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A nuclear magnetic resonance study of vacancy and interstitial motion in scandium hydrides and deuterides

by

Michael Jerosch-Herold
A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

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Iowa State University
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DEDICATION

To

my Mother

and

Diane Marie Fay
INTRODUCTION

The present study is an attempt to obtain a comprehensive understanding of the hydrogen (deuterium) motion in nonstoichiometric transition metal dihydrides and dideuterides. In the monovacancy case and in the absence of particle interactions, the motion of vacancies in dihydrides and dideuterides should resemble a random walk on an empty lattice. The simplicity of this model has to be contrasted with the intricacies of the hydrogen motion for high concentrations where spatial and temporal correlations and particle interactions lead to a considerably more complex description. Furthermore, it was felt that as the vacancy and hydrogen motion are interrelated, the combined study of both vacancy and hydrogen motion should provide a consistency test for any model of hydrogen self-diffusion. Nuclear magnetic resonance measurements of the dipolar $^1$H spin-lattice relaxation rates in transition metal hydrides yield information about the hydrogen motion. Measurements of the quadrupolar relaxation rates of the stationary host lattice metal nuclei should reflect the motion of vacancies if they are the dominant source of the electric field gradient fluctuations at the site of the metal nuclei. The choice of
scandium dihydrides among the transition metal dihydrides was due to a unique combination of properties: $^{45}\text{Sc}$ has 100% abundance and a moderate quadrupole moment which does not produce quadrupolar splitting of the resonance line. The conduction electron contribution to the $^{45}\text{Sc}$ relaxation rate is relatively weak, and it is therefore not necessary for a study of the vacancy motion to measure the spin-lattice relaxation time in the rotating frame of reference, $T_1$.  

We were also interested in extending the measurements considerably beyond the temperature region of the $^{45}\text{Sc}$ quadrupolar and $^1\text{H}$ dipolar $T_1$ minima to high temperatures to investigate the nature of the hydrogen motion in this region. It was thought until recently that the spin-lattice relaxation in the high temperature region would again be dominated by the conduction electron contribution as in the low temperature rigid lattice regime. This expectation is partially based on the assumption that the hydrogen and vacancy hopping frequencies continue to increase with temperature in the high temperature region. The $^{45}\text{Sc}$ Knight shift was measured to study the electronic properties of scandium hydrides and to assist in understanding the nature of the high temperature behavior of the relaxation rates.

The first part of this study gives an overview of the theoretical background, followed by a review of the experimental aspects. The second part consists of a presentation of the results and their discussion.
Metal Hydrides

Metal hydrides have received considerable interest during the last decade. The potential of hydrogen as a future energy carrier replacing fossil fuels, has led to the study of metal hydrides as a storage medium for hydrogen. The finite resources of fossil fuels and environmental considerations will certainly continue to provide strong incentives for the eventual widespread usage of hydrogen as an energy carrier.

Hydrogen may be stored as a gas, a liquid or in easily dissociated compounds such as metal hydrides. Metal hydrides provide a particularly safe and efficient way of storing hydrogen. The number of hydrogen atoms per unit volume is for many metal hydrides larger than in liquid and solid hydrogen or water. The mass or weight ratio of the metal to the stored hydrogen is a disadvantage, when compared with, e.g., liquid hydrogen. The formation of metal hydrides is an exothermic, usually spontaneous and reversible reaction. Metal hydrides are quite stable below their dissociation temperature.

Understanding the properties of metal hydrides has proved extremely important, and the following two examples will illustrate this:

The presence of small amounts of hydrogen will tend to enhance the propagation of cracks through the metal. The
reaction of hydrogen with a metal will, due to phase changes, cause embrittlement. It is certain that most metals do embrittle, sometimes catastrophically. A concentration of one part-per-million of hydrogen in high strength steels is sufficient to cause embrittlement. None of the theories to date appears to provide a general explanation of the mechanism of hydrogen embrittlement. When present in amounts less than necessary for embrittlement, hydrogen can cause a noticeable increase in strength, as long as it can be retained in solution. This field of investigation is very active.

The absorption of hydrogen isotopes by a metallic first wall of a fusion reactor can lead to the spin depolarization of the plasma. This depolarization of absorbed deuterium and tritium will depend on the diffusivity of these atoms and the contents of paramagnetic impurities in the metal. This process might in the case of metallic first walls pose severe problems for the prospective use of spin-polarized plasmas and has added interest to the study of these and related parameters in metal hydrides.

While the technological applications and problems are important, metal hydrides are by themselves a physical system of great fundamental interest. Hydrogen is the smallest impurity which can be implanted in a metal. The basic interactions leading to phase transitions, the change in electronic structure with respect to the metal, the large mobility and
respective isotope effects are some of the topics which have
turned metal hydrides into a physical model system.

Scandium Hydrides and Deuterides

In the present study we investigated scandium hydrides,
deuterides and samples of mixed composition containing 75% $^2D$
and 25% $^1H$. The pressure composition isotherms adapted from a
report by Stampfer\textsuperscript{2} are reproduced in Fig. 1. The samples
were in the $\delta$-phase, which has the CaF$_2$ structure, with the
hydrogen predominantly occupying the tetrahedral interstitial
sites. They ranged in composition from $H$/Sc = 1.75 to close
to $H$/Sc = 2.0. Scandium hydrides do not form a trihydride
phase like YH$_x$ and LaH$_x$. They compare in this respect with
the group IV hydrides TiH$_x$ and ZrH$_x$. Scandium dihydride has a
lattice parameter of 4.738 Å, which is larger than the values
for TiH$_2$ and ZrH$_2$, but smaller than for YH$_2$ and LaH$_2$.

Scandium is the first of the series of transition metals
to have an unfilled d-band. Peterman and Harmon\textsuperscript{3} have
calculated the electronic band structure of scandium dihydride
using a muffin tin approximation. Their results seem to
indicate a transfer of charge from the metal site to the
hydrogen tetrahedral sites. The additional electron charge
within the hydrogen muffin tin sphere is 0.15e. Gupta and
Chatterjee\(^4\) used the composite wave variational method as described by Schlosser and Marcus.\(^5\) The band structure obtained is similar to the results of Peterman and Harmon. The two lowest bands are mainly hydrogen derived bonding bands with strongly covalent character. They have a mixture of metal s, p, and d like character. The mixture of covalency and ionic bonding accounts for the strong stability of these hydrides.

The specific heat \(c_p\) of ScD\(_x\) in the \(\beta\)-phase has been measured by Moss et al.\(^6\) After accounting for the different components of \(c_p\) with harmonic lattice, electronic and dilational terms, their experimental data show a sizeable additional contribution. This contribution increases rapidly with the temperature above 600 K and shows no significant composition dependence. The authors ascribe this fast rise to anharmonic vibrations of the deuterons due to large amplitude thermal motion.

Venturini and Richards\(^7\) discuss their low temperature electron spin resonance spectra of diluted Er in ScH\(_x\) (\(x\) in the range of 1.84 to 2.0) powder samples. They conclude that the octahedral site occupancy at the dihydride composition is certainly less than 0.5%. This is consistent with the fact that Sc does not form a trihydride. Optical\(^8\) and photoelectron spectroscopy\(^9\) confirm that the octahedral site occupancy is negligible.
Beattie\textsuperscript{10} performed acoustic velocity measurements on ScH\textsubscript{1.99}. The longitudinal and shear velocity measured as a function of temperature show an abrupt change in their temperature derivatives between 240 and 250 K. This seems to indicate the possible occurrence of a phase transition. The Debye temperature inferred from these measurements is 759 K.

Venturini and Morosin\textsuperscript{11} report Gd\textsuperscript{3+} electron spin resonance linewidth measurements in Sc\textsubscript{0.995}Gd\textsubscript{0.005}H\textsubscript{1.9}. The half width at half maximum as a function of temperature shows a pronounced change in slope in the region of 120 to 140 K. According to the authors the transition temperature does not depend on the Gd\textsuperscript{3+} contents of the sample.

Several Nuclear Magnetic Resonance (NMR) studies of the Sc-H system have been reported in the literature. Schreiber\textsuperscript{12} measured the metal nucleus Knight shift $K_{\text{Sc}}$ in the metal and ScH\textsubscript{2}. For the latter case, $K_{\text{Sc}} = 0.07\%$ and the ratio of this to the Knight shift in the metal is $0.33 \pm 0.03$. The experimental results are interpreted by Schreiber as evidence for the protonic model where the hydrogen is assumed to donate its electron to the metal d-band. The observed Knight shift seems to indicate a reduction in the density of states at the Fermi level with increasing H-concentration.

The effects of paramagnetic impurities for the NMR results have been systematically investigated by Phua et al.\textsuperscript{13} for yttrium and lanthanum hydrides. They show that the
presence of rare earth impurities at levels as low as 10 parts per million can produce significant effects. Torgeson et al.\textsuperscript{14} report the determination of the proton Korringa product in the dihydride phases of scandium, yttrium, lanthanum and lutetium. They used highest purity Ames Laboratory metals. The quantity $(T_1eT)^{-1/2}$, which is essentially proportional to the density of states $N(e_F)$, was determined to have a value of 0.055 $(\pm 0.002) \text{s}^{-1/2} \text{K}^{1/2}$ at the dihydride composition in all of these systems. Lu\textsuperscript{15} studied the effects of paramagnetic rare earth impurities in scandium hydrides. He also discusses the probability of octahedral site occupancy, based on his $^1\text{H}-T_1$ data. The substantial magnetic moment of $^{45}\text{Sc}$ makes the $T_1$ measurements relatively insensitive to the hydrogen distribution, but the results seem to confirm the previously mentioned evidence from ESR measurements of negligible O-site occupancy.

**Diffusion in ScH$_x$ and ScD$_x$**

In the $\beta$-phase of scandium hydrides and deuterides the metal atoms form a face centered cubic (fcc) lattice and the hydrogen atoms occupy the tetrahedral interstitial sites. These sites form a simple cubic lattice, where alternating cube centers are occupied by the host metal atoms. During
diffusion\textsuperscript{16} the hydrogen atoms move between these equilibrium sites.

For the temperature range where diffusion influences the NMR results in our study, the hydrogen motion is described by classical over the barrier jumps of hydrogen from one equilibrium site to another. The barrier to jumps is mainly due to self-trapping distortion and interactions with the host metal lattice. Classical rate theory\textsuperscript{17} gives the following result for the average dwell time between jumps

\[ \tau = \tau_0 \exp \left( \frac{E_a}{kT} \right). \]  

[1]

The activation energy $E_a$ is related to the difference in potential energy of the saddle point and the minimum configuration. An accurate description will have to take the zero point vibration energies into account. Classical rate theory also predicts an isotope dependence of the prefactor of the form

\[ \tau_0^{-1} = \nu_0 \alpha m^{-1/2}. \]  

[2]

The prefactor is related to the vibrational frequency of the hydrogen atom about its equilibrium position $\nu_0$, the number of available jump paths $Z$ and the probability that a neighboring site is unoccupied by
\[ \nu_0 = \nu_0 \cdot z \cdot (1 - c_H) \quad [3] \]

\( c_H \) gives the hydrogen concentration. In the case of nearest neighbor jumps, \( z \) corresponds to the coordination number. For a certain hydrogen concentration on the tetrahedral sublattice there should exist a very simple relation between the motion of labeled particles and the vacancies

\[ \nu_0^{(H)} \cdot (1 - c_V) = \nu_0^{(V)} \cdot c_V \quad [4] \]

where \( \nu_0^{(H)} \) and \( \nu_0^{(V)} \) are the jump frequency prefactors for particles and vacancies respectively. The vacancy concentration of ScH\(_x\) is \( c_V = 1 - x/2 \). The pictures inferred from observing the hydrogen and vacancy motion separately should be consistent with this relation. We will see that the present study provided an unique opportunity to study the diffusion process from these two viewpoints.

