measurement temperature ($\sigma T$) and are plotted versus reciprocal temperature in an Arrhenius plot as shown in Figure 4.3. The d.c. conduction activation energy ($\Delta E_a$) and the high temperature limiting conductivity ($\sigma_o$) are determined by fitting the data to Eq. (2.6), which is a straight line on an Arrhenius plot. The activation energy can be determined with great accuracy but the error in the prefactor can be large when the log result is converted to
Figure 4.2: (a) Complex impedance plane plots at different temperatures for $0.0025\text{Na}_2\text{S} + 0.9975\text{B}_2\text{S}_3$ glass and (b) $0.56\text{Li}_2\text{S} + 0.44\text{SiS}_2$.
Figure 4.3: Arrhenius plot for 0.0025Na$_2$S + 0.9975S$_2$ and 0.5Li$_2$S + 0.44S$_2$. 

$\text{Re}[\sigma T] \quad (\text{K}/\Omega \cdot \text{cm})$
its linear value. In systems where the parameters are slightly changing than comparison of ac-
tivation energies between glasses is more reasonable than that for the prefactor.

The reader is warned that sometimes the activation energy and the prefactor are reported
by fitting $\sigma$ instead of $\sigma T$. In this case, the reported activation energies are slightly lower and
the pre-exponents are three to four orders of magnitude smaller. Plots of this form, however,
are more informative because the d.c. conductivity for any temperature can be immediately
read of the graph.

The large difference in the conductivity between the two glasses is clearly seen by the lo-
cation of the curves on the x-axis. As pointed out earlier, the sodium glass has to be heated to
higher temperatures to attain the same conductivity as the lithium glass. The steeper slope of
the low sodium content glass implies a larger activation energy.

To compare different glasses, the room temperature conductivity is usually reported.
This value is either measured directly at room temperature or determined through Eq. 2.6 us-
ing the calculated activation energy and prefactor.

4.2.2. Dielectric Parameters

The dielectric constant is the defined as the real part of the complex relative dielectric
permittivity. Dispersion in the dielectric constant spectrum is observed in most glass spectra
and is shown in Figures 4.4 and 4.5 for a high concentration lithium thioborate glass and a low
concentration potassium thioborate glass over a wide range of temperatures. Figure 4.4(a)
shows clearly the different polarization mechanisms in the glass. As temperature increases the
curves shift to the right. At high temperatures or low frequencies, all polarization mechanisms
are active but are dominated by the space charge polarization. Ions in a glass at high tempera-
ture are very mobile and behave similarly to ions placed in electric field for a long time - they
exhibit long range motion. Their forward motion, however, is impeded by physical barriers
that inhibits charge migration. The charge build up contribute to a very large dielectric con-
stant at low frequencies and high temperatures. For the lithium sulfide glass, the measured di-
Figure 4.4: (a) Log and (b) linear plot of the dielectric constant for 0.7Li₂S + 0.3B₂S₃ glass.
electric constant of the glass is approximately $10^3$. In the slightly modified potassium thioborate glass shown in Figure 4.5(a), even at the elevated temperatures and lowest frequencies, the ion mobility is very low and the space charge polarization plateau is not observed.

As frequency increases (shorter time), shorter distances are traveled by the ions and less ions find their motion in the direction of the electric field impeded by physical barriers. Both an increase in conductivity and a decrease in the space charge polarization is expected (this will be discussed later). The decrease in polarization is seen in both Figures 4.4(a) and 4.5(b). The break frequency from the space charge polarization plateau is called the space charge polarization relaxation frequency. From the figures it is apparent that the relaxation frequency is
temperature dependent. Decreasing the temperature, decreases the mobility and the likelihood of ions hoping long distance and running into barriers.

A second polarization mechanism is observed at higher frequencies or lower temperatures as the influence of the space charge polarization goes away. This mechanism is due to orientation polarization of the hopping ions. The thermally activated ions hop in the direction favored by the electric field and their average displacement from the neutral position contributes to the dielectric constant. The dashed line labeled in all the plots in Figures 4.4 and 4.5 are guides to the eye to show the approximate contribution to the dielectric constant by hopping ions. The linear-log plots (b) of both figures are plotted to show the approximate magnitudes. The plateau value defined by the dashed line is used to determined the magnitude of the contribution of the hopping ions to the total dielectric constant. The difference in the magnitude of the ion hopping polarization between the two glasses is a result of the ion mobility and the difference in the ion concentration in the two glasses.

Finally, as frequency further increases, the hopping ions can no longer keep up with the alternating field [34,128,129]. This frequency is called the ion hopping relaxation frequency and is temperature dependent.

With further increase in frequency, the magnitude of the contribution due to orientation and space charge polarization becomes negligible and only the contribution of the electronic, atomic and electronic polarization is measured. This is defined as the high frequency and low temperature dielectric constant \( \varepsilon_\infty \) or the dielectric constant of the glass \( \varepsilon_s \). No relaxation processes are expected for higher frequencies or lower temperatures. Resonance losses do occur, however, at the IR frequency due to the weak ionic bonds between the alkali ion and the host glass and at slightly higher frequencies for the stronger covalent bonds in the glassy network.

The frequency spectrum for each temperature in Figures 4.4(a) and 4.5(a) were normalized to its corresponding electrical modulus peak frequency (described in Section 4.2.4) and plotted in Figures 4.4(c) and 4.5(c). The plots show that the shape of the dielectric spec-
Figure 4.5: (a) Log and (b) linear and for 0.0035K₂S + 0.9965B₂S₃ glass
Figure 5.5(c): Reduced frequency plot of the dielectric constant for $0.0035K_2S + 0.9965B_2S_3$

The spectrum is defined independent of temperature and frequency. The frequency shift is thermally activated similarly to the d.c. conductivity.

Figure 4.4(c) is spectacular. The spectrum is defined over twelve decades of frequency and the superposition of each temperature spectrum is near perfect. The polarization mechanisms described above are clearly seen in this figure. The result for the low alkali glass is not as dramatic because the space charge polarization plateau is not observed but the superposition of the isotherms are near perfect. From similar plots where all the features are apparent, values of $\varepsilon_\infty$ (interchangeable with $\varepsilon_\infty$) and $\varepsilon_i$ are determined.
In the next section, analysis of the orthogonal component of the dielectric constant, the real part of the conductivity, is given. To introduce the next topic, this section is concluded with Figure 4.6.

### 4.2.3. Almond-West Model Parameters

The Almond-West model was discussed in section 2.2.1. Eq. (2.15) is shown below and is fit to the real part of the conductivity data:

$$\sigma' = \sigma_{d.c.} + A\nu'. \quad (4.1)$$
Examples of the Almond-West fits for a lithium thiosilicate glass were shown in Figure 2.5. Fits for the conductivity isotherm for various temperature of a potassium thiborate glass and silver modified thioborate-thiosilicate glass are shown in Figures 4.7 and 4.8, respectively.

To determine the Almond-West parameters in Eq. (4.1), values for the d.c. conductivity, the constant in front of the frequency term \( A \) and the slope \( s \) are provided as initial guesses to a non-linear least-squares fitting routine. The initial guess for the d.c. conductivity can be determined by using the complex plane analysis method described in section 4.2.1 or determined approximately from the conductivity value at the conductivity plateau. The slope \( s \) is typically between 0.7 and 0.8 for most glasses and an initial guess of 0.75 is used. The value
for $A$ is determined from Eq. 2.20 ($A = \sigma_{dc}/\nu_h^*$), where the approximate 'hopping' frequency ($\nu_h$) used is the frequency where the $\sigma'(\nu) = 2\sigma_{dc}$. Good initial guesses are crucial for the fitting routine to converge. The routine iterates until the chi-squared value of less than $10^{-15}$ is obtained. The quality of the fits to the data for all three glasses are excellent and typical for most glass data. Fits for the two high temperature silver sulfide isotherms (Figure 4.8) are not obtained because there are not enough data points available to perform a good fit. The 'hopping' frequency $\nu_h$ is determined from the slope $s$, $A$ and $\sigma_{dc}$ in Eq. (2.20). The activation energy ($\Delta E_e+\Delta E_m$) for $\sigma_{dc}$ and the activation energy ($\Delta E_m$) for $\nu_h$ are determined by plotting $\sigma_{dc}T$ and $\nu_h$ on an Arrhenius plot similarly as shown in Figure 2.4.
Once, $\sigma_{de}$ and $\nu_H$ are known then with appropriate values for the ion hop distance ($\lambda$) and the geometric constant ($\gamma$), the value for the concentration of mobile ions can be calculated through Eq. (2.5) in the following form:

$$n = N_e \exp \left(-\frac{\Delta E_c}{kT}\right) = \left(\frac{kT}{(Ze)^2 \gamma \lambda^2}\right) \left(\frac{\sigma_{de}}{\nu_H}\right)$$ (4.2)

In the case where the space charge polarization and the conductivity dispersion almost overlap in frequency and the d.c. conductivity plateau is not clearly defined, as seen in Figure 4.9 for a $0.1\text{Na}_2\text{S} + 0.9\text{B}_2\text{S}_3$ glass, then the contribution of the polarization has to be accounted for in the Almond-West model. This complication has been accounted for through

Figure 4.9: Example of overlap of space charge polarization and the conductivity dispersion overlap for a $0.1\text{Na}_2\text{S} + 0.9\text{B}_2\text{S}_3$ glass,
a collaboration with Drs. Ernest Hairetdinov and Nikolai Uvarov of the Institute of Solid State Chemistry in the Russian Academy of Sciences and is described here.

To describe the electrode impedance an appropriate expression for the electrode impedance has to be determined. Since blocking gold electrodes are used, the electrode impedance can be modeled in terms of either a capacitor or a Complex Phase Admittance (CPA) [130] in series with the bulk conductivity of the glass as shown in Figure 4.10. A capacitor will exhibit an a.c. conductivity $\sigma_{a.c.} \propto \nu$ as $\nu \to 0$, however, the experimental slope $d(\log \sigma)/d(\log \nu)$ appears to be less than unity. Therefore, the experimentally measured electrode admittance may be better described by the CPA element:

$$Y_{CPA}^* = Y_e \nu^a (\cos \phi + i \sin \phi)$$  \hspace{1cm} (4.3)
where $Y_e$ and $\alpha$ are parameters and $i = \sqrt{-1}$. The bulk complex conductivity for the glass, $\sigma^*_g$, modeled in Figure 4.11 is given by

$$\sigma^*_g(v) = \sigma'_g(v) + i2\pi v\varepsilon_\infty'$$  \hspace{1cm} (4.3)

where $\sigma'_g$ is the real part of the glass a.c. conductivity defined by Eq. (2.23) and $\varepsilon_\infty$ is the limiting high-frequency dielectric permittivity of the glass. The total complex AC conductivity, $\sigma^*$, for the glass and the electrode is determined using the following equation:

$$\sigma^*(v) = \frac{Y^*_\text{CPA}(v) \times \sigma^*_g(v)}{Y^*_\text{CPA}(v) + \sigma^*_g(v)}$$  \hspace{1cm} (4.4)

The real part of the conductivity for the scheme presented in Figure 4.10 is determined by separating the real and imaginary parts of the complex conductivity in Eq. (4.4) and is given below:

$$\sigma'(v, T) = \frac{Y_e v^\alpha \left( \sigma'_g Y_e v^\alpha + \sigma_g^2 \cos(\alpha) + (2\pi v\varepsilon_\infty)^2 \cos(\alpha) \right)}{\sigma_g^2 + 2Y_e v^\alpha \left( \sigma'_g \cos(\alpha) + 2\pi v\varepsilon_\infty \sin(\alpha) \right) + (Y_e v^\alpha)^2 + (2\pi v\varepsilon_\infty)^2}$$  \hspace{1cm} (4.5)

This procedure will only give an approximate description of the electrode impedance. However, the aim of this analysis is to extract from the complex impedance data for the exact values for $\sigma_{de}$, $\nu_h$ and the slope $s$ and not to investigate the electrode effects in detail.

As described above, once $\sigma_{de}$ and $\nu_h$ are known and with appropriate values for the ion hop distance ($\lambda$) and the geometric constant ($\gamma$), the value for mobile ion concentration $n$ can be calculated from Eq. (4.2). This second fitting process was done for both the sodium and potassium thioborate glass system to estimate the charge carriers and the paper included in Appendix D.
4.3.2. Electrical Modulus and KWW relaxation function ($\beta$)

The background for this section is given in Section 2.2.2. The complex electrical modulus $M'$ is the inverse of the complex relative dielectric permittivity. The real part of the conductivity is given in terms of the electrical modulus by Eq. (2.24). Wide temperature electrical modulus data are shown in Figures 4.11 and 4.12 for the 0.0025Na$_2$S + 0.9975B$_2$S$_3$ and the 0.1AgI + 0.9AgPO$_3$ glasses. As in the case of the dielectric constant and the conductivity spectrum, the electrical modulus curves shift to the right with increasing temperature. The $M''$ peak frequency shifts thermally at the same rate as the d.c. conductivity and hence both have the same activation energy. The temperature dependence of the peak relaxation frequency for both glasses is shown in Figure 4.13 from which the frequency prefactor, $\nu_0 = (2\pi\tau_0)^{-1}$, and the activation energy are determined.

The frequency of each isotherm can be normalized by the peak frequency of the imaginary part of the electrical modulus, $M''$. The results of the normalization are shown in Figures 4.11(c) and 4.12(c). The near perfect overlap of the different temperature data, superimposed on the single master curve, illustrates well the quality of the fit and that all dynamic processes occurring at different frequencies exhibit the same activation energy.

The method for fitting the data the KWW function is next described. An initial values for $\beta$ is determined from the magnitude of the FWHM of the $M''$ peak. $\beta$ is then graphically fine tuned by overlapping pre-calculated modulus curves on the experimental data. By varying the magnitude of $M$ and $\beta$ for the fitting curve, the disagreement between the experimental data and the fit is easily minimized with errors in $\beta$ of less than ±0.005. This whole process is computer automated using the impedance spectroscopy analysis software package developed by the author [102]. The smooth line through the modulus data in Figures 4.11(c) and 4.12(c) is the KWW fit to the data.
Figure 4.11: Plots of the isothermal frequency spectra of (a) $M'$ and (b) $M''$ for a series of temperatures for 0.0025Na$_2$S + 0.9975B$_2$S$_3$ glass
Figure 4.11(c): Plots of the superimposed $M'$ and $M''$ for a wide range of temperatures for $0.0025\text{Na}_2\text{S} + 0.9975\text{B}_2\text{S}_3$ glass
Figure 4.12: Plots of the isothermal frequency spectra of (a) $M'$ and (b) $M''$ and (c) the superimposed $M'$ and $M''$ for a series of temperatures for 0.1LiI + 0.9AgPO$_3$ glass.
Figure 4.12: Plots of the superimposed $M'$ and $M''$ for a wide range of temperatures for the $0.1\text{LiI} + 0.9\text{AgPO}_3$ glass
Figure 4.13: Arrhenius plots of the frequency at the maximum value of the imaginary part of the modulus for a sodium thioborate and silver metaphosphate glasses.
CHAPTER 5: COMPOSITIONAL CONTRIBUTION TO THE CONDUCTIVITY

The compositional contribution to the d.c. conductivity and the conductivity dispersion is discussed in this chapter. Glasses in the Na$_2$S + B$_2$S$_3$ and K$_2$S + B$_2$S$_3$ glass families over a three decade range of glass composition have been electrically characterized over a wide frequency (1 Hz - 1 MHz) and temperature (100 - 500 K) range. These wide compositional, frequency and temperature study allow for the first-time ever, many of the ideas and hypothesis presented in the Background chapter to be tested.

The analysis and discussion of results for both these glass families are given together in the Section 5.1. The discussion in the first part (5.1.1) is focused on the d.c. conductivity and then directed to the a.c conductivity and conductivity relaxation in the second part (5.1.2). The summary of conclusions obtained from Sections 5.1.1. and 5.1.2. are given Section 5.1.3.