The macroscopic diffusion constant is related to the mean square displacement \( \langle r^2 \rangle \) in a time interval \( \Delta t \) by

\[ D = f_T \cdot \frac{\langle r^2 \rangle}{6 \cdot \Delta t} \]

where \( f_T \) is a correlation factor which characterizes the non-randomness in space of the motion of a marked atom or tracer. The correlation factor \( f_T \) equals unity unless the directions
of successive jumps of atoms are correlated. For nearest neighbor jumps on a cubic lattice consecutive displacements have the same magnitude. The correlation factor can then be represented in the following form

\[ f_T = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \]

where \( \theta \) is the angle between consecutive jump directions and the angular brackets denote an average. If the vacancy concentration is small we can assume that the vacancies perform a random walk on the cubic lattice. The motion of the H atoms is more complicated. The vacancy will move by exchanging its position with a hydrogen atom. The probability for this vacancy to induce further jumps of the same atom is rather high. At some later time a different vacancy will come by and induce a new sequence of jumps of the atom. Bardeen and Herring,\textsuperscript{18} have shown that successive jumps of a tracer due to the same vacancy are correlated and form what is termed an encounter. During an encounter the angle \( \theta \) between consecutive jump directions of an atom does not fluctuate randomly. For the monovacancy limit we can assume that successive encounters of a given atom with different vacancies will be independent.
Fig. 1: Pressure composition isotherms [Adapted from report by J. F. Stampfer, Jr., published by Los Alamos Scientific Laboratory, Los Alamos, New Mexico (1966).]
Fig. 2: The structure of scandium dihydride
[The metal atoms form an fcc lattice and the hydrogen atoms occupy the tetrahedral interstitial sites.]
NUCLEAR MAGNETIC RESONANCE

The discovery\(^{19}\) by Bloch et al.\(^{20}\) and Purcell et al.\(^{21}\) of nuclear magnetic resonance (NMR) has provided the experimentalist with a versatile technique to study metal hydride systems. NMR enables one to study the diffusion of hydrogen and its isotopes in metal hydrides. It can yield structural knowledge about the distribution of hydrogen among the different interstitial sites; it is sensitive to the electronic structure of the metal hydride system and to the presence of paramagnetic impurities. It furnishes a microscopic picture by probing magnetic and electric fields on an atomic scale. We will next, for the sake of completeness, summarize the fundamental principles of NMR, following the treatments of Abragam\(^{22}\) and Wolf.\(^{23}\) The book by Abragam is considered the definitive treatise on this subject.

We will initially follow a semiclassical treatment. The quantum mechanical expectation values obey the same equations. The magnetic moment of a nuclear spin is related to its intrinsic angular momentum \(I\) by the gyromagnetic ratio \(\gamma\)

\[
\mathbf{M} = \gamma \left( \frac{\hbar}{2\pi} \right) \mathbf{I} .
\]
The magnetic moment experiences in a magnetic field a torque, which by definition is equal to the change in angular momentum.

\[
\frac{dI}{dt} = \gamma \hbar I \times H_0. \tag{6}
\]

The nuclear spin therefore precesses in the magnetic field with an angular velocity \(\omega_0\),

\[
\omega_0 = \gamma H_0, \tag{7}
\]

known as the Larmor frequency. We will henceforth use the convention that \(H_0\) points along the \(z\) direction of our laboratory system of reference. In a reference frame rotating with angular velocity \(\omega = \omega z\) the equation of motion becomes

\[
\frac{dI}{dt} = \gamma \hbar I \times (H_0 - \omega/\gamma)z'. \tag{8}
\]

The effective field is defined by the term in parentheses and refers to the field around which the spin precesses in the rotating frame. Primed quantities refer to a rotating frame of reference. Choosing the rotating frame frequency as \(\omega = \omega_0\), would make the effective field in the rotating frame vanish. In this reference frame \(R'\) the spin would appear stationary. The essential idea consists now in applying an
additional, arbitrarily small, field $H_1$, which appears stationary in this frame $R'$ and allows us to appreciably reorient the magnetic moment. In $R'$ the spin would precess around the effective field, which is given by $H_1$. This means that we should irradiate the magnetic moment with a circularly polarized electromagnetic wave of frequency $\omega = \omega_0$ (Larmor frequency). To be able to invert the magnetic moment, the field $H_1$ has to lie in a plane perpendicular to $H_0$. We define the rotating frame in such a way that $H_1$ appears stationary in that reference frame and points along the $x'$ axis. If its angular velocity equals the Larmor frequency, then we are at resonance. In the case of arbitrary $\omega$, the effective field in the rotating frame is given by

$$\gamma H_{\text{eff}} = (\omega_0 - \omega) z' + \omega_1 x' ,$$

where $\omega_1 = \gamma h H_1$. The direction of the effective field is defined by

$$\tan \theta' = \omega_1 / (\omega_0 - \omega) .$$

At resonance, i.e., $\omega = \omega_0$, we have $\theta' = 90^\circ$, and we will be able to invert the magnetic moment, no matter how weak the field $H_1$ is.

In the language of quantum mechanics we can describe the process in the following way:
The Hamiltonian $H$ of a spin in a uniform magnetic field, neglecting all orbital motion, is

$$H = -\gamma \hbar \mathbf{I} H(t). \quad [11]$$

This is called the Zeeman Hamiltonian. Let $H = H_0z + (H_1/2)\cos \omega t \mathbf{x} + (H_1/2)\sin(\omega t) \mathbf{y}$. In the Schroedinger picture the spin state $|\Psi(t)\rangle$ obeys the familiar equation

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \{-\gamma \hbar (H_0 + (H_1/2)\cos \omega t) I_y + (H_1/2)\sin \omega t I_x \} |\Psi(t)\rangle.$$

In the rotating frame this equation has the following solution:

$$|\Psi'(t)\rangle = \exp \left(-i \tilde{\Omega} S t \right) |\Psi'(0)\rangle,$$

with $\tilde{\Omega}$ given by $\tilde{\Omega} = [\left(\omega_0 - \omega \right)^2 + \omega_1^2]^{1/2}$ and

$$S = \left(\omega - \omega_0 \right)/\tilde{\Omega} I_z + \omega_1/\tilde{\Omega} I_x.$$

If the initial state of the spin is $|\Psi(0)\rangle = |\uparrow\rangle$, the probability, that the spin after time $t$ has flipped to the state $|\downarrow\rangle$, is given by

$$P_{\uparrow\downarrow}(t) = |\langle \downarrow | \Psi(t)\rangle|^2 = \frac{\omega_1^2}{2\tilde{\Omega}^2} \left(1 - \cos 2\tilde{\Omega}t \right). \quad [12]$$
The maximum value of $P_\uparrow\downarrow(t)$ occurs when $\Omega t = \pi$, i.e., after a 180° pulse,

$$P_\uparrow\downarrow(t)|_{\text{max}} = \frac{\omega_1^2}{(\omega - \omega_o)^2 + \omega_1^2} . \quad [13]$$

At resonance the probability is unity. Under this condition the spin has flipped with certainty. For atomic nuclei the Larmor frequency falls into the radiofrequency range.

To perform an NMR experiment we place the magnetic moment in a coil whose axis is oriented perpendicular to the direction of $H_o$. To flip the magnetic moment into the $x$-$y$ plane we apply a 90° rf pulse of frequency $\omega_o$ (Larmor frequency). Its duration $\tau$ is defined by the equation

$$\gamma H_1 \tau = \pi/2 . \quad [14]$$

After this pulse the magnetic moment will be precessing in the $x$-$y$ plane and therefore produce the largest possible flux change in the coil. The induced sinusoidal voltage will, in a real world experiment, decay due to the dephasing of the magnetic moments in the plane of precession and their realignment with the static magnetic field $H_o$. These two relaxation processes are caused by spin-spin interactions and energy exchange of the spins with their environment. The envelope of the decaying sinusoidal is called a Free Induction Decay (FID).
A collection of spins will produce an induced voltage only when exposed to coherent radiation. The coherent radiation will affect every system of a statistical ensemble in the same way, and the individual moments will thus give rise to a macroscopic quantity. The decay of the induced voltage is due to incoherent perturbations and requires ensemble averaging. We will have much more to say about this when discussing spin relaxation. As a preparation, we will introduce the density matrix formalism which facilitates the treatment of an ensemble of spins interacting with their environment.

The quantum mechanical states of the spin system are not describable by a wave function. The spin system is coupled to the outside world by interactions with its local environment. The system is said to be in a mixed state, where we can only specify the probabilities of finding the system in one of its accessible eigenstates. It is for the purpose of treating mixed states that the density matrix formalism has been introduced. The density operator is defined by

\[ \frac{dp}{dt} = \sum_i \{ |i><i| p_i \} \]

where \( p_i \) represents the probability of finding the spin system in the normalized state \( |i> \) and the sum extends over all accessible states. Some obvious identities apply:
The expectation value of some physical observable is determined according to the equation

\[ \langle A \rangle = \text{Tr} \{ A \rho \} . \] \[16\]

If \( \{ \phi_n \} \) constitutes a complete set of orthonormal states of the isolated spin system, satisfying

\[ H \phi_n = E_n \phi_n , \] \[17\]

then the occupation probabilities of these states will be given by the Boltzmann distribution

\[ p_n = c \exp \left( -\frac{E_n}{kT} \right) , \] \[18\]

where \( c \) is a normalization constant. The density operator can thus be cast into the following form

\[ \rho = \exp \left( -\frac{H S}{kT} \right) / \text{Tr} \{ \exp \left( -\frac{H S}{kT} \right) \} . \] \[19\]

For a system of \( N \) magnetic moments with spin \( J \) in a strong magnetic field \( H_o \) we obtain for temperatures \( H S/kT \ll 1 \) for the magnetization
\[ \langle M_z \rangle = \text{Tr} \{ M_z \rho \} = N \gamma^2 \hbar^2 J(J+1)/3kT . \quad [20] \]

This is the well known Curie-Weiss law.

In the Heisenberg picture the density operator obeys the familiar equation

\[ \frac{d\rho}{dt} = i \{ \rho , H \} , \quad [21] \]

which, in this context, is called the Neuman-Liouville equation. It is the starting point of Wolf's theory of spin relaxation.

The Concept of Spin Temperature

The assignment of a temperature to the spin system has been proven a useful concept.\textsuperscript{27} It allows for a simple thermodynamic interpretation of the spin lattice relaxation process. For a spin 1/2 the Zeeman Hamiltonian has two non-degenerate energy levels. We define \( p_+ \) and \( p_- \) as the relative populations of the two eigenstates and the thermal equilibrium ratio is given by the Boltzman factor

\[ \frac{p_+}{p_-} = \exp \left( \frac{\gamma H_0}{kT_S} \right) . \quad [22] \]
$T_s$ is called spin temperature. This procedure is only meaningful when the spins are in a state of internal equilibrium. The motivation for the spin temperature concept stems from the hypothesis that the spin system behaves similarly to other systems for which the thermodynamic concept of temperature has been defined. Given a spin system with spin temperature $T_s$, the thermal contact with a heat bath at $T_L \neq T_s$, will allow the exchange of thermal energy between the spins and the heat bath. Eventually this will lead to the equalization of these two temperatures. This process is called spin-lattice relaxation and in the context of NMR the heat bath is the lattice. In many cases one makes the additional assumption that the lattice has infinite heat capacity. The lattice temperature $T_L$ would then remain constant during spin-lattice relaxation. The establishment of internal equilibrium among the spins is called spin-spin relaxation. After applying a 180° pulse to the spin system the spin temperature will be negative due to the population inversion. The process of spin-lattice relaxation will then reestablish thermal equilibrium between the spins and the lattice. The concept of spin temperature can still be applied when we deal with spins $I > 1/2$, if the Zeeman levels continue to be equally spaced. The relative population ratios between adjacent energy states can, in this situation, still be characterized by a single spin temperature. For nonequal
spacing we have to assign several spin temperatures to the system and this complicates the description of the relaxation process.\textsuperscript{28}

The Spin Hamiltonian

We have until now only taken into consideration the Zeeman term in the spin Hamiltonian, although we admitted the existence of further contributions, when we mentioned the spin relaxation process. The complete Hamiltonian of the entire system, spin plus lattice, may be partitioned as follows

$$
H = H_S + H_{SL} + H_L .
$$

\(H_S(t)\) includes the Zeeman term, as well as internal spin interactions. The weak coupling between spin system and the lattice is characterized by the spin-lattice interaction Hamiltonian \(H_{SL}\). It commutes with neither \(H_S\) nor with \(H_L\). The lattice Hamiltonian \(H_L\) causes phenomena like defect motion.
Dipolar Interaction

We will consider first the dipolar interaction, which can contribute to $H_S$ and $H_{SL}$. The interaction energy between two magnetic dipoles $\mu_1$ and $\mu_2$ can be written as

$$W_{jk} = \frac{1}{r_{jk}^3} \left\{ \mu_j \mu_k - \frac{3}{2} \frac{\mu_j \cdot r_{jk} \cdot \mu_k \cdot r_{jk}}{r_{jk}^2} \right\},$$

where $r_{jk}$ is the vector connecting the magnetic dipoles labeled $j$ and $k$. The corresponding Hamiltonian can be written in terms of tensor operators and then takes the following form:

$$H_D = \xi_q A_{jk}^{(q)} F_{jk}^{(q)} ; (-2 \leq q \leq 2),$$

where

$$A_{jk}^{(0)} = \delta_D/2 \left( 3 I_j I_k - I_j I_k \right),$$

$$A_{jk}^{(\pm 1)} = 3\delta_D/2 \left( I_j I_k^\pm + I_j^\pm I_k \right),$$

$$A_{jk}^{(\pm 2)} = 3\delta_D/4 \left( I_j I_k^\pm \right),$$

with $\delta_D = -\gamma_i \gamma_k h^2$ and $A_{jk}^{(q)} = A_{kj}^{(-q)*}$. The geometrical lattice functions are usually expressed in spherical coordinates $r_{jk}$, $\Theta_{jk}$ and $\phi_{jk}$. $\phi_{jk}$ is measured with respect to the static field direction $H_0$ (z-axis).
\[
F_{jk}(0) = r_{jk}^{-3}[1 - 3\cos^2 \theta_{jk}] = (16\pi/5)^{1/2} Y_{20}(\phi_{jk}, \theta_{jk})/r_{jk}^3 ,
\]

\[
F_{jk}(\pm 1) = r_{jk}^{-3} \sin \theta_{jk} \cos \theta_{jk} \exp(\pm i\phi_{jk}) = (8\pi/3)^{1/2} Y_{21}(\phi_{jk}, \theta_{jk})/r_{jk}^3 ,
\]

\[
F_{jk}(\pm 2) = r_{jk}^{-3} \sin^2 \theta_{jk} \exp(\pm 2i\phi_{jk}) = (32\pi/5)^{1/2} Y_{22}(\phi_{jk}, \theta_{jk})/r_{jk}^3 .
\]

The operators $A_{jk}(q)$ and $F_{jk}(q)$ are second rank tensor operators, and $Y_{2m}$ are second order spherical harmonics. If we want to obtain the representation of the operators $F_{jk}(q)$ in the rotating frame of reference, we therefore have to recall the formally identical rules of transformation to the rotating frame for the second rank spherical harmonics $Y_{2m}(\Theta, \Phi)$. The term in the Hamiltonian, corresponding to $q=0$, commutes with the Zeeman Hamiltonian,

\[
[\mathcal{H}_D^{(0)}, \mathcal{H}_Z] = 0 .
\]

This term is for this reason called the secular part of the dipolar Hamiltonian. It is time independent in the Heisenberg picture. The secular term can be slightly rewritten,

\[
\mathcal{H}_D^{(0)} = \delta_D/r_{jk} (1 - 3\cos^2 \theta_{jk}) [-I_{jz}I_{kz} + 1/4(I_j^+I_k^- + I_j^-I_k^+) .
\]
which shows that this term leads to mutual spin flips. We specialize to the case of like spins, i.e., \( \gamma_j = \gamma_k \), where the mutual flips of two isolated spins conserve energy. If the equidistance of the Zeeman levels is preserved in the presence of dipolar and quadrupolar interactions, the process of mutual spin flips in opposite directions leads to spin diffusion. Spin diffusion homogenizes the magnetization and establishes a uniform spin temperature in the absence of self-diffusion of the spins. The nonsecular terms of the dipolar Hamiltonian produce thermal mixing among the spins and exchange of energy with the lattice. In general the dipolar interaction between like spins \( j \) and \( k \) is more effective than between unlike spins. If spin \( j \) precesses at the Larmor frequency, it produces magnetic field fluctuations at the site of spin \( k \). The frequency spectrum of these fluctuations has a relatively large component at the Larmor frequency of spin \( j \) and gives rise to resonant perturbation of spin \( k \), if \( \gamma_k = \gamma_j \).

**Quadrupolar Interaction**

The presence of an electric field gradient (EFG) will, for a nonspherical charge distribution, make a contribution to the potential energy of the charge distribution. This can be derived from a multipole expansion of the electrostatic energy. The quadrupolar Hamiltonian is given by.
\[ H_Q = \sum_p Q^{(p)} V^{(-p)} ; \quad (-2 \leq p \leq 2). \]  

The operator nuclear quadrupole moments can, using the Wigner-Eckhardt theorem, be represented in the following form

\[ Q^{(0)} = \delta Q/2 \left( 3I_z^2 - I^2 \right), \]  
\[ Q^{(\pm 1)} = 3\delta Q/2 \left( I_z I_\pm + I_\pm I_z \right), \]  
\[ Q^{(\pm 2)} = 3\delta Q/4 \left( I_\pm \right)^2, \]

with \( \delta Q = -eQ/\{4I(2I-1)\} \). The second rank tensor operator \( V^{(q)} \) can be expressed in terms of the EFG tensor components \( V_{\alpha\beta} \)

\[ V^{(0)} = -2V_{zz}, \]  
\[ V^{(\pm 1)} = 2/3 \left( V_{zx} \pm iV_{zy} \right), \]  
\[ V^{(\pm 2)} = 4/3 \left[ (V_{xx} - V_{yy})/2 \pm iV_{xy} \right]. \]

The components of \( V_{\alpha\beta} \) are calculated at the center of the nucleus. The principal axis system of \( V_{\alpha\beta} \) can be characterized by the Euler angles \( \phi, \theta \) and \( \psi \) with respect to the laboratory reference system. We impose the additional condition that \( |V_{zz}| \gg |V_{yy}| \gg |V_{xx}| \). The three Euler angles represent three of the five independent quantities of the traceless, symmetric EFG tensor. The other two are defined as

\[ e_Q = V_{zz} \]
and the asymmetry parameter $\eta$ as

$$\eta = (V_{xx} - V_{yy})/V_{zz}.$$  \[40\]

As a function of these 5 parameters we may, for the special case of axial symmetry ($\eta = 0$), write the operators $v(q)$ as

$$v(0) = eq (1 - 3\cos^2 \theta),$$  \[41\]
$$v(\pm 1) = eq \sin \theta \cos \theta \exp(\pm i\phi),$$  \[42\]
$$v(\pm 2) = eq \sin^2 \theta \exp(\pm 2\phi).$$  \[43\]

Note the formal similarity with the dipolar Hamiltonian for this special case of $\eta = 0$. In nonstoichiometric fcc hydrides, where the hydrogen occupies the tetrahedral sublattice, the gradients at the site of the metal nucleus would be due to vacancies on the hydrogen sublattice. We have to sum the appropriate derivatives of the electrostatic potential $V(r)$, evaluated at the metal nucleus site, over all vacancies contributing to the EFG. In the case of a conductor the effect of linear screening has to be included and will limit the sum in many cases to the terms involving nearest neighbors (n.n.) of the metal nucleus.

There is an additional contribution to the quadrupole coupling that is due to the distortion of the spherical electronic shell of the atom by external charges. The
ZERO, MONO- AND DI- VACANCIES
THEIR PROBABILITIES OF OCCURRENCE

Fig. 3: Probabilities of Occurrence for zero, mono- and di- vacancies on 8 cube vertices
additional induced gradient at the site of the nucleus is
given by \( \gamma V_{jk} \) and the total gradient becomes \((1-\gamma)V_{jk}\). \( \gamma \) is
called the Sternheimer antishielding factor.

Vacancy Distributions

In the case of fcc metal hydrides, the EFG at the site
of the metal nucleus will depend on the distribution of
vacancies in its neighborhood. We assume that the hydrogen
atoms only occupy the tetrahedral sites and study the
distribution of vacancies on the nearest neighbor sites of the
metal nucleus. This seems completely adequate in view of the
conduction electron screening.

The nearest neighbor sites of the metal nucleus form a
simple cube. We assume that the vacancies do not interact and
are distributed at random on the tetrahedral sublattice. The
probability of finding a vacancy at any specific site is
therefore determined by the vacancy concentration \( c_v \) and is
independent of the distribution of vacancies on the
surrounding sites. The probability of finding \( i \) vacancies on
any of the 8 vertices of a cube on the tetrahedral sublattice
for a given vacancy concentration, \( c_v = (1-c_H) \), is

\[
P_8(i,c_v) = (1-c_v)^{8-i} c_v^i \binom{8}{i}.
\]  
[44]
Figure 3 shows the probabilities for the cases $i = 0$, 1, and 2 as a function of vacancy concentration.

For the monovacancy case the EFG parameters $\eta$ and $e_g$ are

$$\eta = 0 \quad \text{and} \quad e_g = v_{zz} = \frac{16e}{a^3} = v_o,$$

where $a$ is the lattice parameter of the tetrahedral sublattice and thus equals half the metal lattice parameter. The $z$-axis of the principal axis system is defined by the direction connecting vacancy and nucleus. To account for electron screening we should substitute the electronic charge $e$ by an effective charge $Z'e$.

For the divacancy case ($i=2$) we have 3 subclasses of possible configurations of the 2 vacancies on the 8 cube sites. It is easiest to specify the configurations in terms of the line connecting the 2 vacancies. The 3 possibilities are cube edge, face diagonal and body diagonal. The probabilities of these 3 configurations occurring are:

- cube edge: $p = \frac{12}{28} = 0.43$
- face diagonal: $p = \frac{12}{28} = 0.43$
- body diagonal: $p = \frac{4}{28} = 0.1$.

A straightforward calculation of the parameters $e_g$ and $\eta$ for these configurations yields:
cube edge: \( n = 1 \) \( \eta \) \( \text{eq} = V_0 \)
face diagonal: \( n = 1 \) \( \eta \) \( \text{eq} = V_0 \)
body diagonal: \( n = 0 \) \( \eta \) \( \text{eq} = 2V_0 \).

The arrangement of 2 vacancies at opposite ends of a body diagonal is a relatively rare event. In a first approximation the change from a monovacancy to divacancy configuration and vice versa thus involves only a change in the asymmetry parameter \( \eta \), with \( \text{eq} \) remaining constant.

The probability of occurrence of a trivacancy reaches 15\% for a vacancy concentration of \( c_V = 0.2 \). For the composition range of the samples used in this study the occurrence of trivacancies is normally negligible. It is interesting to note that for the trivacancy case only the arrangement with two vacancies at opposite ends of a body diagonal will produce nonzero values of \( \text{eq} \) and \( \eta \). Trivacancy configurations are, with one exception, equivalent to the case of zero vacancies, as long as the metal nucleus remains fixed at its equilibrium site.

The parameters \( \eta \) and \( \text{eq} \) are, by definition, calculated in a principal axis system. Its orientation with respect to the laboratory reference system, specified by the Euler angles, changes with different vacancy arrangements. The reorientation of a divacancy will produce a fractional change in the quadrupolar interaction energy. This change is
certainly small, compared with the creation of a monovacancy in a previously undisturbed environment of cubic symmetry.