The conductivity dispersion was analyzed using the widely used electrical modulus formalism and the KWW function to describe the non-exponential relaxation of the conducting ions (see Section 2.2.2). During the course of the writing of this dissertation, the author has questioned the validity of the interpretation of the results using the above method of analysis. Although the data are good and the analyses are correct, the interpretation may be flawed from the outset. The reader is reminded, however, that the analyses using the above technique was a major portion of the author's research project and has previously been peer reviewed. This analysis and the interpretation using the above method on the assumption that it is valid are given in this chapter. Hints of problems with this technique and the predicted results are pointed out through out the discussion of both this and the following chapter and will be explained in fuller detail in Chapter 7.
The number of mobile charge carriers was estimated using the real part of the conductivity data for the sodium and potassium thioborate glasses and the Almond-West model. This work was done in collaboration with Dr.'s Ernest Hairetdinov and Nikolai F. Uvarov of the Institute for Solid State Chemistry at the Russian Academy of Sciences and has been published elsewhere [149,150].

Li₂S + SiS₂ glasses prepared for the NSLR experiment were electrically characterized, and the results for some of these glasses have been previously reported by Pradel et al. [27,28,42]. The conductivity increases and activation energy decreases with alkali concentration. The results on Table 4.3 are in good agreement with those reported by Pradel et al. Any disagreement may be attributed to the non-Arrhenius conductivity exhibited at high temperature by all FIC glasses.

5.1. M₂S + B₂S₃ Glasses

Glasses in the xNa₂S + (1-x)B₂S₃ system in the composition range 0.001 ≤ x ≤ 0.15 and 0.55 ≤ x ≤ 0.80 were batched, melted, cast into disks and electrically characterized using impedance spectroscopy. Parallel potassium and lithium studies to examine the universality of the conductivity trends observed in the sodium thioborate glasses were also performed.

Potassium glasses are typically not studied because of the low ion mobility of the K⁺ ion. In the case of sulfide glasses, however, the mobility is high enough to make the ion conductivity measurable. Glass compositions in range x ≤ 0.4 for the xK₂S + (1-x)B₂S₃ system were prepared and electrically characterized using impedance spectroscopy. IR spectra of these glasses have shown a dramatic increase in oxide contamination with the addition of K₂S in these glasses for x ≥ 0.25 [96]. Conductivity results for these glasses should be analyzed with this oxide contamination in mind.

In the case of the lithium thioborate glasses, a low alkali glass forming region does not exist. The melts phase separate for concentrations of approximately x = 0.1 and crystallize for lower lithium concentration. In the high lithium content region, two glasses of composition x
= 0.65 and 0.70 were prepared and only the $x = 0.70$ was electrically characterized. This glass was intended for ion dynamics studies using NSLR and the discussion of both the electrical and NSLR results are given in Chapter 6.

Although the research direction for the potassium thioborate study stemmed from the initial results of the sodium thioborate system, the results and discussion for both the potassium and sodium thioborate glasses are given together in this section.

The compositional trends in the d.c. conductivity parameters will be related to the Nerst-Einstien equation and the Anderson-Stuart model in the first section. Similarly, the compositional trends in the conductivity dispersion/relaxation using the KWW and electrical modulus formalism will be shown in the second part.

5.1.1. **d.c. Conductivity**

The background for this discussion is found in Section 2.1. The predominant interest in investigating fast lithium conducting glasses has been to optimize the d.c. conductivity for their use as solid electrolytes in solid state batteries. For that reason, less attention has been given to the studies of heavier and less mobile sodium and potassium ion glasses. Furthermore, studies were concentrated in the high alkali region where the ionic conductivity is greatest due to the larger charge carrier concentration. This is first-ever wide composition study of glasses in the low alkali region.

Arrhenius plots of the d.c. conductivity for sodium thioborate glasses in the low and high alkali region are shown in Figures 5.1 and 5.2. Similar plots for sample glasses in the potassium thioborate system are shown in Figure 5.3. As seen in most studies of FIC glasses, the d.c. ionic conductivity increases with an increase in temperature and an increase in alkali ion content.

The true d.c. conductivity activation energies for these glasses are determined by plotting $\sigma_{dc}T$ on an Arrhenius plot and are listed in Tables 4.1 and 4.2. These values are plotted versus the composition in Figure 5.4 for both glass systems. The data on the sodium glasses re-
Figure 5.1: Arrhenius plot for the d.c. conductivities obtained from the complex impedance plots of $xNa_2S + (1-x)B_2S_3$ glasses in the range $x \leq 0.15$. 
Figure 5.2: Arrhenius plot for the d.c. conductivities obtained from the complex impedance plots of $x\text{Na}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses in the range $0.55 \leq x \leq 0.80$
Figure 5.3: Arrhenius plot for the d.c. conductivities obtained from the complex impedance plots of \( xK_2S + (1-x)B_2S_3 \) glasses in the range \( x \leq 0.40 \).
ported by Levasseur et al. [90] and Susman et al. [94] are included on the graph and are in good agreement with these results. The log composition plot of the activation energy in Figure 5.5 is used to expand the low alkali region to show the behavior of the activation energy more clearly. The sodium glass activation energy in the low alkali region decreases from the asymptotic 0.77 eV value (limit as $x \to 0$) to 0.35 eV at $x = 0.3$. In the high alkali region, the activation energy is greater than that for the $x = 0.3$ sodium glass and is weakly dependent on the composition. The potassium data also decrease from an asymptotic 0.83 eV value but does not decrease as rapidly as the sodium data.

Figures 5.4 and 5.5 also show the compositional dependence on the d.c. conductivity prefactor. No obvious trends are apparent in the low alkali region except to say that the compositional dependence on the d.c. conductivity prefactor is weak. In the high alkali region, the prefactor increases by an order of magnitude from the value in the low alkali region. For lithium thiborate glasses studied by Menetrier et al. [97], the increase in the prefactor is of two orders of magnitude.

The d.c. conductivity at 150 °C is given in Figure 5.6. The conductivity increases linearly with composition in the region between $(0.001 \leq x \leq 0.02)$ and increases super-linearly for higher values of $x$ for both glasses. The conductivity for the sodium glass is greater than the potassium glass through the whole glass composition range. This plot is not discussed further because the conductivity at a given temperature has no significance by itself.

The general trends in the parameters have been described above. The predictions of the various models to describe the trends in the conductivity parameter as function of composition are discussed in detail next.

5.1.1.1. **Activation energy** The physics contributing to the dramatic change in the activation energy in the low alkali region is probably very different from the physics in the high alkali region. For that reason, this discussion on the activation energy is first focused on the low alkali region and then directed to the high alkali region.
Figure 5.4: Linear plot of the $x\text{Na}_2\text{S}$ and $x\text{K}_2\text{S}$ compositional dependence of the d.c. activation energy and the conductivity prefactor.
Figure 5.5: Log plot of the $x\text{Na}_2\text{S}$ and $x\text{K}_2\text{S}$ compositional dependence of the d.c. activation energy and the conductivity prefactor
Figure 5.6: (a) Linear and (b) log plot of the $xNa_2S$ and $xK_2S$ compositional dependence of the (a) d.c. conductivity at $T = 150 \, ^{\circ}\text{C}$.
The dramatic decrease in the activation energy in the low alkali region with an increase in concentration is similar to the behavior of the Na*-Na* separation distance and concentration shown in Figure 2.10 in Section 2.2.3. The dependence of the activation energy on the alkali ion-ion separation distance $\alpha$ is shown in Figure 5.7. Density values to determine the alkali ion separation distance have been reported for sodium thioborate glasses by Polewick and Martin [102] and for potassium thioborate glasses by Cho and Martin [96]. The plot shows a smooth connection between two regions of dependence on ion separation distance. The first region, $\alpha < 15 \, \text{Å}$ (for $x > 0.02$), shows a strong positive dependence of the activation energy on the separation distance, $\alpha$. This effect is more pronounced for the sodium glass. The sec-

![Figure 5.7](image)

**Figure 5.7:** $\Delta E_{\text{act}}$ plotted against the average $M^*-M^*$ separation distance, the line is best fit of Eq. 5.1
ond region, $\alpha > 15 \text{ Å}$, shows a weakly dependent activation energy asymptotically approaching $\sim 0.77 \text{ eV}$ and $\sim 0.8 \text{ eV}$, for the sodium and potassium glasses, respectively.

To discuss the above observations, we proceed in the order of decreasing alkali concentration (increasing $\alpha$). For the alkali composition range of $0.02 < x < 0.5$, a strong increase in the activation energy is observed with an increase in $M^+\cdot M^+$ (alkali ion) separation distance. This phenomenon has been widely reported for most alkali glasses in a similar composition range [57-72]. Martin and Angell have explained this phenomenon by suggesting that the activation energy is a function of the amount of overlap between the potential energy wells of cation sites [57,65,70]. They show, through the Anderson-Stuart model [2], that the energy barrier for each cation (i.e. the activation energy) increases as the overlap between potential energy wells decreases due to an increasing alkali-alkali ion separation distance (see Section 2.1.2, Figure 2.2). They assumed here that the jump distance was the alkali-alkali ion separation distance.

At high alkali, $x > 0.05$, the overlap between these potential energy wells, for all practical purposes, has saturated as the ion separation distance saturates at a small value $< 5 \text{ Å}$, and thereafter changes little with added alkali. As the alkali is decreased below $x = 0.05$, however, dramatic increase in $\alpha$ occurs and as such the overlap between potential energy wells decreases.

The trend in the activation energy observed in the very low alkali region of Figures 5.4 and 5.5, to the best of the authors' knowledge, is reported here for the very first time. In this region, the activation energy no longer shows the strong linear dependence on the jump distance as observed in the higher alkali region. $\Delta E_{\text{act}}$ increases asymptotically as $x$ decreases to a final value of $\sim 0.77 \text{ eV}$ and $\sim 0.83 \text{ eV}$ for sodium and potassium glasses, respectively. This behavior suggests that this value may be the fundamental limiting energy barrier affecting the conduction mechanism. This result is in accordance to the Anderson-Stuart model [2], where the activation energy ($\Delta E_{\text{act}}$) is given by the sum of the strain energy ($\Delta E_s$) and the coulombic binding energy ($\Delta E_b$) given in Eqs. (2.7) - (2.9):
\[
\Delta E_{\text{act}} = \Delta E_s + \Delta E_b = 4\pi G r_D \left( r - r_D \right)^2 + \frac{ZZ_0 e^2}{\varepsilon_\infty} \left[ \frac{1}{r + r_o} - \frac{2}{\lambda} \right]
\]  \tag{5.1}

where \( G \) is the shear modulus of the glass; \( r_D, r \) and \( r_o \) are the interstitial window, the mobile cation and the non-bridging anion radii, respectively; \( \lambda \) is the jump distance; \( Z \) and \( Z_0 \) are the charges on the mobile cation and the anion; and \( e \) is the charge on the electron. The variation in the shear modulus and \( \varepsilon_\infty \) for these slightly different glass compositions may be best approximated as constants. The strain energy contribution to the activation energy is therefore expected to be a constant and fairly small, see reference [57] for calculations on Na\(_2\)O + B\(_2\)O\(_3\) glasses. In the coulombic energy part, all the variables are constant except for \( \lambda \). Typically, the value used for the average jump-distance is the \( M^-\cdotM^- \) separation distance \( \alpha \). The line through the data in Figure 5.7 then is the activation energy calculated from the A-S model using \( \alpha \). The trend is in good agreement with the experimental data and shows the rapidly diminishing influence of the jump distance for \( \alpha > 15 \text{ Å} \).

A question which arises from these results for dilute glass systems is what is an acceptable definition for the jump distance? The alkali-alkali ion separation distance has been used as the jump distance for alkali concentrations greater than \( x = 0.02 \). It would seem that the asymptotic behavior of the conductivity activation energy in the low alkali region suggests that whatever the energy barrier, it appears to remain constant. Some hint for the asymptotic value can be gained by returning to the Anderson-Stuart Equation (2.8) and (2.9). The limit as \( \alpha \) goes to infinity for this equation is:

\[
\lim_{\alpha \to \infty} \Delta E_{\text{act}} = \lim_{\alpha \to \infty} \Delta E_s + \lim_{\alpha \to \infty} \Delta E_c
\]

\[
= \lim_{\alpha \to \infty} \Delta E_s + \frac{Z Z_0 e^2}{\varepsilon_\infty} \left[ \frac{1}{r + r_o} - \frac{1}{\alpha} \right]
\]

\[
= \text{const.} + \frac{Z Z_0 e^2}{\varepsilon_\infty} \left[ \frac{1}{r + r_o} \right]
\]  \tag{5.2}
Unfortunately, without values for the shear modulus, $G$, and the interstitial window radius, $r_{\text{D}}$, accurate estimations are not possible. What these equations do suggest, however, is that the activation energy is one where the cation is not jumping into another cation site, but, rather, into some type of defect site. Here if a cation were jumping into a near-neighbour site, then the $\alpha^{-1}$ term would be active. The exact nature of the defect site, however, is unknown at this point. Perhaps one possibility would be for the jumping cation to cause bond interchange according to the reaction shown in Figure 5.8.

![Figure 5.8: Possible ion jump mechanism for conducting ions, especially in the ultra-low alkali limit](image)

This would require a cage activation energy, essentially that of the B-S bond strength. At the low alkali extreme where it is believed such processes may be taking place, the limiting activation energy is $\sim 0.8$ eV (71 kJ/mol). This value is much smaller than the estimated B-S bond strength of 200-300 kJ/mol and suggests that if such a process is occurring, it must be a connected one where bond breaking and reforming processes are acting simultaneously to lower the activation barrier. To answer these questions, molecular dynamics simulations should be
used to determine the actual jump distance and investigate the various possible cation environments in these low alkali glasses.

If the jump distance is assumed to follow a mechanism similar to the one described above then the jump distance with some distribution may be considered to be invariant. With this assumption, a slight modification to the Anderson-Stuart equation could be used to account for the additional effect of the well overlap potential and is given as the following:

\[
\Delta E_{\text{act}} = \left[ \frac{\pi G \lambda (r - r_o)^2}{2} \right] + \frac{ZZ_0 e^2}{\varepsilon_\infty} \left[ \frac{1}{m} \left( \frac{1}{r + r_o} - \frac{2}{\lambda} \right) - \frac{1}{n(\alpha)} \right] \tag{5.3}
\]

The original strain energy term has been replaced by a more realistic strain energy term proposed by McElfresh and Howitt [37] for the passage of a sphere through a dilated cylinder. In the coulomb term, the average jump distance is used to determine the maximum energy required for an ion to be at the saddlepoint between the energy potential well inhabited by the ion and the potential energy well for the future jump site. The \(1/m\) parameter is used to modify the macroscopic dielectric constant parameter to account for the actual polarizability in the microscopic domain of the ions. The second part of the coulomb energy term is the modification of the potential energy barrier between two jump sites due to the effect of overlap of energy barriers of other alkali ions. The \(n\) parameter used to modify the dielectric constant is different from the value \(m\) because of the different amount of shielding by neighboring atoms.

The results of graphically fitting the data to (Eq. 5.3) by varying the parameters \(m\) and \(n\) are shown in Figure 5.9. The value used for the jump distance was 5.6 Å, which is slightly larger than the sum of the diameters of the sulfur and alkali ion. This large value was used because the ionic conduction pathway is thought to be a percolation path through the material, connecting equilibrium diffusion doorways, which has the lowest effective activation energy for all such paths. The measured conductivity activation energy, is then defined as the highest barrier for ionic motion on the conduction pathway or the most difficult, successful hop on the easiest conduction pathway. The exact value for the shear modulus is not available and was...
approximated to $9 \times 10^9$ (Nm$^{-2}$) using the technique demonstrated by Tanaka [131] and, also, by comparing to shear modulus values of the various alkali oxide glasses reported by Fusco et al. [132]. The radius of the interstitial window was calculated assuming that the doorway was made up of four sulfurs in contact with each other. A value of 0.23 Å was calculated ($r_d = (0.225)r_{sulfur}$) and a value of 0.24 Å was used. The value for the dielectric constant was approximated to 6 for the purpose of fitting. The results of the fit and the calculated values for the energy for an ion at the saddle point and the strain energy terms are shown on Table 5.1.

The value for $m$ is reasonable and implies that the polarizability felt by the ions in the glass is 6.5 time greater than that measured macroscopically. The large $n$ value suggests that the effect of the coulomb potential wells of alkali ions are strongly shielded by atoms in the glass.
network but still contribute to a decrease in the coulomb energy. The $n$ value for potassium is twice that of the sodium glass to account for the weaker contribution of the shallow coulomb wells.