**Hyperfine Interaction**

The interaction of electrons with the nuclear spin I is described by the hyperfine Hamiltonian

\[ H_{\text{hfs}} = \gamma_e \gamma_n \hbar \left\{ \frac{1\hbar^2}{r^3} + \frac{1}{r^3} \right\} \left[ 3(s(I)l)(I\hbar)/r^2 - I s \right] + (8\pi/3)I s \delta(r) \], \quad [45]

where \( r \) represents the vector connecting electron spin and nucleus. \( s \) and \( l \) are the electronic spin and electronic orbital angular momentum, respectively. We will concentrate on the case of metals where the conduction electrons behave as a degenerate Fermi gas and occupy Bloch states.

The hyperfine Hamiltonian creates at the site of the nucleus an additional field due to the electrons. For a cubic metal it can be shown that the dipolar term in the hyperfine Hamiltonian vanishes when averaged. Performing an ensemble average using Fermi Dirac statistics the Fermi contact term produces a shift in the resonance frequency. This usually positive, i.e., paramagnetic shift is known as the Knight shift. Spin orbit coupling will produce only negligible
effects if the orbital angular momentum is not already quenched. For transition metals electrons in the partially filled d-shell can polarize inner core s-state electrons. This core polarization makes for the case of d-band electrons a diamagnetic contribution to the hyperfine field, i.e., the hyperfine field due to d-band core polarization is negative.

The hyperfine interaction will also give rise to an indirect coupling, through electrons, between two nuclear spins \( I_j \) and \( I_k \). The Hamiltonian is bilinear in the nuclear spin operators and has an oscillatory behavior as one changes the separation \( r \) between \( I_j \) and \( I_k \):

\[
|H_{\text{ex}} = \frac{(2/9\pi)}{\gamma_e^2 \gamma_n^2 \hbar^2 m^*} |u_{k_F}(j)|^4 x \left[ \sin 2k_F r - 2k_F r \cos 2k_F r \right]/r^4 I_j I_k \quad [46]
\]

where \( m^* \) is the electronic effective mass, \( k_F \) the wavevector at the Fermi surface and \( |u_{k_F}(j)| \) represents the density of electrons at the site of nucleus \( j \), with wavevector \( k = k_F \). A nuclear magnetic dipole moment creates in its immediate neighborhood a small region which favors parallel moments. The perturbed electronic wave function corresponds to the addition of Bloch states with parallel spin, which interfere constructively at the site of the nuclear spin. Interference of these Bloch states, corresponding to a small range of wavevectors around the Fermi wavevector \( k_F \), produces
oscillations of the charge density of the electrons. These oscillations are known as Friedel oscillations and give rise to sinusoidal factors in the above equation.

**Spin-Lattice Relaxation**

Having studied the different contributions to the total Hamiltonian of the system spin plus lattice, we would like to analyze the relaxation process due to these interactions. We will consider the case of strong Zeeman fields, where we can assume that the Zeeman Hamiltonian is the dominant contribution and treat the remaining interactions as perturbations. Especially the coupling between the spins and the lattice is assumed to be weak. If we separate the lattice and spin degrees of freedom, we can write for the total Hamiltonian (Eq. 23)

\[ H = H_S + H_{SL} + H_L. \]

We will concentrate first on the relaxation effects produced by the dipolar and quadrupolar interactions. The Hamiltonian can then also be partitioned as

\[ H = H_Z + H_D + H_Q. \] [47]
The quadrupolar and dipolar Hamiltonian contain products of lattice and spin operators and therefore contribute mostly to $H_{SL}$. We treat $H_{SL}(t)$ as a random and stationary operator. The latter condition implies that the expectation value,

$$\langle H_{SL}(t) H_{SL}(t+\tau) \rangle,$$

is invariant under a shift in time scale. $\langle \rangle$ represents a time average. Any rigid lattice contributions of the dipolar and quadrupolar Hamiltonians are assigned to $H_L$, so that

$$\langle H_{SL}(t) \rangle = 0.$$  \[48\]

This keeps the coupling term $H_{SL}$ as small as possible and guarantees faster convergence of perturbation expansions. The heat capacity of the lattice is assumed to be infinitely large. The exchange of energy between spins and lattice will therefore not produce any changes in the lattice temperature $T_L$. The lattice will remain in thermal equilibrium. We further restrict ourselves to high temperatures, where

$$H_S \ll kT_S.$$

This is certainly true for temperatures above 1 or 2 Kelvin and field strengths of a few Tesla for all nuclei. The density operator can then be approximated by
\[ \exp \left( \frac{H_g}{kT} \right) \rightarrow \frac{1}{Z} \left( 1 - \beta H_g \right), \]  \hspace{1cm} \text{[49]}

where \( Z \) is the partition function \( \text{Tr}\{\exp(H_g/kT)\} \).

Keeping these approximations in mind, we will start our outline of Wolf's relaxation theory with the Neuman-Liouville equation

\[ \frac{d\rho(t)}{dt} = -\frac{i}{\hbar} \left[ H, \rho \right]. \]

This will allow us to determine the time dependence of any operator \( A \)

\[ \langle A \rangle = \text{Tr}_{S+L}\{\rho(t) A\} \quad \text{and} \quad \frac{d\langle A \rangle}{dt} = \text{Tr}_{S+L}\{d\rho(t)/dt A\}. \]

If \( A = H_g \), the latter equation will tell us at what rate the spin reservoir exchanges energy with the lattice. To concentrate on the effects induced by the spin-lattice interaction, we transform to the interaction representation.

\[ \rho^*(t) = \exp[i(H_g+H_L)t] \rho \exp[-i(H_g+H_L)t] \]  \hspace{1cm} \text{[50]}

The exponential spin operator will transform to the rotating frame representation and the lattice operator will eliminate any time dependence due to the lattice degrees of freedom. In this representation the Neuman-Liouville equation of motion becomes
\[
\frac{d\rho^*(t)}{dt} = (-i/h) \left[ H_{SL}^*(t), \rho^*(t) \right]. \tag{51}
\]

The weak spin–lattice relaxation allows an iterative perturbation expansion

\[
\frac{d\rho^*(t)}{dt} = -i/h \left[ H_{SL}^*(t), \rho^*(0) \right] - \frac{1}{h^2} \int_0^t \left[ H_{SL}^*(t'), \left[ H_{SL}^*(t'), \rho^*(0) \right] \right] dt', \tag{52}
\]

where \( \rho^* \) represents the density operator of the whole system, spin plus lattice. We assume that it can be factored into two density operators for the spin degrees of freedom and the lattice degrees of freedom. This would be proper for the case of no interaction between spins and lattice and is a good approximation for weak coupling.

\[
\rho^*(t) = \sigma^*_S(t) P_L^*(t) \tag{53}
\]

In the high temperature approximation we can write

\[
\rho^*(0) = \sigma^*_S(0) - \beta_L H_L . \tag{54}
\]

Using the above approximations and performing a trace over the lattice degrees of freedom leads to
\[ \frac{d\sigma^*(t)}{dt} = \frac{-1}{\hbar^2} \int_0^\infty dt' [H_{SL}^*(t), [H_{SL}^*(t+t'), \sigma^*(t) - \beta_s H_s]] . \]

The trace over the lattice degrees of freedom is represented by a bar and symbolizes an ensemble average. Notice that the upper integration limit has been extended to infinity. The lattice expansion is only valid for times long compared with the correlation time of the fluctuations. On a short time scale the changes of \( H_{SL}(t) \) are rather abrupt and cannot be accounted for by a perturbation expansion. We assume that the nuclear spin density operator is characterized by a single spin temperature \( \theta_s \) and is given by

\[ \sigma_s = \frac{1}{Z} (1 - H_s/k\theta_s) . \]

For a system of \( N \) spins we can approximate the partition function \( Z \) by \((2I + 1)^N\) in the high temperature limit. The expectation value of \( H_s \) is given by

\[ \langle H_s \rangle = \text{Tr}_S \{ \sigma_s H_s \} = (-1/Zk\theta_s) \text{Tr} \{ H_s^2 \} , \tag{56} \]

and its rate of change is

\[ \frac{d\langle H_s \rangle}{dt} = - (1/Zk) \text{Tr}_S \{ H_s^2 \} \frac{d\theta_s^{-1}}{dt}. \tag{57} \]
The rate of change of $\langle H_S \rangle$ is therefore proportional to the inverse spin temperature. This means that if the spin system is losing energy to the lattice, the spin temperature is actually rising. Recalling the above equation 55 one obtains through some lengthy derivation

$$\frac{d\Theta_s^{-1}}{dt} = \left(-\frac{1}{T_s}\right) \{\Theta_s^{-1} - \Theta_L^{-1}\}, \quad [58]$$

where

$$T_s^{-1} = \frac{1}{\langle H_s^2 \rangle} \times \text{Re} \int_0^\infty dt' \text{Tr}_S \{ [H_{SL}^*(t'), H_s][H_{SL}^*(0), H_s] \}.$$

$\text{Tr}_S\{}$ represents a trace over the spin degrees of freedom. We have attributed a physical meaning only to the real part of the integral expression. The expectation value $\langle H_S \rangle$ is a real quantity. We also made use of the fact that the relaxation process is nonoscillatory and eliminated the oscillatory factors. They are an artifact from the transformation to the rotating frame. Our intuitive picture describing spin-lattice relaxation as a process of thermal equilibration between spins and lattice is confirmed by equation 58.

We could now specify $H_{SL}$ for dipolar and quadrupolar coupling and proceed with the calculations. We will skip the
mathematics and present the final results for dipolar and quadrupolar relaxation below.

The above equation 59 for $T_{SL}^{-1}$ already indicates that the relaxation process depends on the temporal correlation of the fluctuating interaction $H_{SL}(t)$. The interactions which commute with the spin Hamiltonian $H_S$ will leave the spin-system unperturbed and do not contribute to the spin-lattice relaxation. They are referred to as secular terms.

For the dipolar interaction the correlation functions are defined by,

$$G(q)(\tau) = \sum_k \sum_j \langle F_{jk}(q)^*(t) F_{jk}(q)(t+\tau) \rangle , \quad [60]$$

where the second rank tensors $F_{jk}(q)$ describe the spatial dependence of the dipolar interaction between two dipoles, labeled j and k. The Fourier transform of the correlation function gives the frequency spectrum of the dipolar fluctuations,

$$J(q)(\omega) = \int_{-\infty}^{\infty} G(q)(\tau) e^{-i\omega \tau} d\tau . \quad [61]$$

For the quadrupolar case the correlation functions are defined analogously

$$G(q)(\tau) = \sum_{\alpha, i} \langle V_{\alpha i}(q)(t) V_{\alpha i}(q)(t+\tau) \rangle . \quad [62]$$
The $V_{\alpha i}(q)(t)$ are derived from the components of the gradient tensor and again relate to the spatial dependence of the quadrupolar interaction. The greek index $\alpha$ refers to the defect, producing the EFG at the site of nucleus $i$.

The operators $P(q)$ and $v(q)$ are lattice operators and we should solve the Schröedinger equation for the lattice Hamiltonian to determine their properties. Since this is impossible in practice, we treat $P(q)$ and $v(q)$ as classical quantities, which vary, reflecting the motion of the spins and/or vacancies.

Lattice vibrations produce normally negligible relaxation in themselves. The dipolar interaction can be replaced by its value averaged over many lattice vibrations, since the jump frequency is in most cases slow compared to the lattice frequencies.

The spin-lattice relaxation rate is expressed as a function of the spectral density, evaluated at the Larmor frequency or an integer multiple. This reflects the fact, that the frequency component at the Larmor frequency of the fluctuating perturbation is most effective in appreciably reorienting the spins.

The spin-lattice relaxation in the rotating frame and the spin-spin relaxation are derived in an analogous way. See Wolf for further details.

The final results for the quadrupolar case are
The constant $d_Q$ is given by

$$d_Q = \left( \frac{Z e^2 gQ}{\hbar} \right)^2 \frac{(2I+3)}{[I^2(2I-1)]}.$$  \[66\]

The results for the dipolar interaction between like spins are given by

$$T_1 = \frac{2}{30} d_Q \left[ J^{(1)}(\omega_0) + 4J^{(2)}(2\omega_0) \right], \quad [63]$$
$$T_{1_p} = \frac{3}{40} d_Q \left[ 3J^{(0)}(2\omega_0) + 5J^{(1)}(\omega_0) + 2J^{(2)}(2\omega_0) \right], \quad [64]$$
$$T_2 = \frac{3}{40} d_Q \left[ 3J^{(0)}(0) + 5J^{(1)}(\omega_0) + 2J^{(2)}(2\omega_0) \right]. \quad [65]$$

$$T_1^{-1} = \frac{3}{2} d_P \left[ J^{(1)}(\omega_0) + J^{(2)}(\omega_0) \right], \quad [67]$$
$$T_{1_p}^{-1} = \frac{3}{8} d_P \left[ J^{(0)}(2\omega_1) + 10J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right], \quad [68]$$
$$T_2^{-1} = \frac{3}{8} d_P \left[ J^{(0)}(0) + 10J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right], \quad [69]$$

with $d_P = \gamma^4 \hbar^2 I(I+1)$.

We would like to introduce the microscopic features of the motion of the hydrogen atoms. For this purpose we change the time average in the definition of the correlation functions to an ensemble average

$$G^q(t) = \int \int P(r_\alpha, r_\beta, t) F_{ij}^q(r_\alpha) F_{ij}^q(r_\beta) \rho(r_\alpha) \, dr_\alpha \, dr_\beta.$$ \[70\]

$p(r_\alpha)$ denotes the probability that some arbitrary spin is located in $dr_\alpha$ at $r_\alpha$. To be more specific we will label this
spin with \( i \). \( P(r^\alpha, r^\beta, t) \) denotes the probability that if spin \( i \) was at time zero located at \( r^\alpha \) relative to spin \( j \), its relative position will will be given by \( r^\beta \) at time \( t \).

The Polycrystalline Case

The explicit form of the dipolar correlation function is

\[
G(q)(t) = \frac{c_H d^2}{Q} \sum_{j<k} Y_{2q}(\Theta_{jk}, \Phi_{jk}) Y_{2q}^* (\Theta_{jk}(t), \Phi_{jk}(t)) r_j^{-1} r_k^{-3} \times P(r_j, r_k, t) . \tag{71}
\]

We are interested in the relaxation rates for a powder sample and have thus to perform the appropriate angular averaging process over all crystal orientations of the correlation function. Wolf\(^{30}\) has shown that for cubic crystals the relaxation rates will have an angular dependence described by

\[ f(\Theta, \Phi) = \sin^2 \Theta + \sin^4 \Theta \sin 2\Phi , \]

where \( \Theta \) and \( \Phi \) give the crystal orientation with respect to the magnetic field direction. Performing an angular average over all field directions will, under the condition \( \omega \tau \ll 1 \), give the following ratio for the dipolar spectral density functions

\[
<J^{(0)}(\omega)>_{\Theta, \Phi} : <J^{(1)}(\omega)>_{\Theta, \Phi} : <J^{(2)}(\omega)>_{\Theta, \Phi} = 6 : 1 : 4 . \tag{72}
\]
These results apply to the quadrupolar case only for an axially symmetric EFG tensor, where $\eta = 0$ and in the absence of electron screening. Only under these circumstances do the quadrupolar lattice functions have a form equivalent to the dipolar lattice functions. They can then be expressed, as in the above dipolar case, in terms of second order spherical harmonics. A nonzero axial symmetry parameter $\eta$ of the EFG will add considerable complexity to the angular dependence of the quadrupolar lattice functions. Electron screening will change the radial and possibly the angular dependence of the lattice functions.

The BPP Model

If we assume that the probability of occurrence of relative jumps of a spin pair is independent of their separation, we can approximate $P(r_\alpha, r_\beta, t)$ by

$$P(r_\alpha, r_\beta, t) = \sum_s w_s(t, \tau) P_s(r_\alpha - r_\beta) . \quad [73]$$

$w_s(t, \tau)$ gives the probability that 2 spins perform $s$ jumps relative to each other in a time interval $t$ and $\tau$ is the mean time between jumps of spin pair members to another lattice site. $P_s(r_\alpha - r_\beta)$ is the probability that the spin pair
separation changes by \((r_\alpha - r_\beta)\) as a result of \(s\) relative jumps. This approximation also assumes that the motion of a spin pair does not depend on the initial absolute positions \(r_\alpha\) and \(r_\beta\) of the spins, but only on \(r_\alpha - r_\beta\). We assume translational invariance. For a random succession of jumps, \(w_s(t, \tau)\) is given by a Poisson distribution

\[
w_s(t, \tau) = (s!)^{-1} \left( \frac{t}{\tau} \right)^s e^{-t/\tau}.
\]  \[74\]

Neglecting all but the \(s=0\) term in the above sum in Eq. 73 is equivalent to the BPP (Bloembergen, Purcell, Pound) approximation,

\[
G(q)(t) = G(q)(0) \ e^{-t/\tau}.
\]  \[75\]

This model involves the trivial assumption that a spin pair does not change its separation as a result of zero relative jumps,

\[
P_0(r_\alpha - r_\beta) = \delta(r_\alpha - r_\beta) .
\]

The BPP model thus neglects the details of the jump process.

For a polycrystalline sample where we can average over all crystal orientations we obtain for the dipolar spin-lattice relaxation time

\[76\]
\[ T_{1}^{-1} = \frac{2}{3} \frac{\omega_{D}}{\omega_{o}} \{ \frac{\omega_{o} \tau}{1 + \omega_{o}^{2} \tau^{2}} + \frac{4\omega_{o} \tau}{1 + 4\omega_{o}^{2} \tau^{2}} \} , \]

with \( \omega_{D}^{2} = (3/5) \hbar^{2} \gamma^{4} I(I+1) \Sigma_{j} (r_{j}^{-6}) \), and the sum extends over all possible spin pairs, with one member fixed at the origin. The inclusion of metal-hydrogen interactions is straightforward. The above expression for \( R_{1}=T_{1}^{-1} \) has a maximum for \( \omega_{o} \tau = 1 \). Its asymptotic behavior for fast (\( \omega \tau \ll 1 \)) and slow (\( \omega \tau \gg 1 \)) motion is

\[ T_{1}^{-1} \propto \omega_{o}^{2} \tau \quad \text{for} \quad \omega_{o} \tau \ll 1 \]

and

\[ T_{1}^{-1} \propto \omega_{o}^{2}/(\omega_{o}^{2} \tau) \quad \text{for} \quad \omega_{o} \tau \gg 1 . \]

If we plot \( \log(T_{1}) \) versus \( T^{-1} \) we see that a BPP type \( T_{1} \) minimum should be symmetric. Recalling that \( \tau = \tau_{0} \exp(E_{a}/kT) \), on a logarithmic scale, the slopes of the minimum will be straight lines and give a measure of the activation energy \( E_{a} \).

We will next outline models which try to improve on the simple BPP approximation. They apply mainly to the dipolar correlation functions.
Torrey\textsuperscript{31,32,33} improved the BPP model by applying the theory of random walks and using an isotropic diffusion approximation. A spin is allowed to jump from its site to any position on a sphere, which is centered at its initial position. Torrey applies this isotropic model to the case of motion on a discrete lattice. The results show great similarity with the ones obtained in the BPP approximation.

Barton and Sholl\textsuperscript{34} refined this model by including the full details of the theory of random walks on a discrete lattice. Wolf\textsuperscript{35} uses a formally equivalent approach, but applies different summation techniques for the slowly converging infinite series which appear in the high temperature limit ($\omega_0 \tau \ll 1$). Barton and Sholl\textsuperscript{36} treat the specific problem of interstitial diffusion in an fcc lattice. This model can be applied to H diffusion in fcc hydrides and includes the dipole-dipole interactions between a migrating spin and the stationary host spins on the fcc lattice.

It is important to notice that all jump models up to this point completely neglect correlation effects. This corresponds to the picture in which spins hop on an empty lattice and is only valid for infinitesimally small hydrogen concentrations. Spatial correlations occur because no two spins can occupy the same site simultaneously. A better
approximation than the random walk model is given by the mean field approximation, which allows only for single occupancy of a site. It assumes that the probability of a given site being vacant is $c_v = 1 - c_H$. The mean field theory has been combined with a reciprocal space formalism by Barton and Sholl\textsuperscript{37} who calculated $J(q)(\omega)$ for sc, fcc and bcc lattices. Pedders and Sankey\textsuperscript{38} have developed the multiple scattering approximation, which seems to yield improved accuracy at the price of considerable mathematical complexity.

The mean field theory can be shown to be exact for $c_H \to 0$ and in the low temperature limit ($\omega_0 \gg 1$), with the exception of the monovacancy case ($c_H \to 1$). The multiple scattering approximation is exact for $c_H = 0$ and $c_H = 1$. Due to the complex dependence of the correlation functions on $c_H$, general tables of the results cannot be generated for the multiple scattering approximation. The random walk model is never exact since the motion of the spin pairs is correlated even in the limit $c_H \to 0$.

At low vacancy concentration the long range diffusion of an atom due to the vacancy mechanism can be described as a sequence of encounters of an atom with a vacancy. An encounter comprises a sequence of jumps of an atom induced by a single vacancy before the vacancy diffuses away. After the initial exchange subsequent jumps of the same spin have a much higher probability of occurrence than the initial jump, since the vacancy is now certainly in the vicinity of the spin.
This rapid succession of jumps in the presence of a nearby vacancy is a sign of temporal correlation. The encounter model was first applied to NMR by Eisenstadt and Redfield. Sholl determined the diffusion correlation factor for motion on a simple cubic lattice of noninteracting particles in the monovacancy limit, obtaining $f=0.65$. The relaxation rates in the low frequency ($\omega_0 \tau << 1$; low temperature) limit have also been determined by Sholl. The numerical values given by Sholl are 60% smaller than the results obtained by either Barton and Sholl or Fedders, based on the mean field approximation. In the mean field approximation the average time before either spin of a spin pair has jumped is simply given by $\tau_S/2$. $\tau_S$ is the mean time between jumps of a single spin. In the monovacancy limit this average time between jumps of either member of a spin pair, would be given by the mean time between encounters $\tau(r_\alpha)$, where $r_\alpha$ gives the initial separation of the two spins forming a pair at the beginning of the encounter. These two quantities, $\tau_S$ and $\tau(r_\alpha)$, are not identical in the monovacancy limit, which accounts for the difference in the results obtained. According to Sholl $\tau_S$ and $\tau(r_\alpha)$ are related by

$$1/\tau_S = [Z(0) + Z(r_\alpha)]/2\tau(r_\alpha)$$

[77]
\(Z(r_\alpha)\) is the mean number of times a randomly walking vacancy, commencing at the origin, visits the \(n'\)th neighboring site \(r_\alpha\). \(Z(0)\) is thus the mean number of times a single vacancy, starting at the origin of a filled lattice, visits the origin during a random walk. The probability of either spin of a pair jumping first being \(1/2\), the mean number of jumps of the members of a spin pair is given by \([Z(0) + Z(r_\alpha)]/2\). In the encounter model the correlation time for dipolar fluctuations depends on the separation of spins and the time scale of these fluctuations is given by the mean time between encounters.

For numerical evaluations of dipolar relaxation rates, it has become customary to list \((aTT_1)^{-1}\) versus \(y = \omega_0\tau\), where

\[
\alpha = \gamma^4 h^2 I(I+1)c_H/(5b^6\omega_0),
\]

and \(b\) is the lattice constant. The tables can be applied for any concentration \(c_H\), within the range of validity of the underlying theory used. A comparison of numerical results for the different models discussed seems to indicate, that the depth of the \(T_1\) minimum is insensitive to the particular model chosen while the value of \(\omega_0\tau\) at the \(T_1\) minimum is sensitive to the model. All models discussed yield an essentially symmetric \(\ln(T_1)\) versus \(T^{-1}\) minimum.