The difference in the values of the activation energy and the rates of decrease in the activation energy with alkali concentration for the sodium and potassium thioborate glass system is made clear from the results of Table 5.1. The magnitude of the coulomb activation energy for the sodium glass is twice that the value of the strain energy term. In the case of the potassium glass, however, the strain energy term contributes twice as much to the total activation energy than the coulomb term. These results are a consequence of the difference in the ionic radius of the two ions. The smaller radius increases the coulomb energy term and decreases the strain energy term as seen in Eq. (5.3). This oppositely related energy terms to the ionic radius are almost balanced in the sodium and potassium thioborate glasses. They both have very different values for the strain and coulomb energy term but the sum is almost the same.

Table 5.1: Fitting parameters in Eq. (5.3) for fits shown in Figure 5.9

<table>
<thead>
<tr>
<th>Ion</th>
<th>$r_{ion}$ (Å)</th>
<th>$m$</th>
<th>$n$</th>
<th>$\Delta E_{Saddle Point}$ (eV)</th>
<th>$\Delta E_{Strain}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>1.02</td>
<td>6.5</td>
<td>24</td>
<td>0.54</td>
<td>0.30</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.38</td>
<td>6.5</td>
<td>10</td>
<td>0.20</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The roll off in activation energy with decreasing jump distance observed for the sodium glass is not as dramatic for the potassium glass data because in the case of the potassium glass system the data approaches the value of the strain energy much sooner. As seen in Eq. (5.3), the overlap of alkali ion energy potential wells with increasing ion concentration, decreases
only the contribution of the coulomb term to the total activation energy. The strain energy is unaffected. This roll off therefore will be most dramatically apparent for glasses with large coulomb terms and/or small strain terms.

The observation of the dominance of the strain energy term to the overall ionic conductivity in glasses is not common. Fusco et al. [132] in their study of alkali metaborate glasses have reported for their glasses the importance of the strain energy contribution to the total activation energy. However, Wang et al. [133], Muller et al [134] and others have concluded that the strain energy contribution to the total migration energy is negligible or non-existent, which clearly contradicts the results of this work.

An alternative possibility for the activation energy plateau for the potassium glass may be due to oxide contamination. IR spectra has shown the increasing oxide contamination of the glasses with increasing addition of K$_2$S. Although IR spectroscopy is extremely sensitive to trace amounts of impurities and impedance spectroscopy is a bulk measurement, the possibility exists that gross level of oxygen contamination exists and the material being studied is actually an oxy-sulfide glass. It is well documented that mixing glass formers improves the glass formation and may well be the reason why the glass forming region for potassium compared to the other alkali glasses is so much more extended. The activation energy reported for K$_2$O + B$_2$O$_3$ by Beekankamp [135] are greater than 1 eV in the low alkali region (x < 0.15). The activation energy data for both the oxide glass and sulfide glass are shown in Figure 5.9 where the dotted lines are the hypothesized curves for pure oxide and sulfide glasses and the glass data is assumed to be an oxy-sulfide.

In the high alkali region, the activation energy for the sodium glass is weakly dependent on the composition. It is apparent that the a minimum in the activation energy occurs between x = 0.3 and x = 0.55 but glasses cannot be formed in this region. The increase in activation energy is contributed to the increase in the glass basicity. $^{11}$B NMR studies on these glasses by Sills [136] show that in the low alkali region, addition of alkali sulfide to the glass composition result in a change of three coordinated boron units to four coordinated boron units with
the incorporation of the sulfur (associated with the alkali ion) into the glass network as bridging sulfurs. The negative charge on these four coordinate units is delocalized and the alkali ion is weakly associated to the whole unit.

Further addition of alkali ions gives rise to the non-bridging sulfurs in the network as the number of four coordinated borons become saturated. These non-bridging sulfurs act as localized traps for alkali ions. These ionic bonds are typically stronger than the delocalized shallow wells and an increase in the activation energy is expected and observed. For compositions of $x = 0.5$ and greater, most of the four coordinated boron units have disappeared and trigonal non-bridging boron units begin to dominate the structure. The glass network becomes more

Figure 5.10: Anticipated change in activation energy with composition due to oxide contamination in potassium thioborate glasses
ionic in nature and little change in the activation energy is expected. Menetreir et al. [97] in the lithium thioborate glass and Martin [101] in the sodium borate glasses have shown that the activation energy increases throughout the high alkali composition range but this is not the case for the sodium thioborate glasses.

5.1.1.2. d.c. conductivity prefactor $\sigma_0$. The d.c. prefactor for both glasses are approximately the same in the low alkali region. There is more scatter in the sodium data but the data for the potassium are very good and are used for the following discussion. The potassium prefactor increases slowly in the low alkali region and then linearly with the composition for $x > 0.1$. In the same region, a linear increase is also observed for the sodium glass system. The super-linear increase observed for the lithium thioborate glasses by Menetrier et al. [97] is shown in Figures 5.4 and 5.5 but is not observed for the sodium glass.

To explain the linear increase in the prefactor, the Nerst-Einstein derivation needs to be examined more closely. The prefactor is given by

$$\sigma_0 = \frac{N_e(Ze)^2 \gamma \lambda^2 v_e}{k} \quad (5.4)$$

where all the variables are assumed to be constant with composition except for $v_e$, $N_e$ and $\lambda$. The vibrational frequency is expected to increase weakly with composition as reported by Kamitsos et al. [137,138] for oxide glasses. They report a gradual increase in the wavenumber from 165 to 237 cm$^{-1}$ and 127 to 185 cm$^{-1}$ for sodium and potassium borate glasses in the composition range $0.05 \leq x \leq 0.35$, respectively. No wide composition data were available for the sulfide glasses except for the single composition study of sodium thioborate for $x = 0.6$ by Susman et al. [94] and it is assumed that a similar increase is expected for sulfide glasses. This increase does not account for the order of magnitude increase in the prefactor but does contribute weakly to the overall increase in the prefactor.

The previous discussion on the activation energy stressed that the jump distance must vary slightly with composition and not play a significant role in the prefactor. For that reason,
the linear increase in the prefactor with concentration in the composition range \( x > 0.1 \) must be indicative of the strong dependence of the prefactor on \( N_e \).

In the ultra low alkali region \( (x < 0.1) \), there is a decrease in the prefactor showing a weaker dependence on the concentration. It is hypothesized that other electronic conductors are present in the glass which are not accounted for and contribute to the prefactor and their base contribution dominates in the ultra low alkali region and the overall conductivity. The dotted line in Figure 5.11 shows the expected decrease in the prefactor due to the contribution of the alkali ions only. The horizontal (or could have been increasing) dotted line is the assumed base impurity or electrons contributing to the prefactor. The sum of the two different
types of charge carriers contribute to the measured prefactor and hence the reason for the change in slope.

The possibility of electronic conduction is very high in these glasses and should be examined in the future. They are green in color and electronic transitions may occur due to optical excitations. Furthermore, reports of electronic conduction has been reported in some chalcogenide glasses by Souquet et al. [137]. The other possibilities is impurities. The reader is reminded that the amount of alkali sulfide added to a two gram batch of boron trisulfide is less than 0.5 mg. Any dust in the glovebox falling on the batch could contribute to the conductivity. The purity of composition is very difficult to maintain at this concentrations. Other experiments and analysis techniques are necessary to determine the contribution of impurities.

5.1.2. Conductivity Relaxation

The purpose for studying ultra-low alkali glasses is to verify that the conductivity dispersion with frequency was a result of non-exponential relaxation of conducting ions and the non-exponentiality was a result of ion-ion interaction. It is anticipated that by increasing the alkali ion-ion separation distance, the amount of ion-ion interaction should decrease and single exponential time relaxation behavior should be approached. The background for this discussion and analysis is found in Sections 2.2.2 and 2.2.3.

Isothermal frequency plots of the real part of the conductivity for the $x = 0.005$ sodium and $x = 0.05$ potassium composition glasses are shown in Figures 5.12(a) and 5.13(a). All analyses data for these two different glasses will be show in parallel to each other through out the discussion. The data show a frequency independent conductivity for low frequencies and high temperature followed by an increase in conductivity for higher frequencies and lower temperatures. The switch from the frequency independent to the dependent region signals the onset of the conductivity relaxation phenomena. In order to relate the conductivity to the relaxation of the mobile ions, one can rely on the phenomenological nature of the electric modulus [7], or on the generalized Nerst-Einstein formalism [34]. The electrical modulus ap-
Figure 5.12: (a) Conductivity isotherms showing frequency dependent conductivity for a series of temperatures for 0.005Na₂S + 0.995B₂S₃ glasses. (b) Master plot of the normalized $\sigma_{dc}$ conductivity plotted against normalized $M^*$ peak frequency.
Figure 5.13: (a) Conductivity isotherms for a series of temperatures for $0.05\text{K}_2\text{S} + 0.95\text{B}_2\text{S}_3$ glasses. (b) Master plot of the normalized $\sigma_{dc}$ conductivity plotted against normalized $M^+$ peak frequency of the corresponding temperature.
proach to analyze the relaxation phenomena is preferred as it is easier to relate to other properties, especially the dynamical mechanical modulus, and can be written as a single function of the conductivity.

The real part of the conductivity, $\sigma'$, is related to the complex electrical modulus through Eq. [2.24]. Any change in the spectra of the real part of the modulus, $M'$, is indicative of a change in the "stiffness" of the material under test, and the frequency region where this change occurs is emphasized by a "loss" peak in the imaginary part of the modulus.

Using Eqs. (2.24), the conductivity can also be related directly to the relaxation function, $\phi(t)$. Macedo et al. [7] have already shown that for a non-exponential relaxation the conductivity will exhibit a strong frequency dependence. To examine this, Figure 5.12(b) shows a master plot of a series of a.c. conductivity curves for the sodium glass where the frequency has been normalized by the peak frequency for that temperature of the imaginary part of the electrical modulus and the conductivity scale has been reduced by the d.c. conductivity, $\sigma_{d.c.}$. The same is done for the potassium glass in Figure 5.13(b). As expected, the curves are superimposable in accordance with the temperature independence of the relaxation function and the superposition principle. Figures 5.14 and 5.15 show similar plots but are now of a series of glasses in each glass family. Here all the temperatures were chosen such that each glass would have approximately the same relaxation frequency, $\sim 1$ kHz. In this way, each curve would have about the same data region above and below the peak frequency in the imaginary modulus. Figure 5.14 and 5.15 shows that as alkali is added to the glass, the frequency dependence of the conductivity appears to increase. Note that for low alkali glasses, there is a range of frequencies above $v/v_{c} = 1$ where the conductivity remains frequency independent. The conductivity dispersion, however, does eventually occur for all glass compositions. The data for the potassium glass in Figure 5.15 clearly show that the conductivity dispersion at higher frequencies has approximately the same slope independent of glass composition. It is not clear at this point whether the increase in conductivity especially at lowest $x$ and highest
Figure 5.14: Conductivity for a series of $x\text{Na}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses
Figure 5.15: Conductivity for a series of $xK_2S + (1-x)B_2S_3$ glasses
frequency arises from conductivity relaxation, from another loss mechanism or an artefact of
the construction. This question will be further investigated in Chapter 7.

Parts of the next discussion have been mentioned in the background section but are re­
peated here to remind the reader of the common interpretation of the electrical modulus and
also to guide the reader through the logic of the experiment. Figures 5.16 and 5.17 show a
series of isothermal frequency spectra of (a) $M'$ and (b) $M''$ and (c) the superimposed $M'$ and
$M''$ for the same sodium and the potassium glasses. The low frequency value of $M'$ is zero
and represents a lack of restoring force for the electric-field-induced mobile sodium ions. As
frequency increases, $M'$ increases to a maximum asymptotic value defined as $M'_m$. It is envi­sioned that as frequency increases, each ion moves a shorter and shorter distance as it changes
direction to keep up with the steadily increasing frequency electric field until finally, the elec­
tric field changes so rapidly that the ions only "rattle" within the confinement of their poten­tial energy wells. At these frequencies, the glass appears to have become "stiffer" because the
mobile ions have been frozen into the structure of glass.

The spectra of $M''$ shows an asymmetric peak approximately centered in the dispersion
region of $M'$. The region to the left of the peak is where the ions are mobile over long dis­tances, and the region to the right is where the ions are spatially confined to their potential
wells. The region where the peak occurs is indicative of the transition from long range to
short range mobility or more quantitatively defined as the condition where $\omega \tau = 1$, where $\tau$ is
defined as the most probable ion relaxation time.

The superimposed plots in Figure 5.16(c) and 5.17(c) were obtained by scaling each fre­
quency by the frequency of the maximum loss in $M''$. The near perfect overlap of the different temperature data, superimposed on the single master curve, illustrates well that all
dynamic processes occurring at different frequencies exhibit the same thermal activation en­
ergy. This result was also observed in Figure 5.12(c) and 5.13(c) for the conductivity. The
temperature dependence of the peak relaxation frequency for the sodium and potassium glass
are shown in Figure 5.18. The d.c. activation ($\alpha_{dc}$ instead of $\alpha_{dc} T$) energy and the $M''$ peak
Figure 5.16: Plots of the isothermal frequency spectra of (a) $M'$ and (b) $M''$ for a series of temperatures for $0.005\text{Na}_2\text{S} + 0.995\text{B}_2\text{S}_3$ composition glasses
frequency activation energy from Figure 5.18 agree quite well. This result explains why the isothermal conductivity spectrums shift to the right and up by 45° with increasing temperature. The temperature independence of the loss peaks may contradict the idea of a distribution of activation energies which has been suggested to explain the conductivity dispersion [58-72], however, the possibility exists that the distribution of activation energies may be frequency and thermally activated with the same d.c. activation energy. Alternatively, the possibility that the conductivity dispersion may be due to a second mechanism that contributes to the total conductivity and has a constant slope on a log frequency plot and is temperature independent.
Figure 5.17: Plots of the isothermal frequency spectra of (a) $M'$ and (b) $M''$ for a series of temperatures for $0.05K_2S + 0.95B_2S_3$ composition glasses.
Figure 5.17(c): Plots of the isothermal frequency spectra of (a) $M'$ and (b) $M''$ for a series of temperatures for $0.05K_2S + 0.95B_2S_3$ composition glasses

Plots similar to those shown in Figures 5.15 and 5.16, obtained for other glass compositions, differ only in the maxima value and the magnitude of the Full Width Half Maximum (FWHM) for $M''$ loss peak.

At this point, some peculiarities of the conductivity data obtained are pointed out. The conductivity and dielectric constant data for the sodium thioborate glasses in the range $0.02 \leq x \leq 0.04$ show no gross anomalous features but the conversion of the impedance data to the electrical modulus revealed two peaks in the imaginary component and corresponding increases in the magnitude of the real component. The low frequency peaks are similar in appearance and behavior to those of glasses with just one $M''$ peak, while the high frequency
peaks were extremely broad and their behavior not familiar. At the end of this section in Figure 5.25, the electrical modulus data plots for these glasses are shown. Since the second peak occurred at high frequency, it was attributed to the possibility that the impedance bridge was failing. An alternative optimistic idea proposed was that phase separation had occurred in the glass and somehow impedance spectroscopy had detected the different phases and therefore, could be used in the future to probe the glass microstructure. The d.c. conductivity parameters for these glasses, however, were easily obtained using the impedance data in form of the conductivity data but determination of the $\beta$ parameter was not possible. The author believes that this unusual behavior is not an artefact of the preparation of the glass, phase separation or
instrumentation but is a real phenomenon and has not observed before because very few studies in the low alkali region have been performed. This result is further discusses in Chapter 7.

The compositional dependence of the shape of the electrical modulus curves is quite apparent from the normalized frequency complex modulus plots for various sodium composition and potassium composition glasses shown in Figure 5.19 and 5.20, respectively. Here as with Figures 5.14 and 5.15, the temperature for each glass was chosen such that the relaxation frequency is about the same, ~1 kHz. The dramatic narrowing with decreasing x is quite evident and suggests the strong role that composition has upon the conductivity relaxation in the low alkali region.

The shape of each spectrum for each glass composition is quantified with a β value obtained by fitting the M' and M" curves to the Kohlrausch relaxation function by the method described in the last chapter. The smooth line through the modulus data in Figures 5.16(c) and 5.17(c) are a typical examples for the various glass compositions of the close agreement between the experimental data and the curve fit. The glasses in Figure 5.16(c) and 5.17(c) have a β value of 0.83 and 0.50, respectively. β values obtained for other composition glasses are given in Table 1 and plotted in Figure 5.21 against composition.