Another important approach to the calculation of correlation functions are Monte Carlo computer simulations.
Bustard\textsuperscript{41} performed such a simulation. In his averages over collections of spin pairs, he assumed that the motion of a spin pair is statistically independent of the motion of all other spin pairs, including spin pairs with common spins. This independent spin pair model agrees well with the random walk model and the encounter model in the appropriate limits.

All of the above mentioned models are based on the assumption that the spins and vacancies do not interact with each other. Including any form of such interaction in the calculation of the correlation functions adds considerable complexity.

\textbf{Interacting Particles}

We will present Richards' model\textsuperscript{42} of interacting particles on a regular lattice. The effects of strong particle repulsions at the saddle point will be considered qualitatively. A particle will jump to a neighboring vacant site only in the presence of a second nearby vacancy. Otherwise the particle is not able to overcome the repulsion of adjacent particles. This situation corresponds to the case of infinite barrier height for a single neighboring vacancy. The frequency spectra of vacancy and labeled particle motions for finite particle repulsion will have qualitatively similar
features. It seems that this model developed by Richards should be relevant to the case of high concentration metal hydrides. For the analytic treatment of this model we refer the reader to the above mentioned paper by Richards.

We first consider the case of no particle interactions. For labeled particles we have two possible initial configurations. If the particle is near a vacancy it can hop at a rate \( v_v \), where \( v_v \) is the vacancy hopping rate. In the absence of a vacancy on one of the nearest neighbor sites the particle is restricted to its site for an average time \( 1/v_v c_v \), since \( v_v c_v \) is the mean rate at which a vacancy diffuses into the neighborhood of the particle. The frequency spectrum of the labeled particle motion would in this simple-minded picture have two components, one at zero frequency and a second at a frequency corresponding to the vacancy hopping rate \( v_v \). The zero frequency component is broadened on the order of \( v_v c_v \) due to the finite lifetime of the occupied site state, while the other component is motionally narrowed. The labeled particle, which had a vacancy on one of its nearest neighbor sites, will loose this environment favorable to jumping at a rate \( v_v \). This is the transition rate between the two environments considered: a vacancy on a neighboring site and no vacancies on neighboring sites. It also corresponds to the frequency separation of the two peaks of our labeled particle motional frequency spectrum. This observation and
standard stochastic theories lead to the conclusion that the two peak structure will merge into a single peak. The labeled particle will hop on the average at the frequency at which vacancies enter its neighborhood, $v_v c_v$. This rate corresponds to the standard mean field result. The vacancy motion is trivial for the monovacancy case and no interactions. The vacancy will hop at a rate $v_v$.

We now consider particle interactions and specialize to the case of infinite particle repulsion in the presence of a single vacancy and nonzero hopping rate when a second vacancy is on one of the neighboring sites thereby reducing the particle repulsions at the saddle point of the potential barrier. As a particle now only jumps in the presence of a vacancy pair a single vacancy cannot diffuse. The vacancy pair moves at a rate $v_v/2$, while the single vacancy motion gives rise to a peak in the frequency spectrum at zero frequency. The rate of transition between these two environments corresponds to the rate of arrival of a vacancy pair in the neighborhood of a single vacancy, $v_v c_v^2$. The rate at which a single vacancy-environment can be altered by a vacancy pair is therefore too small to produce a merger of the two frequency peaks and this gives rise to a nonmean-field type behavior. Based on our model a labeled particle will only hop in the presence of a vacancy pair. The vacancy pairs arrive in the neighborhood of a labeled particle at an average
rate $\nu_c c_v^2$, and the zero frequency component is therefore again lifetime broadened. The broadening is of the same order as the mean field particle hopping rate, $\nu_c c_v^2$. The hopping rate of a particle with a divacancy in its neighborhood is $\nu_v$, but the relative weight of the spectrum at this frequency is $c_v^2$. In the presence of particle interactions the labeled particle motion remains mean-field-like with a hopping rate corresponding to an average over the distribution of hopping rates. In contrast, the vacancy motion is nonmean-field like and the frequency spectrum consists of two peaks.

A more realistic model allows a particle with only a single vacancy in its neighborhood to jump at a nonzero rate $\nu'$. If $\nu'$ were on the order of $\nu_c c_v$ we would be back to the case where the two frequency peaks for vacancy motion can merge. A divacancy can now be broken up by a single vacancy at a rate $\nu_c c_v$, which corresponds to the mean field vacancy hopping rate. As long as $\nu' < \nu_c c_v$, vacancy hopping will display non-mean-field behavior. According to Richards, these two types of frequency spectrum for vacancies and labeled particles can lead to sizeable differences in the jump rate prefactors, on the order of $c_v Z$, where $Z$ gives the number of possible sites the particle or vacancy can reach in one step.
Quadrupolar Relaxation

Quadrupolar relaxation cannot in general be described by a simple exponential decay, corresponding to a single $T_1$. If the system can be characterized by a single spin temperature, we will also obtain a single $T_1$ for the spin-lattice relaxation process. This implies that the nuclear energy levels have to be equally spaced. In many cases any inequality in the spacing of the nuclear energy levels is smaller than the dipolar linewidth and the system can then again be assigned a single spin temperature. There are two cases of quadrupolar relaxation which are of greatest interest in the context of this study.

First we consider a stationary nuclear spin relaxing due to the fluctuating EFG’s generated by the mobile vacancies. For the fcc metal hydride $\text{ScH}_x$, the $^{45}\text{Sc}$ nuclei correspond to the stationary nuclei, and the EFG sources are the vacancies on the tetrahedral sublattice for nonstoichiometric compositions. The second case of interest is the quadrupolar relaxation of a mobile nucleus due to EFG’s produced by surrounding particles as well as by the motion of the mobile nuclear spins themselves.

For the case of dipolar relaxation all models discussed determine only the pair correlation functions and neglect three particle and higher correlation terms. For the case of
quadrupolar relaxation, three particle correlations have been shown by Barton^{43} to be of importance. The quadrupolar relaxation depends on the total EFG at the site of the relaxing nucleus and is determined by the radial and angular positions of the EFG sources. The three particle correlation function reflects the angular distribution of EFG sources around the relaxing nucleus.

We first discuss the above mentioned case of quadrupolar relaxation of a stationary nuclear spin. If we have very small vacancy concentrations the three particle correlations involving the stationary spin and two nearby vacancies can be neglected. In other words, the probability of occurrence of a divacancy configuration should be negligible. For vacancy concentrations \( c_v > 0.5 \) the three particle term will even become dominant, compared with pair correlation. In the monovacancy regime the exclusion of three particle terms will give accurate results and the spectral density functions could be taken over from the models for dipolar relaxation, if the gradients are due to an unscreened Coulomb potential \( V(r) \propto r^{-1} \). In the case of \( \text{ScH}_x \) we will most certainly have to include the electron screening. The effects of electron screening on quadrupolar relaxation have been discussed by Barton and Seymour.\(^{44}\) Comparison of the results for screened potentials and an unscreened Coulomb potential indicate that the screening not only decreases the depth of the \( T_1 \) minimum,
but also produces a shift of the position of the \( T_1 \) minimum towards lower temperatures. This shift towards lower temperatures becomes more pronounced with increasing hydrogen concentration. To make quantitative predictions, it would be necessary to have a detailed knowledge of the electronic band structure as a function of hydrogen concentration. The radial dependence of the lattice functions will be changed and would therefore force a recalculation of the correlation functions. To obtain accurate results for the effects of electron screening is thus not straightforward. The calculations for a free electron gas presented by Barton and Sholl seem to indicate a difference of at least 20\% in the value of \( \omega_0 \tau \), evaluated at the minimum of \( T_1 \).

Quadrupolar Relaxation of Deuterium

The tetrahedral sites of the \(^{2}D\) sublattice in a fcc deuteride possess cubic symmetry. Thus the average EFG experienced by the \(^{2}D\) nuclei is zero. At some instant in time the deuterium nuclei can have noncubic arrangements, as not all neighboring sites are occupied in a nonstochiometric sample. Obviously the motion of the \(^{2}D\) nuclei is only possible with the presence of vacancies. The EFG fluctuations experienced by the \(^{2}D\) during a jump due to the metal
nuclei can be ignored, if the time of flight is negligible compared with the dwell time.

Quadrupolar relaxation is dominant in the relaxation of the deuterons. The deuterium gyromagnetic ratio $\gamma_D$ is a factor of 6.5 smaller than for protons and dipolar interaction is nonsignificant. It is interesting to compare the features of the $T_1$ diffusion minimum for the $^1H$ and $^2D$ resonances. Barton and Seymour predict that the $T_1$ value at the minimum for deuterons in metal deuterides is approximately two orders of magnitude larger than the minimum $H-T_1$ value in the hydrides of corresponding composition. The temperature at which we observe the $T_1$ minimum is always lower for the deuterides.

Barton and Seymour emphasize that this should be particularly true in the fcc deuterides and hydrides, where the interstitials occupy the tetrahedral sites. We expect some differences between the $^1H$- and $^2D$- $T_1$ results on the basis of the isotope effect, but this can certainly not account for the effects described by Barton and Seymour. As indicated earlier, the three particle correlation functions can dominate over the pair correlation functions for concentrations above $c_D = 0.5$. Conduction electron screening reinforces some of the effects produced by three particle correlations. In particular, the position of the $T_1$ minimum will be shifted to a lower temperature as a consequence of
electron screening and this effect increases with the density of conduction electrons. Barton and Seymour applied the mean field approximation to obtain quantitative predictions. They used a free electron gas model and determine the depth and position of the $T_1$ minimum for several fcc deuterides.

Another approximation used to account for electron screening consists in cutting off the $r^{-1}$ Coulomb potential for distances larger than the nearest neighbor separation between nucleus and vacancy. This conceptually simple model still produces the same qualitative effects. The peculiarities of the specific conduction electron screening model chosen are thus of little importance. This gives us confidence in expecting similar effects for $\text{ScD}_x$, where the free electron gas presumably constitutes a poor approximation.

Conduction Electron Relaxation

The contact term in the hyperfine interaction of conduction electrons with the nuclear spin provides a rather effective relaxation mechanism. It can be shown that the electronic contribution to the relaxation time can be described by the Korringa relationship

$$T_{1e} T \propto N(\varepsilon_F).$$

[79]
$N(\varepsilon_F)$ is the density of electronic states at the Fermi level. During a nuclear transition an electron is scattered from some initial state of wave vector $k$ and spin orientation $s$, to some final state $k', s'$. The average kinetic energy of the electrons is much larger than the thermal energy $kT$. The change in kinetic energy during a mutual spin flip of electronic and nuclear spin is small, and therefore the Pauli principle predicts that only electrons close to the Fermi level can participate in this scattering process.
Fig. 4a: Block diagram of phase-coherent NMR spectrometer
Fig. 4b: Cross section of high temperature probe
[Not drawn to scale. Height of probe is roughly 13 in. and diameter is close to 2 in.]
PULSED MAGNETIC RESONANCE PROBE CIRCUITS

TAPPED PARALLEL TUNED ($f_0 \leq 20\text{MHz}$)

![Parallel Tuned Circuit Diagram]

TAPPED SERIES TUNED ($f_0 \leq 20\text{MHz}$)

![Series Tuned Circuit Diagram]

Fig. 5: RF matching circuits
DUPLExer using 2/4 coaxial cables and crossed diode switches

Fig. 6: Duplex circuit
Fig. 7: Quadrature Detection
The spin relaxation time measurements were made with a phase-coherent pulsed NMR spectrometer shown in Fig 4a. Operation at different frequencies involved only minor adjustments: retuning of the NMR probe and RF amplifier, exchange of quarter-wavelength cables connecting probe, receiver and transmitter and of the bandpass filters in the video amplifier. The RF coil and tank circuit were tuned to 50 Ω input impedance and 0° phase shift. A watercooled furnace allowed high temperature measurements extending up to 1400 K. The temperature was measured with a Pt/Pt-10%Rh thermocouple and controlled with a current feedback system. A digital pulse programmer with autoincrement circuit was used to generate the required pulse sequences. Several pulse sequences were used for the measurements: inversion recovery and saturation comb sequences for T₁ measurements, Hahn echo and Carr-Purcell-Meiboom-Gill (CPMG) sequences for T₂ measurements and spin-lock sequence for T₁p measurements. During most of the measurements we integrated the free induction decay (FID), sampled and digitized the peak value of the integrated signal and stored it in the memory of a multichannel signal averager. For the T₂ measurements
involving the CPMG pulse sequence the echo peak values were directly digitized. Spin relaxation times were determined by nonlinear least squares fitting of exponential curves to our data. In subsequent sections we will cover the spectrometer components and experimental techniques in more detail.