The β parameter decreases with decreasing concentration from ~0.5 to a minimum value of ~0.35 for the x = 0.05 Na₂S composition glass and then rapidly approaches 1 for x < 0.05. In the case of the potassium system, the β parameter is between 0.46 and 5.75 up to x = 0.02, and then increases rapidly to 0.9 but not as fast as in the sodium system. Even for the more dilute potassium glass composition x = 0.0005, β = 0.93 is not approached in comparison to the x = 0.001 sodium glass having twice as many alkali ions. Reasons for this behavior will be given in later. The general trend of the β with alkali composition is first discussed.

It is believed this is the first ever report clearly showing the transition between the non-exponential and exponential relaxation phenomena in glass. This approach towards exponential relaxation with reduced alkali content agrees well with the predictions of Simmons et al. [69], Ngai et al. [61] and Martin [65]. The electrical modulus data with a β of 0.93 for the
Figure 5.19: (a) the real and (b) imaginary part of the electrical modulus plotted against normalized frequency for selected glasses in the series $x\text{Na}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses
Figure 5.20: (a) the real and (b) imaginary part of the electrical modulus plotted against normalized frequency for selected glasses in the series $x\text{K}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses
Figure 5.21: Variation in the $\beta$ parameter versus $xM_2S$ where $M = \text{Na or K}$

$x = 0.001 \text{ Na}_2\text{S}$ glass in Figure 5.22 shows a nearly single exponential relaxation, almost identical to the modulus response of an ideal R-C circuit.

To further investigate the hypothesis that the approach to single exponential relaxation ($\beta \rightarrow 1$) may be associated with the lack of cation-cation interactions [61,69], $\beta$ is plotted against the average alkali-alkali ion separation distance ($\alpha$) in Figure 5.23, similar to Figure 2.11. The $M^+ - M^+$ ion separation distances were calculated using the assumption that the cations were uniformly distributed throughout the glass, from the composition and the density data of Martin and Polewik [102] and Cho [95] described in the last section. The results in Figure 5.23 show that $\beta$ increases almost linearly from 0.5 to 1 as the $M^+ - M^+$ separa-
tion distance increases from ~6 to ~50 Å and strongly suggests that the conductivity relaxation is inherently tied to the separation parameter. The last two sodium glass data points on this graph, the ones at B approximately equal to 0.46 and 0.35 fall of the linear curve and the reason for this is unknown at this point. However, the electrical modulus curves like those shown for x = 0.05 in Figure 5.19(b), do show enormous broadening, beyond what might be expected [68]. This may suggest that in the high alkali range x > 0.05, extra contributions exists than just the ion conductivity relaxation.

The fact that the β value rises to unity only at the lowest alkali fraction suggests that a long range force, such as the coulombic force, is responsible for the interaction leading to non-exponentiality. Another possible mechanism might be that, as others have suggested, the
mobile cations cluster, rather than disperse themselves randomly in the glass. Such an effect would cause the relaxation to retain its non-exponential character to levels of alkali below that where the cations would be thought to be jumping independently of one another. At present, we cannot refute nor corroborate this possibility.

An alternative possibility is that relaxation processes, independent of ion interaction, may have a distribution of relaxation times due to the inherent disorder in the glass network and uniqueness of each jump site. This contribution to non-exponential relaxation in a very primitive analysis may account for the continued presence of non-exponentiality even in the most dilute glasses, $\beta_{\text{uter}} = (1 - 0.93)$. What this last statement implies is that both serial and parallel
electrical relaxation processes are occurring in the glass but the non-exponentiality is dominated by the latter.

In any case, the results shown in Figure (5.23) and combined with those of Figure (2.11) are shown in Figure 5.24 and show a universal behavior for all glasses examined to date. It is believe that this is the first such universal mapping of the $\beta$ parameter with a structural parameter of the glass. Others, especially Martin and Ngai [61] have correlated $\beta$ with a "primitive" activation energy, $\beta E_{act}$. Although this correlation does work well for many glasses, the correlation to fit $\beta$ to a structurally recognizable variable, the alkali ion separation distance, is perhaps more significant.

Figure 5.24: $\beta$ parameter plotted against the average alkali ion ($M^-$- $M^+$) separation distance for various glasses
Figure 5.24 shows that the $\beta$ parameter for germanate glasses modified by rubidium is larger than that for sodium for the same ion-ion separation distance [66-68]. If a decrease in ion-ion interaction contributes to larger $\beta$ then it must be the case that rubidium ion interacts less than the sodium ion. The conduction activation energies for these rubidium glasses are not dramatically different from those of sodium glasses, but are slightly greater implying that the rubidium ions are less mobile and do not run into each other as frequently, and hence, maybe the reason for the larger $\beta$.

In the case of the thiborate glasses studied here, the $\beta$ values for the potassium glasses are less than those for sodium glasses over the whole composition range. This result is opposite to that observed for the germanate glasses. It is possible that the intrinsic conduction due to electrons or impurities in the potassium glasses described in the d.c. conductivity section may be contributing to non-exponential conductivity relaxation. Impedance spectroscopy is a bulk property measurement and parallel conduction modes are difficult to separate if they have the same relaxation times.

Angell [70] recently correlated $\beta$ to the extent of decoupling between the fast ion diffusional motion of the mobile ion populations and the viscous liquid motions of the host glass network. Here the hypothesis is that as the ions become more and more decoupled, i.e. more mobile at constant scaled temperature (by the viscosity), they become more likely to correlate (couple to) each others motions. Ions which are highly coupled to the network of the glass are, likewise, much less likely to couple to each others motion. Using the conductivity data from Tables 4.1 and 4.2 to calculate the decoupling index, $R_g = \tau_\eta / \tau_\varphi$ for each glass and taking $\tau_\eta \sim 100$ seconds at $T_g$ and $\tau_\varphi = \sigma_0 / M_c \sigma_{dc}$, Figure 5.25 shows that the data for the sodium and potassium thioborate glasses are stark exceptions to Angell's master plot. In fact the data appear to be well correlated along a straight line but this line has a completely different slope and intercept than Angell's master plot. Other exceptions to this correlation are also known. It is also not clear from the graph what the physical significance would be for the apparent and dramatic "bend over" at high $\beta$ in order for the alkali thioborate data to meet up at the pro-
posed correlation point of $B = 1$ and $R = 1$. Our data do, however, suggest that though there may well be certain classes of glasses that can be placed onto the $B$ versus $R$ universal map, there are certain exceptions to the correlation. Indeed, it may well be that such anti-correlation can be used to gain better insights into the exact nature of the non-exponential relaxation in glass.

Figure 5.25: $\beta$ parameter plotted versus decoupling index $R$. 
5.1.3. Conclusions

This is one of the first complete high to extremely low alkali (three decades) composition studies of the effect of glass composition on the d.c. conductivity and a.c. conductivity.

1. The d.c. conductivity activation energy plotted against the alkali-alkali jump distance show two distinct regions where different conductivity mechanisms are proposed to be active. At high alkali concentrations, the amount of overlap of potential energy wells between alkali sites strongly affects the activation energy. At the low alkali concentration, the effect due to overlap of energy wells is non-existent and the activation energy is independent of jump distance. A possible model has been developed to explain the limiting behavior of the activation energy with concentration in the extreme dilute region.

2. The data in both regions agree well with the Anderson-Stuart model but to account for a constant jump distance in both regions a modification to the equation (Eq. 5.3) has been proposed. This model gives meaningful results and could be used as a predictive tool. The amount of contribution to the activation energy due to the overlap of potential wells is strongly dependent on how the activation energy is divided between the strain and coulomb energy term. The potassium thioborate conduction activation energy is dominated by the strain energy term and the rapid decrease in the activation energy of the coulomb-dominated activation energy for the sodium thioborate glasses is not observed.

3. The activation energy for the sodium glass in the high alkali region shows little compositional dependence, unlike those observed for the lithium thioborate glasses and the sodium borate glasses.

4. The conductivity prefactor has a linear dependence on the composition for $x > 0.1$ and it has been suggested that this is due to addition of alkali ions to the glass. In the low alkali region, the prefactor dependence on the composition is slight and it
has been that suggested that there may exist a base amount of conductive contami-
nation or intrinsic electronic conduction in the glass contributing to the conductivity
and prefactor.

This is also one of the first-ever examination of the effect of glass composition on the ex-
tent of the non-exponentiality of conductivity relaxation. The transition from non-exponential
to exponential relaxation in the electrical modulus formalism is reported for both sodium and
potassium thioborate glasses.

1. The results show that the $\beta$ parameter in the Kohlrausch relaxation function corre-
lates well with the alkali-alkali separation distance. It is inferred that the narrowing
of the electrical modulus spectrum ($\beta \to 1$) implies an approach to single exponen-
tial relaxation for the conducting ions. It is the non-exponential ion relaxation which
contributes to the conductivity dispersion. This result verifies the hypothesis that
ion-ion coupling is the reason for the conductivity dispersion in frequency.

2. Although near single exponential fits for the electrical modulus have been calculated
for some of these glasses, conductivity dispersion is still observed for all glasses. In
fact, Figures 5.14 and 5.15 shows that for a wide composition of glasses with a wide
range of $\beta$ values describing their electrical modulus spectrum, all compositions
show approximately the same amount of dispersion. It has been proposed that addi-
tional relaxation mechanisms may be active outside the region of the fit of the elec-
trical modulus peak.

3. The alternate possibility is that the narrowing of the electrical modulus and the con-
ductivity dispersion are not related. Some other parameter is contributing to the
narrowing of the electrical modulus spectrum The electrical modulus and its rela-
tionship to the conductivity dispersion are examined in detail in Chapter 7.

To end this section, the reader is reminded that conductivity dispersion is universally ob-
served for most materials, including semi-conductors and liquids. The conductivity dispersion
mechanism must therefore be independent of the unique properties of glasses, semiconductors or liquids.

![Graph](image)

**IMAGINARY MODULUS**

\[ x\text{Na}_2\text{S}_3 + (1-x)\text{B}_2\text{S}_3 \text{ Glass} \]

- Peak decreasing \( \rightarrow \) with \( x \) increasing.
- Peak growing \( \leftarrow \)

**Figure 5.26:** Anomalous behavior of the electrical modulus for sodium thioborate glasses in the range \( 0.01 \leq x \leq 0.05 \)
CHAPTER 6: RELATIONSHIPS BETWEEN NSLR AND IONIC CONDUCTIVITY

The background for ion conductivity relaxation, nuclear spin lattice relaxation (NSLR), relationships between NSLR and conductivity, optimum glasses to study this phenomena and the proposed plan of study were given in sections 2.2.2 and 2.4-2.6. A brief review of that background is given here to introduce the Results and Discussion sections.

It has been ubiquitously observed that the activation energies determined from the temperature dependence of fixed-frequency \((v > 10 \text{ MHz}) T_1\), measurements are 2-5 times lower than those of the d.c. ionic conductivity activation energies \([25,28,79,81,83,84,89]\). This disagreement has been most frequently attributed to the notion that spin-lattice relaxation can occur without substantial long-range diffusion and hence the \(T_1\) activation energy measures a ‘local’ activation energy and not the entire activation energy ‘landscape’ that the d.c. ionic conductivity does.

Martin \([25]\) and Angell and Martin \([89]\) have suggested that the source of the discrepancy may reside in the fact that perhaps the comparison is one that is flawed from the outset. They pointed out that for most oxide glasses, the conductivity at 10 MHz is frequency-dependent even at elevated temperatures whereas the d.c. ionic conductivity is always measured as a frequency independent quantity. They hypothesize that a lower activation energy is measured in the NSLR experiment because measurements are not performed over a wide enough and overlapping frequency range, as the d.c. ionic conductivity.

One of the purposes of this study is to examine measurements of the ionic conductivity and \(T_1\), in fast lithium conducting thiosilicate and thioborate glasses under conditions where both quantities are: (i) frequency-independent, and (ii) where both quantities are measured in the frequency-dependent region but at the same frequency.
The NSLR $T_i$ is related to the spectral density of the position-position correlation function (CF) and thus probes the local charge-density fluctuations. The frequency-dependent conductivity on the other hand, measures the macroscopic relaxation properties of the electric field and thus probes the dissipation due to long-range diffusion of charges [18]. The purpose of this work, then, is to examine the relationships between the NSLR and ionic-conductivity relaxation in the light of the fact that they depend on ion motion, but measure fluctuations in the case of the former and dissipations in the latter.

The electrical modulus formalism, $M^*$, is often used (assumed) to describe the relaxation of the electric field in a host glass by mobile ions. The broadening of the electrical modulus spectra is interpreted as the non-exponential relaxation of the electric field due to the non-exponential relaxation of the ions. With this assumption in mind, the electrical modulus formalism is used in this study to model and characterize the conductivity relaxation. An alternative analysis is given in Chapter 7.

The relaxation of the microscopic position-position correlation function due to the fluctuations introduced by the cation thermal hopping motion is also non-exponential. The KWW function will be uses as the CF of choice to fit both sets of experimental data because it has been found to reasonably successful in treating the conductivity relaxation for a wide variety of oxide and sulfide glasses as well as crystalline solids. It has not been widely used to study NSLR because of the lack of good wide frequency and temperature NSLR data. For the few instances, however, it has been shown to provide a reasonable fit to the CF for the NSLR.

The scope of this work is, therefore, to examine the extent to which a universal description of the conductivity and NMR relaxations can be developed by properly accounting for the non-exponentiality of both processes. In doing this, it is essential to verify experimentally the relationships between the measurements of the relaxation (ionic conductivity) and fluctuation ($T_i$) using the two different techniques on the same glass system over wide and similar ranges of temperatures and measuring frequencies. To the author's knowledge, besides this study [79,147,148], no other study of both the frequency-dependent ionic conductivity and NSLR
$T$, on the same FIC system where the frequency dependence of both phenomena has been carefully examined.

The results of the NSLR and conductivity data are reported for various fast lithium conducting glasses which were specifically chosen because of their very high room temperature conductivity. The maximum NSLR $T_{1/2} (R)$ for these glasses occurs at a low enough temperature so that both the high and low-temperature sides of the $R$ peak can be investigated as a function of measuring frequency and compared with the d.c. and a.c. ionic conductivities. In this way, the most accurate comparison of the CF's for both processes will be possible.

6.1. NSLR (4 MHz - 40 MHz) Results

A 0.56Li$_2$S + 0.44SiS$_2$ glass was made by the technique described in section 3.3.3 and sealed in a silica tube for the NMR experiment. $^7$Li measurements of the spin lattice relaxation time $T_1$ for the glass were taken at 4, 7, 12.2 and 40 MHz over a wide temperature range (100 - 600 K) using the inversion recovery method in collaboration with Mark Trunnel, a graduate student of Dr. Ferdinando Borsa in the Solid State Physics Department of Iowa State University. This work has been reported in his M.S. Thesis [30] and is summarized here.

The $^7$Li nucleus has a nuclear spin of 3/2 and as the result exhibits quadrupolar interactions between the electric moment of $^7$Li nucleus and electric field gradients in the glass. The $^7$Li spectral line width changes as a function of temperature due to motional effects of the Li$^+$ cations, but the quadrupole effects remain small (~35 kHz) and as is shown in Figure 6.1. This effect is small enough such that both the central and satellite lines can be saturated using a short pulse sequence.

The wide temperature and frequency measurements of the 0.56Li$_2$S + 0.44SiS$_2$ glass are shown in Figure 6.2 and agree well with results reported earlier [100]. Note that the curves are significantly asymmetric and that the maximum in the curves, where condition $\omega_c \tau = 0.64$ holds, where $\omega_c$ is the Larmor frequency, shifts to higher temperatures, the higher the fre-
Figure 6.1: $^7$Li spectrum for 0.56Li$_2$S + 0.44SiS$_2$ at 22 MHz and ~193 °K

The wide temperature NSLR data for $^7$Li in the 0.56Li$_2$S + 0.44SiS$_2$ glass cannot be adequately described by the BPP single exponential model.

The Cole-Davidson (CD) distribution function (see Eqs. 2.50 and 2.51) has been used to account for the asymmetry in the curve but never has it been tested for a series of frequencies using the same parameters. The results of the fit using the CD function for all four frequencies are shown in Figure 6.3. Additionally, as in the case of conductivity relaxation in glasses,
good fits can also be obtained by using the KWW stretched exponential relaxation function for the form of the correlation function.

The NSLR $R_1$ that is related to the spectral density $J(\omega_L)$ of the fluctuations due to the Li$^+$ hopping motion was given in Eq. (2.47) and (2.52) as:

$$\frac{1}{T_1} = R_1 = C[J(\omega_L) + 4J(2\omega_L)]$$  \hspace{1cm} (6.1)

where

$$J(\omega) = Re \int_{-\infty}^{\infty} e^{-\{(t/\tau)^\beta\}} \cos(\omega t) e^{-\{(t/\tau)^\beta\}} dt.$$  \hspace{1cm} (6.2)
Figure 6.3: Fits of the NSLR data for 0.56Li$_2$S + 0.44SiS$_2$ glass to the Cole-Davidson function. The following parameter values $\Delta E_{\text{act}} = 0.353$ eV, $\tau_o = 4.5 \times 10^{-14}$ s, $C = 7.9 \times 10^9$ (rad sec)$^3$ and $\alpha = 0.28$ were used in Eq. 2.51.

The KWW function is used as the CF to describe the time decay of the internal magnetic field due local interactions of diffusing Li$^+$ ions. The KWW fit is shown in Figure 6.4. The values for $\Delta E_{\text{NaR}}$ and $\beta$ can be easily determined from $R_i$ measurements since there are data available for both the high and low temperature sides of the $R_i$ maximum. The frequency and temperature limits of the above equations are found on Table 2.3 are reproduced here to help explain how these two parameters are determined.

$$\omega_L \tau_c \ll 1 \quad \frac{1}{T_1} = R_i \propto \tau_c = \tau_o \exp \left( \frac{\Delta E_{\text{NaR}}}{kT} \right)$$

(6.3)
\( \omega_L \tau_c \ll 1 \quad \frac{1}{T_1} = R_1 \propto \omega_L^{-(1+\theta)} \tau_o^{-\beta} \exp \left( \frac{\beta \Delta E_{\text{NMR}}}{kT} \right) \quad (6.4) \)

\( \Delta E_{\text{NMR}} \) is determined from the slope \( (\Delta E_{\text{NMR}}/k) \) of the high temperature side of the \( T_1 \) curve (see Eq. 6.3). \( \beta \) is determined from the ratio of the low temperature slope \( (\beta \Delta E_{\text{NMR}}/k) \) to the high temperature slope \( (\Delta E_{\text{NMR}}/k) \). The KWW fit to the NSLR data is performed using a similar technique to that of the method used to fit the KWW function to the electrical modulus data [30]. Since the values for the coupling constant \( C \) and \( \tau_o \) are independent of each other, they can be adjusted until the curve for the KWW data for a particular \( \beta \) and the experimental data begin to overlap. The values for the \( \beta \) and the \( \Delta E_{\text{NMR}} \) are readjusted to improve the fit.

Figure 6.4: \(^7\)Li data for 0.56Li$_2$S + 0.44Si$_2$S$_3$ glass with theoretical fits using the KWW form of the correlation function, fit parameters are found on Table 6.1
The results of these fits and the parameters are found on Table 6.1 in Section 6.3. The predictions of Eqs. (6.1 - 6.4) are approximately borne out in the experimental results as shown in Figure 6.4 and confirms the general validity of a description of the NMR data in terms of the stretched-exponential relaxation (KWW) function. At the lowest temperatures, significant deviation from linearity is observed for all the curves and results from possibly the onset of a second low-temperature relaxation mechanism.

Measurements of the spin lattice relaxation time $T_1$ were also determined for a 0.1LiI + 0.9(0.5Li$_2$S + 0.5SiS$_3$) glass were taken at 7, 24, 40 and 135 MHz using the same inversion-recovery technique (see Figure 6.5) described above by Hui Wang, a graduate student of Dr.

![Figure 6.5: $^7$Li data for 0.1LiI + 0.9(Li$_2$S + SiS$_3$) glass with theoretical fits using the KWW form of the correlation function. Fit parameters are found on Table 6.1](image)
Ferdinando Borsa in the Physics Department of Iowa State University. In this case, the recovery of the nuclear magnetization for the glass is also exponential. The NSLR $R$, parameters determined from the temperature and the frequency dependence of $R$, are found on Table 6.1 and the KWW fit to the data is shown in Figure 6.5.

To study the universality of the NSLR, $^7\text{Li} T_1$ measurements were performed on a glass with a different glass network, in particular, the $0.7\text{Li}_2\text{S} + 0.3\text{B}_2\text{S}_3$ glass. Measurements at 4, 7, 22 and 40 MHz were done by Kyung Kim, a Ph.D. student in the Physics Department, and are shown in Figure 6.6. Data collected at 4 MHz appear very similar to those of the silicon sulfide glass data. For higher frequencies, the data cannot be fit well to the KWW function. A problem which can be seen also in the data in Figures 6.4 and 6.5. The results may be due

Figure 6.6: $^7\text{Li}$ data for $0.7\text{Li}_2\text{S} + 0.3\text{B}_2\text{S}_3$ glass with theoretical fits using the KWW form of the correlation function. Fit parameters are found on Table 6.1
to iron contamination in the glass which gives rise to an additional contribution to the measured NSLR not included in the fit. Compositional analysis of the glass has shown that there is approximately 50 ppm of iron in the composition. This data is not analyzed here and is being further explored by Kim Kyung.

6.2. High Frequency (1 Hz - 200 MHz) Conductivity Results

Conductivity measurements on the $0.56\text{Li}_2\text{S} + 0.44\text{SiS}_2$ glass were performed over the same temperature and frequency range as the NSLR $T_i$ measurements. Ionic conductivity data collected on both the low and high frequency impedance workstation are shown in

![Graph showing conductivity data for the 0.56Li₂S + 0.44SiS₂ glass](image)

Figure 6.7: (a) Wide temperature and wide frequency (1 Hz - 200 MHz) conductivity data for the $0.56\text{Li}_2\text{S} + 0.44\text{SiS}_2$ glass
Figure 6.7: (b) Wide temperature and wide frequency (1 MHz - 200 MHz) conductivity data for the 0.56Li₂S + 0.44SiS₂ glass collected in the same frequency range as Figure 6.7(a) and data just for the high frequency bridge are shown in Figure 6.7(b). The data collected by the two bridges are near identical in the overlap frequency region (Figure 6.7(a)). The scatter in the data in that region is due to the low frequency bridge. The data do not overlap as well at high temperature because the measurement temperatures are not the same for the two isotherms measured by the two bridges.

At lowest temperatures and high frequencies, we can see that the conductivity is frequency dependent but for this highly FIC glass even at these low temperatures the d.c. conductivity plateau is observed. As temperature increases, space charge polarization begins to dominate and conductivity dispersion is seen at the lowest frequencies. As frequency increases, the d.c. conductivity plateau is observed. At highest temperatures, the space charge
dispersion dominates up to 10 kHz followed by the d.c. conductivity plateau and only at highest temperatures do we see the conductivity dispersion.

Figure 6.8 shows the real part of the measured ion conductivity at various fixed frequencies corresponding to the NSLR $T_j$ measurement frequencies $\omega_c$ and $2\omega_c$. The isofrequency data all converge asymptotically with increasing temperature to the d.c. conductivity line. The apparent activation energy for the a.c. conductivity is substantially less than that for the d.c. conductivity and the higher the frequency, the higher the temperature where the departure of the isofrequency curve from the d.c. conductivity occurs. In fact, at lowest frequencies the conductivity is almost temperature independent.

Figure 6.8: The real part of the measured ion conductivity for the 0.56Li$_2$S + 0.44SiS$_2$ glass at various fixed frequencies against reciprocal temperature
Figures 6.9: Plots of the isothermal frequency spectra of (a) $M'$, (b) $M''$ for a series of temperatures for $0.56\text{Li}_2\text{S} + 0.44\text{SiS}_2$ glass and
 Isothermal curves of the real and imaginary part of the electrical modulus are shown in Figures 6.9(a) and 6.9(b). The M'' spectra shows an asymmetric peak approximately centered in the dispersion region. As temperature increases, the imaginary part of the complex electrical modulus peak shifts to higher frequency. The peak frequency shifts thermally at the same rate as the d.c. conductivity and hence both have the same activation energy. The temperature dependence of the peak relaxation frequency for the glass is shown in Figure 6.10 from which the frequency prefactor, $f_o = (2\pi \tau_0)^{-1}$, and the activation energy are determined.

Figure 6.9(c) is the superimposed plot obtained by scaling each frequency by the frequency of the maximum loss in M''. The near perfect overlap of the different temperature
Figure 6.10: Arrhenius plot of the frequency at the maximum peak value of $M''$ for $0.56\text{Li}_2\text{S} + 0.44\text{SiS}_2$ glass. The dotted line is the expected rollover due to the decreased temperature d.c conductivity dependence (see Eq. 6.7).

data, superimposed on the single master curve, illustrates well the quality of the fit and that all dynamic processes occurring at different frequencies exhibit the same activation energy.

The method for fitting the data the KWW function has been described before but is reviewed again. An initial values for $\beta$ is determined from the magnitude of the FWHM of the $M''$ loss peak. $\beta$ is then graphically fine tuned by overlapping pre-calculated modulus curves on the experimental data. By varying the magnitude of $M$ and $\beta$ for the fitting curve, the disagreement between the experimental data and the fit is easily minimized with errors in $\beta$ of less than $\pm 0.005$. This whole process is computer automated using the impedance spectros-
Figure 6.11: (a) Wide temperature and frequency (1 Hz - 10 MHz) range conductivity data for the 0.1LiI + 0.9(Li$_2$S + SiS$_2$) glass, (b) the conductivity at various fixed frequencies against reciprocal temperature.
Figure 6.11: (c) The reduced temperature (140 - 200 K) plots of $M'$ and $M''$ for 0.1LiI + 0.9(Li$_2$S + SiS$_2$) glass. The line through the data is the KWW fit to the data using the parameter set given in Table 6.1.

copy analysis software package developed by the author [102]. The smooth line through the modulus data in Figure (6.9c) is the KWW fit to the data.

The value for the activation energy for d.c. conduction, the KWW $\beta$ parameter and $\tau_o$ were determined in the same manner for both the 0.1LiI + 0.9(0.5Li$_2$S + 0.5SiS$_2$) and the 0.70Li$_2$S + 0.30B$_2$S$_3$ glasses and plotted in Figures 6.11 and 6.12. Plots of the (a) conductivity against frequency, (b) isofrequency conductivity against reciprocal temperature and (c) reduced electrical modulus are given for each glass. The graphs for all three very different glasses look very similar. The calculated parameters are summarized on Table 6.1.
Figure 6.12: (a) Wide temperature and frequency (1 Hz - 10 MHz) range conductivity data for the 0.7Li₂S + 0.3B₂S₃ glass and (b) the conductivity at various fixed frequencies against reciprocal temperature.
Figure 6.12: (c) Reduced temperature (150-210 K) plots of $M'$ and $M''$ for 0.7Li$_2$S + 0.3B$_2$S$_3$ glass. The line through the data is the KWW fit to the data using the parameter set given on Table 6.1.
6.3. Results

The results of fitting the data to determine the temperature dependence and the degree of non-exponentiality for both conductivity and the NSLR rate are summarized on the Table 6.1. The activation energies for NSLR and the conductivity for the three glasses are approximately the same, however, the correlation time ($\tau_c$) for the NSLR is an order of magnitude larger than that for the conductivity. Furthermore, the KWW parameter $\beta$ is not the same for the two processes. Note that the parameter values are glass composition independent for both the NSLR and the conductivity. These results are analyzed in the following section.

Table 6.1: Values of the parameters for KWW function used to fit the conductivity and experimental data

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\Delta E_{\text{Act}}$ (eV)</th>
<th>$\beta$</th>
<th>$\tau_c$ (sec)</th>
<th>$C$ (rad sec)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56Li$_2$S + 0.44SiS$_2$ NSLR</td>
<td>0.39</td>
<td>0.35</td>
<td>4.5 x 10$^{-14}$</td>
<td>3.8 x 10$^9$</td>
</tr>
<tr>
<td></td>
<td>$\sigma(\omega)$</td>
<td>0.36</td>
<td>0.48</td>
<td>1.3 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.1LiI + 0.9(Li$_2$S + SiS$_2$) NSLR</td>
<td>0.34</td>
<td>0.34</td>
<td>2.1 x 10$^{-14}$</td>
<td>3.8 x 10$^9$</td>
</tr>
<tr>
<td></td>
<td>$\sigma(\omega)$</td>
<td>0.35</td>
<td>0.48</td>
<td>2.5 x 10$^{-15}$</td>
</tr>
<tr>
<td>0.70Li$_2$S + 0.30B$_2$S$_3$ NSLR</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\sigma(\omega)$</td>
<td>0.36</td>
<td>0.48</td>
<td>9.4 x 10$^{-16}$</td>
</tr>
</tbody>
</table>
6.4. Relations between NSLR and Conductivity

6.4.1. Activation Energies For The Two Processes

The hypothesis that the activation energy for NSLR rate in the frequency independent region will be equal to the d.c conductivity activation energy is verified for the three studied glasses. In fact, the activation energies (see Table 6.1) for the NSLR are slightly larger than those for the d.c. conductivity. The decrease in the a.c. conductivity activation energy for high frequencies was shown through Figures 6.7, 6.11(b) and 6.12(b). A numeric value for the activation energy from the slope of the constantly changing curve is extremely difficult to determine and may be meaningless (see Figure 6.11(b) and 6.12(b)). This result is in agreement with the lower activation energy measured from the frequency dependent side of the NSLR rate curve. The values of the activation energy in the different regions support the hypothesis and predictions made by Martin [25] and Angell and Martin [89].

6.4.2. Correlation Functions

Cole-Davidson function: The results of the fit using the Cole-Davidson distribution function is seen to badly represent most of the data curves. At high temperature, it predicts too sharp a decrease with temperature (too high an activation energy), whereas at lower temperature it predicts too low an activation energy. This effect cannot be simply taken out by adjusting the $\alpha$ parameter in the CD function. However, the slope can be accounted for by combining together the single parameter Cole-Davidson and Cole-Cole (CC) function [140] to form the two parameter Havriliak and Negami (HN) function [141]. The slope on each side of the curve can be easily fit with the additional parameter. Wang and Bates [142] have shown the differences in the distribution relaxation times for the CD, CC and HN functions and the similarity between the KWW and HN function. Since the KWW is a single parameter ($\beta$) function, it is also a simpler choice for the correlation function.
KWW correlation function: The predictions of the equations on Table 2.3 to the experimental data are shown by the KWW fits in the figures and confirm the general validity of using the KWW function to describe the NSLR and conductivity data.

The deviation of the NMR data from the curve generated from the best-fit parameters at lowest temperatures (see Figures 6.4-6.6) could be due to an additional frequency-independent contribution to relaxation. This effect becomes pronounced only at lowest temperatures and highest frequencies. Similar $^7$Li relaxations have been reported in other fast ion conductors including oxide glasses [30,86,87]. The origin for the discrepancy is not yet clear and should be explored further. One should point out that the deviation from the experimental data from the theoretical fitting curves at low temperatures and high temperatures could also be a shortcoming in the description of the CF in terms of a stretched exponential function.

The deviation of the $\sigma(\omega)$ data from the theoretical curve at low temperature and high frequency is ascribed to the known failure of the KWW function at high frequency [7,8]. To date, no satisfactory explanation has been given for this failure. It is not clear whether the function simply can not fit the data or whether there is an "extra" relaxation at high frequencies that contributes to the imaginary part of the electric modulus keeping it from going to zero as the frequency goes to infinity. It was shown in the last chapter for both the $xNa_2S + (1-x)B_2S_3$ and the $xK_2S + (1-x)B_2S_3$ glasses that the more non-debye like the conductivity, i.e., the more $\beta$ deviates from unity, the greater the high frequency failure of the KWW function. The difficulty in fitting the data may be attributed to the failure of the KWW function or, more importantly, to the fundamental interpretation of the electrical modulus. This is the topic of discussion for the next chapter.