The NMR High Temperature Probe

For the measurements extending to close to 1200° C a high temperature probe was custom built. Figure 4b shows a cross section of the probe. A water jacket with an outer diameter of 44.5 mm and inner diameter of 35.5 mm, surrounded the high temperature furnace and coil assembly. The water jacket consisted of two concentric brass cylinders with grooves, allowing for the waterflow, forming a spiral on the outer surface of the inner brass cylinder. O-rings between the two brass cylinders at opposite ends prevented any water leaks. The outer brass cylinder touched the magnet pole faces and it was therefore important to prevent any heat up of the pole surfaces. A waterflow of 300 ml/min proved sufficient at all temperatures.

The furnace winding was made from nickel chromium alloy wire. Alumina beads were strung on the wire, which was then coiled noninductively. This was done by folding the wire
around its midpoint and then winding it on a cylindrical piece of wood. The surface of the heater coil formed by the threaded beads was coated with a layer of 'Sauereisen Electrotemp Cement No. 8'\textsuperscript{50} to give the furnace mechanical stiffness and rigidity. This cement has a very high dielectric strength and withstands thermal shock. After letting the cement dry, the outside of the heater was covered with 2 layers of 'Zirconia'\textsuperscript{51} felt, a commercial refractory fiber textile, which provided excellent thermal insulation between the brass cylinder and the furnace. The felt has a thermal conductivity of 0.14 W/mK at 1100° C. 'Zirconia' rigidizer was applied to the felt to give it stiffness. The furnace was cured in an oven by raising the oven-temperature by 30° C/hour to a maximum of 700° C, thereby incinerating the inner wood form. The curing process is very important, as it allows the organic binders in the rigidizer to escape. If the heating rate is too fast, the organic binders will carbonize, and this can lead to electrical shorts during later use of the furnace.

The RF coil was made out of #15 platinum wire. Platinum was chosen to avoid oxidation at high temperatures. The coil had about 17 turns and an inner diameter to accommodate 10 mm OD quartz tubes containing the polycrystalline samples.

The thermocouple was placed close to the bottom end of the RF coil. We used a Pt – Pt/10% Rh thermocouple with the
wires threaded through a 3 mm thick double bored alumina tube. On the outside of the probe the thermocouple wire was connected to 2 pF grounded capacitors to suppress the intrusion of RF noise into the probe. The furnace and the RF coil were held in place by pieces of aluminum silicate, machined to cylindrical shape, with two parallel holes for the coil legs and a center hole for the alumina tube with the thermocouple wires.

We initially experienced some problems, due to RF coupling between the furnace and RF coil. The wires connecting the furnace to the outside power supply were therefore shielded with wire braid and the wire braid was grounded. The elimination of ground loops was a rather lengthy process. A worthwhile future modification would be the insertion of a platinum foil between furnace and RF coil to eliminate RF coupling and create a more uniform temperature distribution. The furnace had a resistance of 9 Ω and was connected to a 1000 W DC power supply, which provided a maximum voltage of 75 V. A good regulator with low ripple factor is of importance.

The watercooled brass cylinder with coil and furnace inside were mounted on a tuning box containing resistors and tuning capacitors. The RF matching circuits were a parallel tuned circuit and a series tuned circuit for operation at 24 MHz and 12.2 MHz, respectively (Fig. 5). The circuit
components and load were tuned to an input impedance of 50Ω and 0° phase angle at the Larmor frequency. This matches the characteristic impedance of the coaxial cable leading to the probe and thus avoids reflections of signals. The tuning process was performed with a sweep generator and a 10 db directional coupler. One of the four ports of the coupler is terminated in $Z_0$, the impedance of the coaxial cable. The coupled path connects the probe and detector. This setup provided good isolation (10 db) between the RF output of the sweep generator and the diode detector. The demodulated output of the detector was fed to an oscilloscope.

The Q value of the RF probe gives the ratio of stored energy to the energy dissipated per cycle. An increase in Q value will improve the signal to noise ratio and decrease the frequency bandwidth of the probe. After an RF pulse has been absorbed by the probe, the resonant circuit will continue to oscillate until sufficient energy has been dissipated. This latter rate of energy dissipation is determined by Q. The same coil is used for transmission and reception and thus an increase in Q will lead to a lengthening of the ringdown time of the coil and saturation time of the receiver, preventing detection of the nuclear signal. The Q value of our probe was in the range of 10 to 20, which led to a maximum receiver dead time of approximately 15 to 20 μs in the frequency range 12.2 to 24. MHz. This ringdown and accompanying receiver
saturation did not constitute a serious problem in our experiments, and most of the information contained in the free induction decay (FID) was captured.

**NMR Signal Detection and Processing**

We now consider the network connecting the probe to the transmitter and receiver. The basic function of this circuit is to decouple the transmitter and receiver, while maintaining good contact between these components and the probe at appropriate times. This so called duplexer is realized with crossed diodes and quarter wavelength coaxial cables. The design used is similar to the one described by Lowe and Tarr and is shown in Fig [5]. The \( \lambda/4 \) cables act as an impedance transformer according to \( Z_i Z_o = |Z|^2 \), where \( Z_i \) and \( Z_o \) are the input and output impedance of the cable, and \( Z \) is the characteristic impedance of the coaxial cable. When the transmitter is on, the diode switches are conducting and the low impedance of the grounded diode switch is transformed to a high impedance by the \( \lambda/4 \) cable. If the probe is perfectly matched no RF energy will reach the receiver during the RF transmission phase. When the transmitter is off, it will be decoupled from the remaining circuit and a \( \lambda/2 \) length path now connects probe and receiver. The input impedance of the
transmission line as seen from the probe is simply equal to the receiver input impedance.

The receiver consists of preamplifier stages followed by a phase sensitive detector. The extremely fast recovery time receiver has been described by Adduci et al. Its building blocks are wideband limiting amplifiers, which do not saturate from overload, but only clip the signal. These amplifier stages are interconnected by bandpass filters. The maximum receiver recovery time is 2 μsec. The amplified RF signal is then led to the phase sensitive detector. This quadrature demodulator transforms the incoming signal to an intermediate frequency (IF) as in a heterodyne receiver. A double balanced mixer or multiplier heterodynes the input signal with a ω₀+30MHz reference. A power divider rejects the upper band signal and splits the lower band input into two in-phase signals of equal amplitude and 30 MHz IF. These intermediate frequency signals are now mixed with two quadrature 30 MHz references, respectively. The two 30 MHz quadrature references are produced by a 90° hybrid. We thus obtain two demodulated in quadrature signals as output, which represent the FID as seen along 2 perpendicular axes in the rotating frame. The upper band signals of frequency 30 + 30 MHz are discarded. The bandwidth and gain of the receiver can be adjusted manually.
In most experiments we integrated the FID and digitized the integrated signal. The digitized signal was stored in consecutive memory locations of a 'Nicolet' signal averager. The data could then be transferred to a 'Digital Equipment Corporation' PDP-11 computer and processed.

For the $T_1$ measurements we used the inversion recovery sequence and in some cases the saturation comb sequence. For the $T_2$ measurements the CPMG and Hahn echo sequence were applied. The microprocessor controlled pulse programmer is capable of generating a large variety of NMR pulse sequences involving up to four channels. The pulse sequences are entered through a video terminal using a simple special purpose programming language. The programming language provides an auto timebase advance function to facilitate automatic relaxation time measurements. The pulse programmer has an internal 30 MHz quartz oscillator, which is used as reference throughout the system. Pulse length and repetition times for the pulse sequences are adjusted with manual controls. The RF switch allows for the adjustment of the relative phases of the four RF channels.

The radio frequency signal was generated by a frequency synthesizer, whose output was fed to the RF switch. The RF switch which is under control of the pulse programmer outputs the RF pulses to a gated amplifier. The gating signal originates from the pulse programmer. The transmitter was
able to deliver approximately 1 kW of rf power into a 50 Ω load.

The Magnet

The static magnetic field was produced by a 'Varian Associates' electromagnet, which could reach a maximum field strength of approximately 2.4 T. The magnetic field was stabilized by a Hall Effect regulator leading to a temporal stability of the magnet of about 1 in 10^5 per hour. The field homogeneity over a typical sample volume is 1 in 10^6.

Temperature Control

The thermocouple was connected to a 'Leeds and Northrup' 7553-5 Type K-3 potentiometer whose potentiometer balance was monitored by a null detector with feedback to the furnace power supply. The Pt/Pt-10%Rh thermocouple was placed as close as possible to the bottom of the RF coil holding the sample tube without causing arcing. Due to the relatively large temperature gradients, it was necessary to calibrate the thermocouple by inserting a dummy sample tube, with a second thermocouple inside, into the RF coil. All data presented in
this study have been properly corrected to account for this temperature difference. It is interesting to note that the temperature difference recorded is nearly negligible at the highest temperatures above 1200 K and obviously around room temperature. In the intermediate region we noticed a rather large difference of up to 23 K. The thermal conductivity of the samples seems large enough to greatly reduce any temperature inhomogeneity within the sample itself.

Data Processing

Based on phenomenological arguments Bloch proposed the following equations for the nuclear magnetization

\[ \frac{dM}{dt} = \gamma M \times H - \frac{(M_x i' + M_y j')}{T_2} - \frac{(M_z - M_0)}{T_1}, \]  

[80]

where \( M_0 \) is the magnetization at equilibrium. According to this equation the magnetization follows an exponential law during relaxation. For the \( T_1 \) measurements we thus used the following equation to fit the data

\[ M_z(t) = M_0[1 - xM_0 \exp(-t/T_1)], \]  

[81]
where \( \chi \leq 2 \) for an inversion recovery and \( \chi \leq 1 \) for a saturation comb pulse sequence. The upper bounds on \( \chi \) correspond to the ideal case of complete inversion or saturation. We used an iterative nonlinear least squares fit to the above function or a combination of several exponentials, when the presence of several relaxation processes was tested for. The fitting procedure follows closely the algorithms outlined by Bevington. We feel that this approach is more reliable than taking the logarithm of the magnetization and fitting the data to a straight line. First of all, this only works for a single exponential and secondly it assumes an accurate knowledge of \( M_0 \) and \( \chi \), necessary for a good fit.

For the \( T_2 \) data the FID, as determined by the CPMG method, was fit by a very similar method. At high temperatures, where we expect fast diffusion, the presence of magnetic field gradients at the surface of the hydride grains produces a significant loss of phase coherence not related to the field inhomogeneity. The time interval \( \tau \) between consecutive 180° pulses of the CPMG sequence was changed to extrapolate the value of \( T_2 \) for \( \tau = 0 \). We thus eliminated this contribution to the spin-spin relaxation rate due to random magnetic field gradients in the polycrystalline sample. It vanishes for \( \tau = 0 \) as can be seen from the following expression

\[
\frac{1}{T_{2D}} = \left( \frac{1}{3} \right) D \gamma^2 G^2 \tau^2 ,
\]  

[82]
where $D$ is the diffusion constant and the average $G$ the gradient strength. The extrapolation was made by plotting $T_2$ versus $\tau^2$ and determining the intercept with the $T_2$ axis.