The comparison of the NMR and conductivity data has been considered by others [25,26,87,89], but not in the cases where the behavior could be tested over wide ranges of temperature and frequency as is done here, thus leading to a fortuitous agreement between the two $\beta$ parameters. The difference found here for the values of $\beta$ and the order of magnitude difference in the values of $\tau_0$ for conductivity and NSLR (Table 6.1) implies a different time
dependence of the CF's. Let us first discuss the observed difference between NMR and conductivity in terms of a homogeneous correlation function. The conductivity CF refers to the relaxation of the electric field, which is a macroscopic quantity at $q = 0$, where $q$ is the electric field wavevector

$$
\phi_\sigma(t) \propto \langle E_{q=0}(t)E_{q=0}(0) \rangle
$$

while in the NSLR, the relaxation function is a local CF and is thus the result of collective fluctuations at all $q$ vectors,

$$
\phi_{NSLR}(t) \propto \langle u_i(t)u_j(0) \rangle \propto \sum_q \langle V_q(t)V_{-q}(0) \rangle,
$$

where $u_i$ is a local atomic coordinate [143]. In the presence of cooperative effects in ionic diffusion, the relaxation of the collective modes can be different for the various $q$ values, thus leading to different time dependence for $\phi(t)$ in the two processes. This is the case for all three glasses studied where the $\tau_\sigma$ values differ by an order of magnitude.

A possible explanation to describe the order of magnitude difference between the two processes is given here. In an electric field, the ion hops from one potential energy well to another are favored in the direction of the electric field and each hop in that direction contributes to the decay of the applied electric field in the glass. In the NMR, it is the same hopping ions which contribute to the decay of the magnetic field, however, it is conceivable that an ion in a high magnetic spin state may not have a magnetic interaction during a hop and change its spin state. What the experiment results suggest is that the probability of an ion hop in the direction of the electric field in the conductivity experiment is ten times more likely then the likelihood of a magnetic interaction during any hop in a glass.

The correlation time prefactor for both the NMR and the conductivity are much smaller then the IR resonance time ($10^{-12}$ s) for a Li-S bond and therefore unrealistic. These results were obtained by extrapolating the correlation frequency ($1/\tau_\sigma$) at infinite temperature in an Arrhenius plot of the peak frequency of $M''$ and $R_\nu$. The Arrhenius plot of the real part of the
d.c. conductivity show that at high temperatures the conductivity begins to 'rollover' from the low temperature extrapolated d.c. curve and is shown in Figure 6.11(b). The predicted low temperature d.c. conductivity prefactor is between two to three orders of magnitude greater than that predicted by the high temperature d.c. conductivity. This result is not seen in $M''$ peak frequency because the $M''$ peaks move to right and out of the frequency window at a higher temperature and therefore no data are available at high temperature for fitting. The conductivity and the $M''$ peak frequency, however, are related through the host glass dielectric constant

$$f_{m''} = \frac{\sigma_{dc}}{2\pi\epsilon_0\epsilon_\infty}. \quad (6.7)$$

From the above relationship, a lower correlation time is predicted by the conductivity data at highest temperatures and is shown as a dotted line in Figure 6.8. Similar results are expected for the NSLR correlation time. At higher frequencies, the Arrhenius plot of the $R_\ast$ peak frequency may very likely show a rollover at high temperatures away from that predicted by the low temperature data. For this reason the expected value for the correlation time for the conductivity should be almost three orders of magnitude less than the calculated correlation time prefactors and is more reasonable. The same result is expected for the NSLR rate. It is very likely that the infinite temperature correlation time should be the same for the two processes and the conductivity data may crossover to the NSLR correlation times with increasing temperature.

In the previous section, a strong correlation was shown to exist between $\beta$ and ion-ion separation distance. It was hypothesized and shown that the non-exponentiality was due to ion-ion interaction (coupling) speeding individual ion relaxations at short times and impeding ion relaxations at long times and only in the case for large separation distance was single exponential behavior expected and observed. It can be argued that the coupling between ions should affect in different ways the local NMR CF and the conductivity CF, thus leading to different $\beta$ values. The difference between $\beta_o$ and $\beta_{NMR}$ should then be useful in learning about
the nature of the cooperative behavior if a theory can be developed that relates quantitatively
the value of $\beta$ to the microscopic parameter $[144]$.

**Direct comparison:** Instead of fitting the NSLR and conductivity data to a correlation
function and solving for the activation energies, a direct comparison of two processes is possi­
ble through Eqs. 2.54 and 2.55. Plotting the conductivity data as a relaxation rate and com­
paring the data to the NSLR data would show immediately the similarity and differences
between the two processes. This comparison has never been done before due to the lack of
high frequency conductivity data in the same frequency range as the Larmor frequency $\omega_L$ and
$2\omega_L$. The high frequency impedance spectroscopy workstation was constructed for this pur­
pose and provides the first-ever comparison of the relaxation rate of the conductivity and
NSLR over the same temperature and measuring frequency range.

Figure 6.13 shows the electrical conductivity relaxation rate at 3.9, 6.9, 12.0 and
41.7 MHz determined from the high frequency data shown in Figure 6.7(b) in terms of the
electrical modulus form (Figure 6.9(b)). The appearance of the data looks very similar to the
asymmetric peaks observed for data collected from NSLR experiments. The parameters $\tau_o$, $\beta$
and $\Delta E_{\text{act}}$ can be thus be determined using the technique described for the NMR data in
Section 6.1. The calculated values for $\tau_o$, $\beta$ and $\Delta E_{\text{act}}$ are $2.9 \times 10^{-15}$ s, 0.41 and 0.324 eV,
respectively. The lower activation energy is in agreement with the decreasing activation en­
ergy observed at high temperatures for fast ion conducting glasses. The values of the param­
ters for this fit are in excellent agreement to those calculated using the technique described in
Section 6.2 for the conductivity and found on Table 6.1. This result shows that the different
mathematical techniques used by the Physics and Glass Research Group to determine $\tau_o$, $\beta$
and $\Delta E_{\text{act}}$ yield the same result validating the comparison of the parameter values in the earlier
discussion.

The data for the conductivity relaxation rate and the NSLR for the lithium thiosilicate
glass are plotted on the same graph in Figure 6.14. The magnitude of all the conductivity rate
curves were normalized to the NSLR data at 40 MHz for comparison. It is clear that the cor-
Figure 6.13: Conductivity relaxation rate determined from $M''$ and Eq. 2.55 at comparable NMR frequencies for the 0.56Li$_2$S + 0.44SiS$_2$ glass

relation times for the two experiments are not the same. The peaks of the curves for the two different experiments would have lined up otherwise. This is further apparent by the larger amount of frequency independent (d.c.) data for the conductivity than for the NSLR curves. The d.c. activation energy for the NMR is slightly larger than that of the conductivity because of the steeper high temperature side slope of the rate curve. The activation energy difference, however, is small as observed by the similarity in the temperature shifts of curves with frequency ($\omega_c \tau_c \approx 1$). It is interesting to note that for both results that the slope of the curve at low temperature data deviates from the expected $\beta(\Delta E_{\text{act}})$ slope.

To compare the shape of the curves for the two experiments, the conductivity data were further normalized to the temperature at which the peak occurs for the 40 MHz NSLR data
Figure 6.14: Direct comparison of the conductivity rate to the NSLR rate for the 0.56Li,S + 0.44SiS₂ glass. The conductivity rate is normalized to the peak magnitude of the NSLR rate for the 40 MHz data.
Figure 6.15: Comparison of the conductivity rate to the NSLR rate for the 0.56Li$_2$S + 0.44SiS$_2$ glass. The conductivity rate is normalized to the peak magnitude and temperature of the NSLR rate for the 40 MHz data.
and is shown in Figure 6.15. This plot makes it very clear that the conductivity rate curve is much narrower than that for the NSLR and this observation is in agreement with the larger $\beta$ value determined for the conductivity. This visual formalism immediately shows that the two relaxation processes are different even though they result from the same basic ion motion.

6.5. Conclusions

Much of the confusion surrounding the agreement or disagreement of activation energies taken from the NSLR relaxation and the d.c. conductivity has arisen because of the fact that the frequency dependence of both phenomena is not entirely understood. Most NSLR studies were done on oxide glasses in which the conductivities are low even at temperatures close to $T_g$. The d.c. conductivity plateaus are seldom observed for frequencies greater than 1 MHz. Hence, the NSLR studies have typically reported activation energies from the frequency dependent side of the NSLR rate curve because data were not available from the frequency dependent side. With the development of highly conductive sulfide glasses, wide temperature ranges where the frequency independent NSLR rates can now be measured and compared to the d.c. conductivity. The conclusions from the analysis are given below.

1. The results of this study show that the activation energies for the ion hops in both the conductivity and the NSLR experiments are not as different as previously reported before, but are approximately the same.

2. The data also verify that the NSLR and the conductivity in the frequency-dependent region become less and less temperature dependent, hence if the activation energy were measured in this region then a lower activation energy would have been measured.

3. These results support the hypothesis that the difference in the previously reported activation energies for the ionic conductivity and the NSLR rate was due to the fact that the ionic conductivity activation energies were reported from data in the fre-
quency independent region, while the NSLR values for the activation energy were reported from data in frequency dependent region [25,89].

The relationship between the fluctuation driven $^7$Li NSLR rate and the relaxation driven Li$^+$ ionic-conductivity have been examined over wide ranges of comparable temperature and frequency for three glasses. The highly non-exponential behavior of the data was fit using the Cole-Davidson and the Kohlrausch-Williams and Watts KWW function. The conclusions from these fittings and analyses are given below.

1. The fit of the Cole-Davidson distribution function as the correlation function to the NSLR data shows that the function models the data for individual frequencies very well but fails when it is simultaneously fit to all the curves.

2. Both the NSLR and the electrical modulus form of the conductivity were accurately modeled using the KWW function, but different $\beta$ parameters were required to fit the data for the two processes. Interestingly, for all three glasses the fitted $\beta$ parameter for the NSLR rate was approximately the same. This was also true for the conductivity.

3. The NSLR prefactor $\tau_0$ is an order of magnitude greater than the conductivity prefactor suggesting that the ions are relaxing at a faster rate in the conductivity than in the NMR. These differences, although unexpected from the outset, were used to suggest the dynamics of fluctuation driven NSLR rate and the relaxation driven ionic conductivity are different in detail but have gross features in common.

Finally, Figures 6.14 and 6.15 show the results of the first-ever measurements of the conductivity and the NSLR rate in the same glass system over the same temperature range and measuring frequency. The figures verify the above conclusions.

1. The activation energies are approximately the same due to the similarity in the NSLR and conductivity slopes in the frequency independent region.
2. The correlation time for the conductivity is far less than that for the NSLR rate because conductivity data peaks occur at lower temperatures hence a large frequency independent region.

3. The width of the conductivity curve is less for than that for the NSLR rate. This means that the extent of non-exponentiality in the NMR is much greater than that in the conductivity.
The peak frequency of the imaginary part of the electrical modulus is often interpreted as the average ion hopping frequency. Furthermore, the conductivity dispersion and the broadening of the electrical modulus spectra are attributed to the non-exponential electric field decay in the time domain [7,145,146] and the process is referred to as 'conductivity relaxation'. One hypothesis for the non-exponential behavior is that it is a result of series electrical relaxation processes, strongly coupled in some manner, such that each relaxation event constrains the relaxation of another.

This hypothesis was tested in the Chapter 5 by performing an ultra-low alkali ion conductivity study in the sodium and potassium thioborate glass systems. In this study, it was hypothesized that the electrically-active mobile ions decay the electric field non-exponentially because of ion-ion interactions, and by increasing the ion-ion separation distance to the limit where the ion-ion interactions are minimized, then and only then, would single exponential behavior be observed. The results of these experiments show a dramatic narrowing of the electrical modulus spectra and the approach to near-single exponential relaxation behavior with increasing ion separation distance. Although these results were striking and supportive of the above hypothesis, the conductivity dispersion for all glasses, independent of ion-ion separation distance, continued to exhibit approximately the same frequency dependence. This result contradicts the predictions that the approach to single exponential behavior in the electrical modulus should also result in a dispersion free conductivity (see Table 2.2).

A second inconsistency is the failure of the Kohlrausch-Williams-Watts (KWW) function to fit the electrical modulus data at high frequencies. This high frequency failure was reported by Moynihan et al. [8] in the first-ever report of the application of the KWW function to the electrical modulus and, to the author's knowledge, no example of a successful high frequency
fit has ever been reported. This discrepancy and the failure of the KWW parameter $\beta$ to predict the conductivity slope (Eq. 2.35) has been accounted for by suggesting that a new and additional conductivity relaxation mechanism becomes active at high frequencies. This argument has been applied to glasses where the KWW parameter $\beta$ is typically less than 0.6 but may also be applied here to explain the conductivity dispersion in the ultra-low alkali glasses for which the KWW parameter $\beta$ is typically much greater than 0.6.

However, careful examination using various impedance-related formalisms of impedance data collected in this work show that the narrowing of the electrical modulus spectra is a consequence of a less complicated process, namely the contribution of the alkali ion orientation polarization to the total dielectric constant. This point is quite significant in the understanding of the electrical modulus spectra and will be discussed in detail below.

A second question raised in this chapter is the validity of the interpretation of the peak frequency of the imaginary part of the electrical modulus as the ion hopping frequency and/or the conductivity relaxation frequency. It is important to point out that the shape of the electrical modulus spectrum is a result of both the conductivity dispersion and the sum of the dielectric contribution of both the ion-hop polarization and the ionic, atomic and electronic polarization of the host glass. The conductivity spectrum is a result of the response of the ions to an electric field, whereas the dielectric constant is a result of polarization mechanisms due to both the host glass and the ions. In order to study the ion conductivity relaxation, only the ion contribution to the dielectric constant should be used. It is pointed out that the shape and peak frequency of the electrical modulus spectra is heavily weighed by the dielectric constant of the host glass and, therefore, interpreting the $M''$ peak frequency as the ion hopping frequency may not be correct. This is discussed more fully in the next section and is quite significant in resolving the order of magnitude difference between the ion hopping frequency measured from the electrical modulus and NSLR experiment.

To establish the groundwork for this discussion, the fundamentals of the electrical modulus are reviewed simultaneously with the examination of experimental data to explain the low
and high frequency limits and shape of the electrical modulus. The contribution of the dielectric relaxation and conductivity dispersion to electrical modulus spectra is pointed out.

7.1. Fundamentals of the Electrical Modulus Formalism

The real part of the conductivity and the dielectric constant are orthogonal components and can be used to derive all the impedance related formalisms. The complex conductivity is related to the relative dielectric permittivity by \( \sigma^* = j\omega\varepsilon\varepsilon^* \), where the real and imaginary components are given below:

\[
\sigma' + j\sigma'' = j\omega\varepsilon_0(\varepsilon' - j\varepsilon'')
\]

\[
\sigma' + j\sigma'' = \omega\varepsilon_0\varepsilon'' + j\omega\varepsilon_0\varepsilon'
\]  

(7.1)

The electrical modulus in terms of the conductivity and the dielectric constant is given below:

\[
M^* = M' + M'' = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''}
\]

\[
= \frac{\varepsilon' + j\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} + j\frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2}
\]  

(7.2)

By substituting the real part of the conductivity for \( \varepsilon'' \), the following form is obtained,

\[
M^* = M' + M'' = \frac{\varepsilon'}{(\varepsilon')^2 + \left(\frac{\sigma'}{\omega\varepsilon_0}\right)^2} + j\frac{\frac{\sigma'}{\omega\varepsilon_0}}{(\varepsilon')^2 + \left(\frac{\sigma'}{\omega\varepsilon_0}\right)^2}.
\]  

(7.3)

The frequency limits of Eq. (7.3) are summarized on Table 7.1. Note that these results are dependent on the exact nature of the frequency dependence of the conductivity and dielectric constant spectra. The \( M'' \) peak frequency, however, is approximately given by Eq. (7.4b).
Table 7.1: Limiting frequency behavior of the electrical modulus as a function of the dielectric constant and the conductivity

<table>
<thead>
<tr>
<th>Region</th>
<th>$M'$</th>
<th>$M''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon' \ll \sigma' / \omega \varepsilon_0$</td>
<td>$\omega \ll \sigma' / \varepsilon_0 \varepsilon'$</td>
<td>$\varepsilon' \left( \frac{\varepsilon_0}{\sigma'} \right)^2 \omega^2$</td>
</tr>
<tr>
<td>$\varepsilon' \approx \sigma' / \omega \varepsilon_0$</td>
<td>$\omega \approx \sigma' / \varepsilon_0 \varepsilon'$</td>
<td>$\frac{1}{2\varepsilon'}$</td>
</tr>
<tr>
<td>$\varepsilon' \gg \sigma' / \omega \varepsilon_0$</td>
<td>$\omega \gg \sigma' / \varepsilon_0 \varepsilon'$</td>
<td>$\frac{1}{\varepsilon'}$</td>
</tr>
</tbody>
</table>

The reduced frequency plot of the dielectric constant and the real part of the conductivity for various isotherms for the 0.02K$_2$S + 0.98B$_2$S$_3$ glass is shown in Figure 7.1. It is apparent as mentioned above that the shape of the spectrum for each temperature is identical and is scaled by the frequency with the same activation energy as that for the d.c. conductivity. Similar plots to Figure 7.1(a) were shown in Figures 4.4 - 4.6. The plots in Figure 4.4 and 4.6 are outstanding because they contain all the textbook features of polarization. The analysis given in this section deals with the frequency region where the space charge polarization is negligible and only the dielectric contribution of the mobile ions and the host glass network, the mobile ion relaxation and the high frequency (host) dielectric constant are considered. Attention is drawn also to the fact that the onset of the conductivity dispersion begins at approximately the same frequency as the dielectric relaxation frequency of the ion-hopping polarization mechanism.

The method for obtaining values for the individual dielectric contributions of each mechanism were discussed in Chapter 4. The approximate dielectric values for the summed effect of the ion-hopping mechanism and the glass network are shown in Figure 7.1(a). The reduced frequency plot of the electrical modulus spectra for the same data is shown in Figure
Figure 7.1: The reduced frequency plot of the (a) dielectric constant and the real part of the conductivity and (b) for the electrical modulus for various isotherms for the 0.02K₂S + 0.98B₂S₃ glass
7.1(b) exhibiting the typical broad dispersion and a lower peak $M''$ value. At highest frequencies, $M'$ is increased towards a value of $1/\varepsilon_{\text{glass}}$, but in the case of $M''$, the slope of the decreasing $M''$ function changes to a more gentler slope and the $M''$ value does not reach zero, as is expected. The following analysis is performed to explain these features.

Values for $\varepsilon_{\text{ion+glass}} = 12.98$, $\varepsilon_{\text{glass}} = 6.44$ and $\sigma_{\text{d.c.}} = 6.6 \times 10^9$ /Ωcm were extracted from the spectra of Figure 7.1 and are shown as dotted lines for an isotherm in Figure 7.2. Combinations of $\varepsilon_{\text{ion+glass}}$, $\varepsilon_{\text{glass}}$ and $\varepsilon'(\omega)$ were then used with $\sigma_{\text{d.c.}}$ and $\sigma'(\omega)$ to generate electrical modulus spectra using Eq. (7.2). The two dielectric constant values and the d.c. conductivity

![Figure 7.2: Plot showing values for $\varepsilon_{\text{ion+glass}} = 12.98$, $\varepsilon_{\text{glass}} = 6.44$ and $\sigma_{\text{d.c.}} = 6.6 \times 10^9$ /Ωcm as dotted lines for a select isotherm used in Figure 7.1](image-url)
with the raw conductivity and dielectric constant data give the following six possible combinations listed below

(a) \( \varepsilon_{\text{ion+glass}} \) and \( \sigma_{\text{d.c.}} \): The electrical modulus spectrum for a process with an invariant dielectric constant \( \varepsilon_{\text{ion+glass}} \) and constant conductivity \( \sigma_{\text{d.c.}} \).

(b) \( \varepsilon_{\text{ion+glass}} \) and \( \sigma'(\omega) \): The electrical modulus spectrum for a process with an invariant dielectric constant \( \varepsilon_{\text{ion+glass}} \) and dispersive conductivity \( \sigma(\omega) \).

(c) \( \varepsilon_{\text{glass}} \) and \( \sigma_{\text{d.c.}} \): The electrical modulus spectrum for a process with an invariant dielectric constant \( \varepsilon_{\text{glass}} \) and constant conductivity \( \sigma_{\text{d.c.}} \).

(d) \( \varepsilon_{\text{glass}} \) and \( \sigma'(\omega) \): The electrical modulus spectrum for a process with an invariant dielectric constant \( \varepsilon_{\text{glass}} \) and dispersive conductivity \( \sigma(\omega) \).

(e) \( \varepsilon'(\omega) \) and \( \sigma_{\text{d.c.}} \): The electrical modulus spectrum for a process with dielectric relaxation \( \varepsilon'(\omega) \) and constant conductivity \( \sigma_{\text{d.c.}} \).

(f) \( \varepsilon'(\omega) \) and \( \sigma'(\omega) \): The electrical modulus spectrum calculated from the with dielectric relaxation \( \varepsilon'(\omega) \) and dispersive conductivity \( \sigma(\omega) \) for the glass data.

Figure 7.3 show linear plots and Figure 7.4 show the log plots of the (a) the real and (b) the imaginary part of the electrical modulus for the six setups described above. The curves generated for each setup are compared to each other and to the results of the (f) raw data. Values for \( M'(\omega) \), \( M''(\omega) \), \( M' \) peak, the peak frequency and the high frequency slope of \( M'' \) are found on Table 7.2. The slope \( s \) is the conductivity slope described in Table 2.2 and \( \delta \) is the slope of the dielectric constant at highest frequencies. The slopes for the \( M' \) and the low frequency \( M'' \) are in agreement with the predictions of Eq. (7.3a) and are not discussed further. Discussion of the results on Table 7.2 and Figures 7.3 and 7.4 will be used to point out some of the common misconceptions of the electrical modulus and explain special features of the spectrum.
Figure 7.3(a): Linear plot of $M'$ for the various configurations described in the text
Figure 7.3(b): Linear plot of $M''$ for various $\sigma'$ and $\varepsilon'$ combinations as described in the text
Figure 7.4(a): Log plot of $M'$ for various $\sigma'$ and $\varepsilon'$ combinations as described in the text.
Figure 7.4(b): Log plot of $M''$ for the various $\sigma'$ and $\varepsilon'$ combinations as described in the text
Table 7.2: Parameters to quantify the electrical modulus spectra in Figures 7.3 and 7.4

<table>
<thead>
<tr>
<th>Configuration</th>
<th>M'(\infty)</th>
<th>M'' Peak Value</th>
<th>Peak Freq. (\omega_p) [Hz]</th>
<th>M''(\infty)</th>
<th>M'' Slope (\omega \gg \omega_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (\varepsilon_{\text{ion}} + \varepsilon_{\text{glass}} &amp; \sigma_{\text{dc}})</td>
<td>0.077</td>
<td>0.0385</td>
<td>914</td>
<td>0.0000</td>
<td>1</td>
</tr>
<tr>
<td>(b) (\varepsilon_{\text{ion}} + \varepsilon_{\text{glass}} &amp; \sigma'(\omega))</td>
<td>0.077</td>
<td>0.0385</td>
<td>1,064</td>
<td>0.0011</td>
<td>s - 1</td>
</tr>
<tr>
<td>(c) (\varepsilon_{\text{glass}} &amp; \sigma_{\text{dc}})</td>
<td>0.155</td>
<td>0.0775</td>
<td>1,842</td>
<td>0.0001</td>
<td>1</td>
</tr>
<tr>
<td>(d) (\varepsilon_{\text{glass}} &amp; \sigma'(\omega))</td>
<td>0.155</td>
<td>0.0776</td>
<td>2,543</td>
<td>0.0045</td>
<td>s - 1</td>
</tr>
<tr>
<td>(e) (\varepsilon'(\omega) &amp; \sigma_{\text{dc}})</td>
<td>0.150</td>
<td>0.0443</td>
<td>1,323</td>
<td>0.0001</td>
<td>(-\delta) - 1</td>
</tr>
<tr>
<td>(f) (\varepsilon'(\omega) &amp; \sigma'(\omega))</td>
<td>0.150</td>
<td>0.0460</td>
<td>1,645</td>
<td>0.0043</td>
<td>s - (\delta) - 1</td>
</tr>
</tbody>
</table>

7.1.1. Existence of a M'' Peak For Constant \(\sigma\) and \(\varepsilon'\)

The electrical modulus spectra for configuration (a) and (c) show single exponential relaxation behavior with a peak frequency equal to 914 Hz and 1064 Hz and agree with all the predictions of Table 7.1. This result should clear a common misconception that the occurrence of the peak is a result of ion conductivity dispersion or ion dielectric relaxation, where in fact, it is the condition of electrical circuit where the conduction and displacement current are equal. In an ideal RC circuit, the conductivity and the relative dielectric permittivity and real part of the conductance are independent of frequency but the imaginary part of the conductance (displacement current) is proportional to \(\omega \varepsilon'\). At low frequencies, the imaginary part of the conductance is small, but with increasing frequency the imaginary part equals the real part of the conductance and a peak in M'' is observed.
7.1.2. Relationship Between $M''$ Peak Frequency and Ion-Hopping Frequency

From the reasons mentioned in the last paragraph, it should be apparent the frequency where the $M''$ peak maximum occurs is a result of the electrical circuit defined by Eq. (7.4b), and probably has no relationship to the characteristic ion hopping frequency. Alternative choices for the characteristic ion-hop frequency are the frequency where the a.c. conductivity is twice that the value of the d.c. conductivity [12-16], the frequency where the loss peak maximum occurs or the relaxation frequency of the ion-hop polarization mechanism contributing to the dielectric constant. Figures 7.1 and 7.2 show that the approximate frequency where the ion-hop relaxation frequency occurs is also the frequency where the conductivity dispersion begins and therefore significant. Furthermore, this frequency is almost an order of magnitude smaller than the $M''$ peak maximum frequency.

The activation energy of a particular process defined at any location along the dielectric spectrum has the same value as that of the d.c. conductivity. This is validated by the superpositioning principle which allows the scaling of the dielectric, electrical modulus and conductivity spectra.

Determining the ion-hopping frequency from the dielectric constant spectrum and the realizing that the ion-hopping activation energy is the d.c. conductivity activation energy alleviates the discrepancy in the results reported in Chapter 6 between the NSLR and the conductivity. The activation energy for the ion-hops are approximately the same and the ion-hop relaxation time prefactors would be approximately the same for the two processes, strongly suggesting that both experiments are measuring the same ion dynamics.

7.1.3. Frequency Dependence of $M''$ at High Frequencies

The combination of the constant dielectric constant with the experimental conductivity data (b) diamonds and (d) squares) show a similar but slightly broader spectrum than that of (a) and (c). The $M''$ peak frequency and $M''$ maximum values are also slightly greater than that
of (a) and (c) and are a result of using a larger value for the conductivity in Eq. (7.4b) due to
the conductivity dispersion.

At high frequencies, the conductivity dispersion contributes strongly to the deviation of
$M''$ for both (b) and (d) from the single exponential behavior of (a) and (c), and the shape of
curve of $M''$ in both cases approaches that of the experimental result of (f). This result is
even more clearly made clear by the log plot of $M''$ in Figure 7.4(b).

The slope of the $M''$ is strongly dependent on the conductivity dispersion at high frequen­
cies. In the same frequency region, the experimental dielectric constant is weakly decreasing
with frequency with a slope (δ) and contributes slightly to the slope of $M''$ as shown below
through Eq. (7.4c):

$$M'' \propto \frac{\sigma'}{\varepsilon} \omega^{-1} \propto \frac{\omega^{\delta}}{\omega^\alpha \omega^{-1}} = \omega^{(\alpha - \delta - 1)}. \quad (7.5)$$

Since, conductivity dispersion is observed for all glasses, the slope of $M''$ at high frequencies is
expected to always be modified by the conductivity slope. In the extreme case where the dif­
fERENCE of the slopes of the conductivity and the dielectric constant sum to one then a fre­
quency independent $M''$ will be observed.

The effect of the conductivity dispersion does slightly broaden the electrical modulus
spectra at frequencies greater than the $M''$ peak frequency but the dominant contribution to the
electrical modulus is seen at the highest frequencies. Conductivity dispersion is the main rea­
son for the continued presence of the $M''$ tail at high frequencies and is quantified by
Eq. (7.5).

7.1.4. Compositional Contribution to Non-Exponentiality

The electrical modulus spectra determined from the configuration with a constant d.c.
conductivity and the experimentally measured dielectric constant are shown (triangles) in Fig­
ures 7.3 and 7.4. The calculated $M'$ spectrum closely approximates the $M'$ spectrum of the
glass data. The peak value of the calculated $M''$ is also approximately the same as that for the experimental data.

The magnitude of the maximum peak value of $M''$ and the rate of approach of $M'' = 1/\epsilon_{\text{glass}}$ is strongly determined by $\epsilon'(\omega)$. For frequencies greater than the peak frequency, the value of $M'$ is the reciprocal of the dielectric constant. As long as the dielectric constant continues decreasing due to dielectric relaxation then the value of $M'$ will increase at the same rate.

Three hypothetical dielectric relaxation paths are shown in Figure 7.5, where the $M''$ peak is centered in the transition region of Path B. For all three paths, the same processes are observed except that the magnitude of the $M''$ peak and the rate of approach to $M' = 1/\epsilon_{\text{glass}}$ will be different. If the relaxation rate is slow, as in path C, then a $M''$ peak will be observed at the lowest frequency defined by Eq. (7.4b) with an approximate magnitude equal to $1/(2\epsilon_{\text{ion+glass}})$. $M'$ will increase rapidly to the value of $1/\epsilon_{\text{ion+glass}}$ and then appear to level off, but will actually continue to gradually increase with frequency at the same rate as the decrease in the dielectric relaxation rate to the final value of $1/\epsilon_{\text{glass}}$. The slope on the right side of the $M''$ peak will be increased slightly by the contribution of the decreasing slope of the dielectric relaxation. A very slow relaxation rate would give rise to a narrow Debye-like response for the peak width with a broadening at high frequencies due to contribution of the conductivity dispersion.

In the case of Path A, the rapid transition from $\epsilon_{\text{ion+glass}}$ to $\epsilon_{\text{glass}}$ shifts the circuit relaxation frequency to the right and this results in a $M''$ peak height closer in magnitude to $1/(2\epsilon_{\text{glass}})$ and a rapid approach of $M'$ to the value of $1/\epsilon_{\text{glass}}$. The $M''$ peak in this case would also exhibit a narrow Debye-like peak width, but with broadening at high frequencies due to the conductivity dispersion.

Most paths between these two extreme transition ranges would result in a $M''$ peak frequency between that observed for path A and C and with a peak height magnitude between
Figure 7.5: Three possible dielectric relaxation paths for the transition from $\varepsilon_{\text{ion+glass}}$ to $\varepsilon_{\text{glass}}$ for a $M^*$ peak centered in the transition region of Path B.
1/\(2\epsilon_{ion,\text{glass}}\) and 1/\(2\epsilon_{\text{glass}}\). \(M'\) will rapidly approach twice the value of the \(M''\) peak and then increase at a rate approximately equal to the dielectric relaxation rate to the final value of 1/\(\epsilon_{\text{glass}}\). This result is typically observed for most glasses. For the limiting case where \(\epsilon_{ion}\) is small (near zero), then a result similar to that predicted by path A is observed.

The \(M''\) peak value for glasses is always typically much less than half the value of the 1/\(\epsilon_{\text{glass}}\) and the dispersion region of \(M'\) and \(M''\) is broadened due to the combined effects of the dielectric relaxation and conductivity dispersion. The above discussion does not include all the possible relaxation paths and locations of the \(M''\) peak. Examples of results obtained for alternate transitions, especially those occurring close to the \(M''\) peak frequency, show multiple

![Graph showing compositional dependence of the \(M''\) peak value and frequency.](image-url)

Figure 7.6: Compositional dependence of the \(M''\) peak value and frequency
peaks like those seen in Figure 5.26. In these cases, two separate circuit relaxation frequencies give rise to two peaks.

Since the dielectric relaxation rate is not well understood, the ability to control the relaxation rate for glasses by manipulating the chemistry is unclear and the examination of the above statements is difficult. Instead of changing the relaxation rate, the above statements can be investigated by varying the ion concentration in a glass, hence controlling the amount of ion contribution to the orientation polarization. Assuming that the relaxation rate is fairly constant for similar chemistry glasses, then Figure 7.6 shows that the paths A, B and C shown in Figure 7.5 can be reproduced by varying the ion contribution to the dielectric constant by varying the alkali ion concentration. Path A corresponds to a glass with a low concentration of alkali ions for which the frequency width of the dielectric relaxation transition from \( \varepsilon_{\text{ion+glass}} \) to \( \varepsilon_{\text{glass}} \) is small. Path C corresponds to glasses with high concentrations of alkali ions for which the transition occurs over a wide frequency range. The hypothetical peak frequencies for various constant values of \( \varepsilon_{\text{ion+glass}} \) and for \( \varepsilon_{\text{glass}} \) using Eq. (7.4c) are marked in Figure 7.6. From the previous discussion, the magnitude of the experimental \( M'' \) should increase and the shape narrow with decreasing ion contribution to the polarization.

The \( (\varepsilon_{\text{ion}}) \) orientation polarization contribution to the dielectric constant for the sodium and potassium thioborate glasses studied are found on Tables 4.1 and 4.2. Figure 7.7 shows the KWW parameter \( \beta \) and the log \( \varepsilon_{\text{ion}} \) plotted against log composition for (a) sodium and (b) potassium thioborate glasses. \( \varepsilon_{\text{ion}} \) varies linearly with the composition in the low alkali region. This result is expected because the polarization is the sum of all polarizing ions and increasing the ion concentration should therefore increase linearly the number of polarizing ions. A corresponding linear decrease in the KWW parameter \( \beta \) is observed for values of \( x < 0.05 \). For larger \( x \) values, both the dielectric constant and \( \beta \) become almost compositionally independent. The linear increase observed for \( \varepsilon_{\text{ion}} \) at low \( x \) should be continuous throughout the whole composition range but, for larger \( x \) values, it becomes more and more difficult to determine
Figure 7.7 KWW parameter $\beta$ and $\varepsilon_{\text{ion}}$ plotted against log composition for (a) sodium and (b) potassium thioborate glasses.
Figure 7.8: KWW parameter $\beta$ plotted against the (a) linear and (b) log $\varepsilon_{\text{ions}}$. 
the value of $\varepsilon_{\text{ion}}$, because of the overlap of the space charge polarization and ion-hop polarization due to higher ion mobility for these glasses.

To show further the relationship between the KWW parameter $\beta$ and $\varepsilon_{\text{ion}}$, the two parameters are plotted against each other in Figure 7.8. Both the (a) linear and (b) log plots show the strong correlation between this two variables. For the sodium glass with $\beta = 0.93$, shown in Figure 5.22, the $\varepsilon_{\text{ion}}$ contribution to the dielectric constant is 0.48. Although, near exponential behavior is observed for this glass, the conductivity dispersion will always raise the high frequency tail of $M''$ and broaden the electrical modulus spectra to the point that observing $\beta = 1$ is highly improbable. In any case, Figure 7.8 shows for two glass systems a possible universal mapping of the $\beta$ parameter with a directly measurable quantity $\varepsilon_{\text{ion}}$. Previously, $\beta$ was related to the ion-ion separation distance because of the strong correlation shown in Figure 5.4, but the relationship only exists because of the strong dependence for both $\varepsilon_{\text{ion}}$ and the ion-ion separation distance to the alkali ion concentration.

In summary, it is proposed that the shape of the electrical modulus spectra is dominated by $\varepsilon_{\text{ion}}$, the dielectric relaxation, and $\varepsilon_{\text{glass}}$. The presence of the high frequency $M''$ tail is due to conductivity dispersion. The electrical modulus spectra has been fit using the KWW function for data on the left side of $M''$ peak, the $M''$ peak frequency and approximately one decade to the right side of the $M''$ peak and therefore the fit has never truly probed the conductivity dispersion which affects the high frequency tail of $M''$. This is discussed in the next section.

### 7.1.5. Reasons For The Failure Of The KWW Function

There is no dispute of the observation by Charles [145] and Macedo et al. [7] that the conductivity dispersion is a result of the non-exponential decay of the electric field in the time domain. The use of the KWW function to describe the non-exponentiality is an excellent choice for the relaxation function, which was first suggested by Moynihan et al. [8]. The problem arises when this function, instead of being directly fit to the conductivity dispersion data, is fit to the electrical modulus data.
The electrical modulus is result of the dielectric constant and the real part of the conductivity (see Eq. (7.3)). The problem here is that conductivity is a measure of the mobile ions only, while the dielectric constant is a measure of all mechanisms contributing to the dielectric constant including that of polarizing ions and the host network. The host glass dielectric constant dominates the overall response of the electrical modulus by shifting the $M''$ peak to the right and pulling the $M'$ value to that of $1/\varepsilon_{\text{glass}}$ and then masking the ion-hop relaxation by leveling off.

Figure 7.9 shows the contribution of the different mechanisms to the total dielectric constant. Even when the measured dielectric constant appears to no longer be changing due to instrumental measurement limits, the polarization due to each mechanism continues decreasing.
indefinitely with frequency. It is the combination of the real part of the conductivity and \( \varepsilon_{\text{ion}} \) which should be analyzed to fully understand the conductivity relaxation.

Subtracting off \( \varepsilon_{\text{glass}} \) from the high frequency dielectric constant and analyzing this data would show more clearly the response of the ions. A \( M'' \) peak would only be observed if the dielectric current of the ions and the ion conduction current were equal. Because of conductivity dispersion and an ever decreasing value for \( \varepsilon_{\text{ion}} \), it is unlikely that a peak shall be observed unless either the conductivity or \( \varepsilon_{\text{ion}} \) levels off.

The KWW function given below should be used to directly fit the real part of the conductivity data. Normalized electrical modulus data files were generated and the method described in Section 3.2.6.1 for \( \beta \) values in the range \( 0.3 \leq \beta \leq 1 \). The electrical modulus data is

![Graph showing fit of the KWW function (\( \beta = 0.3 \)) to the real part of the conductivity and the dielectric constant for the \( 0.56\text{Li}_2\text{S} + 0.44\text{SiS}_2 \) glass.](image)

**Figure 7.10**: Fit of the KWW function (\( \beta = 0.3 \)) to the real part of the conductivity and the dielectric constant for the 0.56Li\(_2\)S + 0.44 SiS\(_2\) glass
then converted to the real part of the conductivity and the dielectric constant using the following equations:

\[ \sigma' = \frac{\omega \varepsilon_0 M''}{(M')^2 + (M'')^2} \]  

(7.6)

and

\[ \varepsilon' = \frac{M'}{(M')^2 + (M'')^2}. \]  

(7.7)

Figure 7.10 shows the fit of the KWW function for the real part of the conductivity and the dielectric constant for the 0.56Li2S + 0.44 SiS2 glass. The conductivity was normalized by the d.c. conductivity and the KWW fit frequency allowed to vary. The dielectric constant was fit by rewriting Eq. (7.7) to the following form:

\[ \varepsilon_{fit}' = (\varepsilon_{glass} - \varepsilon_{a(ion)}) + \frac{M'\varepsilon_{a(ion)}}{(M')^2 + (M'')^2}. \]  

(7.8)

where \( \varepsilon_{a(ion)} \) is the effective atomic and electronic contribution of the alkali ions to the total dielectric constant measured at highest frequencies and coldest temperatures. The high frequency dielectric constant \( \varepsilon_{glass} \) is 15 and the fit was optimized by using a value of 4 for \( \varepsilon_{a(ion)} \). Approximately 37% of all the atoms in the lithium thiosilicate glass are alkali, but their total polarizability is much less than that for sulfur, and therefore, attributing 27% of the total atomic and electronic contribution to the alkali ion seems quite reasonable.

The KWW fit using \( \beta = 0.3 \) is quite good for both the conductivity and the dielectric data curves. A lower value of \( \beta \) may have fit the conductivity data slightly better but tables for lower \( \beta \) values are difficult to generate because of non-convergence of the fits described in Section 3.2.6.1.
This low $\beta$ value (0.3) for the conductivity dispersion is significant when compared to the $\beta$ value (0.36) obtained for the NSLR experiment in Section 6.3. From the discussion in this chapter, the KWW fit to the conductivity and the NSLR data and the average ion hopping rate obtained from the results of the two different experiments are approximately the same. It was shown in Chapter 6 that the thermally activated energy for the ion-hops for the two experiments was also approximately the same. Combining these results strongly suggest, as was hypothesized, that dissipation and fluctuation occurs through the same ion dynamic processes.

The KWW function has been shown to describe the conductivity dispersion and the dielectric constant spectrum very well. The failure of the KWW function to predict the conductivity dispersion while fitting to the electrical modulus is summarized through the following alternative expression for the relaxation function:

$$\phi(t) = g_{\text{glass}} \exp\left(-\frac{t}{RC}\right) + G_{\text{ion}} \exp\left(-\frac{t}{\tau}\right)^\beta$$

(7.9)

where the sum of $g_{\text{glass}}$ and $G_{\text{ion}}$ is equal to one and $G_{\text{ion}} << g_{\text{glass}}$. The first term accounts for the circuit relaxation where the displacement current equals the conduction current and the second term accounts for the ion relaxation contributing to both the conductivity dispersion and the dielectric relaxation. Eq. (7.9) should be used to fit the electrical modulus data. The problem, however, is that the second term can be further expanded into a series expansion of single exponential relaxation functions where the $\Sigma g_i = G_{\text{ion}}$ and is given below:

$$\phi(t) = g_{\text{glass}} \exp\left(-\frac{t}{RC}\right) + \sum_{i=1}^{\infty} g_i \exp\left(-\frac{t}{\tau_i}\right).$$

(7.10)

The circuit relaxation term is also a single exponential relaxation function and can be incorporated into the KWW series expansion. The series can then be rewritten as the KWW function. The point of this exercise was to show that the KWW function does account for the circuit relaxation and the ion relaxation. The logic in applying the KWW function to the electrical
modulus function is therefore valid. The mathematics, however, fails to extract the finer features of the conductivity relaxation because of the dominant $g_{\text{glass}}$. The fit is to heavily weighed by $g_{\text{glass}}$. The fit to the conductivity data revealed a $\beta$ value of 0.3. Typically, the $\beta$ value reported for most glasses is 0.5 or greater. The circuit relaxation term pulls the fit towards one. By deconvoluting the two terms it should be possible to extract values of $\beta$. This is a fairly complicated process, and instead, the user should directly fit the data to conductivity dispersion and the dielectric constant.

7.2. Conclusions

1. The $M''$ peak occurs when the displacement current approximately equals the conduction current, even in the absence of dielectric relaxation or conductivity dispersion.

2. The frequency where the $M''$ peak occurs has no significance to the ion-hopping frequency. To obtain the ion-hop frequency, the frequency of the onset of the conductivity dispersion or the frequency of the onset of the dielectric relaxation of the ion-hop mechanism should be used. The $M''$ peak frequency is affected by conductivity dispersion and the dielectric relaxation but still is an artefact of the electrical circuit relaxation. Approximate values for $\sigma_{\text{d.c.}}$, $\varepsilon_{\text{glass}}$ and the $M''$ peak frequency can, however, be determined if two of the three parameters are known.

3. The continuous presence of the high frequency tail of $M''$ is a result mainly of the conductivity dispersion and has been quantified through Eq. (7.5). The dielectric relaxation also contributes to the value of $M''$ but extremely weakly.

4. The height of the $M''$ peak is determined by the position of the circuit relaxation frequency on the dielectric relaxation path. If dielectric relaxation of the ion-hop mechanism has not begun than the $M''$ peak will be small $(1/\varepsilon_{\text{ion+glass}})$ and $M'$ will increase to the value of $1/\varepsilon_{\text{glass}}$ over a wide frequency. If the circuit relaxation frequency is centered on the transition, then the value of $M''$ peak will be between that
of $1/e_{ionic\,glass}$ and $1/e_{glass}$. Finally, if the circuit relaxation frequency is located in the region where the dielectric relaxation transition is no longer observed then the $M''$ peak will be closer in value to $1/e_{glass}$. $M'$ will also approach its maximum value much more rapidly.

5. Alternatively, decreasing the ion-hop contribution to the total dielectric constant decreases the width of the dielectric relaxation transition and the magnitude difference between $1/e_{glass}$ and $1/e_{ionic\,glass}$. The peak difference will therefore be slight and the transition of $M'$ from $1/e_{ionic\,glass}$ to $1/e_{glass}$ indiscernible and result in a Debye-like peak.

6. The narrowing of the electrical modulus spectra observed with decreasing alkali ion concentration in the thioborate glasses is a result of the decreasing contribution of the ion-hop polarization (see last point).

7. Although the ion-ion separation distance increases with decreasing alkali ion separation distance, there is no indication in the conductivity spectra of a decrease in the amount of dispersion. The statement that the conductivity dispersion is a result of the non-exponential decay of the electric field in the time domain is still valid but the hypothesis that the non-exponentiality is a result of ion-ion interaction is questioned by this broad composition study where glasses were synthesized with calculated ion-ion separation distances of almost 50 Å.

8. The KWW fit of the electrical modulus is predominantly fit to the parameters of the circuit relaxation. The conductivity contribution in the electrical modulus is observed mainly at high frequencies where the fit is generally ignored. The problems of deconvoluting the two relaxation processes in the electrical modulus may be simplified by directly fitting the ion relaxation to the conductivity spectrum. The result of such a fitting was done on the $0.56\text{Li}_2\text{S} + 0.44\text{SiS}_2$ glass.
9. The alternative suggestion of using the ion-hop relaxation frequency as the ion-hopping frequency, the KWW fit of the conductivity spectrum and the measured activation energy show strong similarities to the values of these parameters obtained from NSLR measurements. The dissipation (electrical measurements) and fluctuation (NSLR measurements) processes in the glass for each experiments are a result of mobile ions and their dynamics seem to be very closely related as hypothesized.
CHAPTER 8. CONCLUSIONS

1. A state-of-the-art wide frequency (1 Hz - 200 GHz) and wide temperature (100 K - 500 K) range fully automated, temperature controlled and hermetic impedance workstation has been developed.

2. The first-ever full compositional (three decades) range examination of the ionic conductivity in Na$_2$S+B$_2$S$_3$ and K$_2$S+B$_2$S$_3$ systems is reported.

3. The activation energy is modeled using a modified Anderson-Stuart model that predicts well the results for the low alkali glasses.

4. The a.c. conductivity is examined through the electrical modulus formalism and the Kohlrausch-Williams-Watts decay function. The first-ever compositional study of the approach to exponential relaxation with decreasing alkali concentration or ion-ion separation distance is reported.

5. Although single exponential relaxation is approached, the amount of conductivity dispersion remains unchanged independent of alkali concentration, suggesting possible flaws in the interpretation of the KWW fit to the electrical modulus and the implied non-exponentiality in the relaxation of the electrical field in the time domain.

6. Closer examination of the electrical modulus spectrum shows that its shape is dependent on the conductivity and the dielectric constant. The approach to single exponential behavior correlates well with the decrease in the ion-hopping contribution to the dielectric constant with decreasing alkali concentration.

7. Fitting the KWW function to the electrical modulus yields values for $\beta$ strongly influenced by the glass dielectric constant and the conductivity relaxation. The non-
The exponentiality of the conductivity relaxation is more accurately obtained by fitting the KWW function to the conductivity spectrum.

8. The ion-hopping dielectric relaxation frequency should be used as the characteristic ion-hopping frequency instead of the frequency where the $M''$ peak maximum which may have no physical meaning.

9. The first-ever study of ion dynamics through conductivity and nuclear spin lattice relaxation for three FIC lithium chalcogenide glasses (over the same frequency and temperature range) are reported.

10. For all glasses, the NSLR and the conductivity activation energies are approximately the same. The relaxation time and the KWW $\beta$ parameter are also approximately the same if obtained using the techniques suggested in (7) and (8). These results strongly support the hypothesis that the ion dynamics in the conductivity and the NSLR experiment are the same.

The data obtained from this wide composition, frequency and temperature range impedance spectroscopy study has been used to test the Anderson-Stuart model, the electrical modulus and the KWW function. Modifications have been proposed to the Anderson-Stuart model and flaws in the fitting of the KWW function to the high frequency electrical modulus have been pointed out as a result of this study. Alternative fitting of the conductivity dispersion has been proposed. Finally, comparison of the NSLR and the conductivity results show that the ion dynamics for the two processes may not be that different.

The data collected in this work has already been used to test the Almond-West model [149,150]. This wide range of data should be used to test other d.c. and a.c. conductivity models.
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APPENDIX A.  AUTOCAD DRAWINGS