Sample Preparation

The scandium hydrides, scandium deuterides and samples of mixed composition ($25\% {^1}\text{H}, 75\% {^2}\text{D}$) were prepared B. J. Beaudry and A. Johnson in the Ames Laboratory. Most of the samples used for our measurements were prepared by B. J. Beaudry and we will describe his preparation method first. The Ames Laboratory metal of very high purity was first analyzed by spark source mass spectrometry, which confirmed the negligible impurity contents. The level of paramagnetic impurities was in the region of a few parts per million. The metal was carefully electropolished and placed in a standard high vacuum system, which was evacuated to a pressure of $2\times10^{-1}$ Torr. A known volume was filled with hydrogen and/or deuterium, purified by a Pd sieve. The metal was heated to $670^\circ \text{C}$ for high composition samples ($2.0 < x < 1.9$) and to $780^\circ \text{C}$ for lower compositions. Next the metal was exposed to the hydrogen and/or deuterium gas and the system was allowed to reach equilibrium for up to 12 hours. The existence of some back pressure at the end of this process eliminates the
possible formation of a mixed phased sample, with one phase being the dihydride phase in an outer layer of the metal piece. Any residual pressure after cooling was carefully measured and figured into the final composition. The rather brittle sample was afterwards crushed in a mortar in a helium filled drybox, sieved through a 200 mesh sieve and sealed in quartz tubes. The particle size was large enough to completely rule out effects due to bounded diffusion on the NMR data, though small enough to guarantee complete RF penetration of the grains. For the samples prepared by A. Johnson the metal was exposed in a high pressure, high vacuum system to hydrogen at a known gas pressure and temperature. The hydrogen contents was determined after hydriding by extracting the hydrogen from a known amount of sample powder.
SC SPIN–LATTICE RELAXATION TIME

SAMPLE: SCD 1.99 (#33)

Fig. 8: $^{45}$Sc spin-lattice relaxation times for SCD 1.99
Fig. 9: $^{45}$Sc spin-lattice relaxation times for ScH 1.82
Fig. 10: $^{45}$Sc spin-lattice relaxation times for ScD 1.81
SC SPIN–LATTICE RELAXATION TIME

SAMPLE: SCH 1.64 (#28)

Fig. 11: $^{45}$Sc spin–lattice relaxation times for Sch 1.64 [The actual dihydride-phase sample composition is estimated at H/Sc=1.75.]
Fig. 12: Nonlinear least squares fit of BPP function and Korringa term to Sc-T₁ data
Fig. 13: Nonlinear least squares fit to experimental Sc-T<sub>1</sub> data for ScD 1.81
SC–T1 FOR SCD 1.98 (#234)

LARMOR FREQ.: 12.2 MHZ

Fig. 14: Nonlinear least squares fit to experimental Sc–T1 data for ScD 1.98
MAXIMUM QUADRUPOLAR RELAXATION RATE
for ScH \( x \) and ScD \( x (2-x = 2c) \) at 24 MHz

![Graph showing the maximum quadrupolar relaxation rate as a function of vacancy concentration. The graph includes data points for hydrides and deuterides, with a line representing the theoretical curve.]

Fig. 15: Maximum quadrupolar relaxation rate
LOW AND INTERMEDIATE TEMPERATURE RESULTS

The spin-lattice relaxation rates were measured for $^{45}$Sc, $^1$H and $^2$D in scandium hydrides, scandium deuterides and samples of mixed composition (75% $^2$D, 25% $^1$H) at Larmor frequencies of 12.2 MHz and 24.0 MHz. Most measurements were made in the temperature range from room temperature to approximately 1170 K. The $^{45}$Sc and $^1$H $T_1$ measurements were also in a few cases extended to low temperatures to determine the Korringa constant $T_{1eT}$. For the hydrides we made $^1$H-$T_2$ measurements from a temperature in the vicinity of the $^1$H-$T_1$ minimum at the same Larmor frequency to approximately 1170 K.

We will first concentrate on the low and intermediate temperature results and discuss the measurements at high temperatures ($> 800$ K) in a subsequent chapter.

$^{45}$Sc-$T_1$ Results

The relaxation rates of the metal nucleus provide the opportunity to study the vacancy motion when the dominant relaxation mechanism is given by fluctuations of the quadrupolar interaction. The quadrupolar spin relaxation
depends on the probabilities of occurrence for different vacancy configurations. The fluctuations of the EFG at the site of the metal nucleus are due to changes in the vacancy distribution on neighboring tetrahedral sites. The restriction to nearest neighbor sites seems reasonable in view of the strong electron screening present in a metallic conductor.

Figs. [8-11] show some of the Sc-T\(_1\) results for scandium-deuterides and -hydrides. The quadrupolar Sc-T\(_1\) minimum reflecting the vacancy motion is clearly visible for all samples, which is a consequence of the relatively weak conduction electron relaxation. It was therefore not necessary to measure T\(_{1p}\). The comparatively large values of the Korringa constant for the group III transition metals turned out to be an advantageous property for the present study. It is the quadrupolar relaxation which provides insight into the vacancy motion while the conduction electron relaxation is insensitive to diffusion.

We will attempt to analyze the main features of the BPP-type \(^{45}\)Sc-T\(_1\) minimum induced by vacancy diffusion. When we try to calculate the \(^{45}\)Sc quadrupolar relaxation rate we face several uncertainties. The correlation functions should ideally include the effects of electron screening, particle interactions, three particle correlations and the presence of divacancies on the relaxation process. To the author's
knowledge, no model has been presented in the literature which accounts for all of these aspects, but they are expected to be important for the present study. We point out as an example that divacancies produce in most cases a nonaxially symmetric EFG at the site of the metal nucleus. The additional terms in the quadrupolar Hamiltonian increase the complexity of the mathematical expressions significantly. As a consequence the contributions from nondiagonal elements of the EFG tensor are ignored in nearly all calculations of the particle pair correlation functions in favor of the simpler case of axial symmetry. It is therefore necessary to start with a simple model and estimate later the corrections due to features neglected in the model. In view of these uncertainties, the BPP model seems to be a good starting point to analyze our results. We initially assume the EFG to be axially symmetric and thereby limit our calculations to the monovacancy case. Electron screening is accounted for in a rudimentary way by substituting for the charge e of a vacancy an effective charge Z'e, discarding the change in radial dependence of the quadrupolar lattice functions. For a polycrystalline sample we would thus obtain in a first approximation \[ R_{1Q} = \frac{3\pi^2}{20} \frac{2I + 3}{I^2(2I-1)} \frac{c_v}{h^2} \left( \frac{Z'e^2qQ}{h^2} \right)^2 \left[ \frac{y}{1 + y^2} + \frac{4y}{1 + 4y^2} \right] . \]
with $y = \omega \tau_v$. The quadrupole moment for $^{45}\text{Sc}$ is $0.22 \times 10^{-24} \text{cm}^2$ and $I = 7/2$. The vacancy jump rate $\tau_v^{-1}$ is assumed to follow an Arrhenius relationship $\tau = \tau_0 \exp(E_a/kT)$. A fitting procedure showed good agreement of this model with the experimental results only on the low temperature side and in the vicinity of the $T_1$-minimum of the BPP curve. Figs. [12-14] show the experimental data on the low temperature side of the Sc-$T_1$ minimum and the curve produced by a BPP function and a Korringa term which were fit to the experimental data. The activation energy $E_a$ and jump-attempt frequency are variable parameters, while the depth of the minimum $T_1|_{\text{min}}$, the Larmor frequency $\nu_L$ and Korringa constant $T_1eT$ were provided as input parameters and kept fixed. It is not possible to determine the vacancy concentration $c_v$, the effective charge $Z'e$, or the component $e\gamma$ of the field gradient tensor separately. This fitting procedure just determines the combination of these values as they enter into the prefactor in Eq. 84.

The width of the $\ln(T_1)$ versus $T^{-1}$ minimum is wider than expected for a BPP type $T_1$ minimum as described by the above equation. Notice in figs. [12-14] that the experimental Sc-$T_1$ data for the samples with high vacancy concentrations do not follow the BPP curve as it turns up after going through its minimum $T_1$ value. On the high temperature side of the $\ln(T_1)$ minimum the experimental data have for high vacancy concentrations ($c_v \geq 0.1$) a substantially smaller slope than
on the low temperature side. Only for low vacancy concentrations \((c_v = 0.05)\) do the experimental data yield a symmetric minimum as expected from the BPP model. The frequency dependence of the \(\ln(T_1)\) versus \(T^{-1}\) minimum follows a \(\omega_0^2\) dependence on the low temperature side of the minimum, as predicted by the BPP model. At the minimum itself the \(T_1\) values show a frequency dependence which is weaker than \(\omega_0\) and therefore not in complete agreement with the BPP model. If we denote the frequency dependence of \(T_1|_{\text{min}}\) by \(\omega_0^x\) we obtain values of \(x\) ranging from 0.3 to 1.0. For the scandium hydrides the values of \(x\) closer to 1 coincide with the higher hydrogen concentrations.

**Depth of Sc-\(T_1\) Minimum**

The maximum \(^{45}\text{Sc}\) relaxation rate, \(R_1|_{\text{max}} = (T_1|_{\text{min}})^{-1}\), does not seem to follow the expected linear dependence on vacancy concentration \(c_v\). Fig. 15 shows the dependence of \(R_1|_{\text{max}}\) on the vacancy concentration of the sample for a Larmor frequency of 24.0 MHz. The scandium hydride with a nominal composition of 1.64 was assumed to have a dihydride composition close to the phase boundary between the mixed phase and dihydride phase, which corresponds roughly to \(H/\text{Sc} = 1.75\) \((c_v=0.125)\). An expression for the theoretical curve
shown in the Fig. 15 will be derived below. For both scandium hydrides and deuterides the maximum value of the relaxation rate increases very rapidly in the range of vacancy concentrations from \( c_v = 0 \) to 0.02. The data points are not sufficient to confirm a linear dependence on \( c_v \) in this region. The maximum relaxation rate does not increase much further for vacancy concentrations above 0.02 and in the case of the hydrides seems to show a small gradual decrease for large vacancy concentrations. This saturation of the maximum relaxation rate with concentration is not in agreement with the predictions of Eq. 84.

It is interesting to recall the calculations of the EFG for different vacancy configurations to explain this behavior of \( R_{1Q} \max \). For a transition from a divacancy to a monovacancy we have for the most probable divacancy configurations (in 86% of all divacancy to monovacancy transitions) only a change in the asymmetry parameter from \( \eta = 1 \) to \( \eta = 0 \). The transition from a divacancy to a monovacancy configuration thus produces on the average a considerably smaller EFG fluctuation than the appearance of a monovacancy in a previously undisturbed environment of cubic symmetry. The creation of a divacancy involves two vacancies but seems to make a less effective contribution to the spin relaxation than a monovacancy. On the basis of this comparison, we should therefore not expect a linear increase of \( R_{1Q} \) beyond
the monovacancy regime. If the vacancies do not interact and are distributed randomly over the lattice our calculations showed that for a vacancy concentration of $c_v = 0.1$ the ratio of monovacancies to divacancies reaches 2.5. The probability of occurrence of mono- and di-vacancies becomes equal at about $c_v=0.22$ vacancy concentration. This raises the obvious question why we observe the saturation behavior of $R_{1Q}\max$ already for vacancy concentrations in the neighborhood of $c_v=0.02$. One possible reason could be that vacancies do not occur at random and experience an attractive interaction favoring the formation of vacancy pairs. This seems to be consistent with the model proposed by Richards\(^\text{57}\) to explain the observed labeled particle jump frequency prefactors for scandium hydrides. We recall that Richards considers classical hopping of interacting particles on a lattice and concludes that strong repulsions between particles at the saddle point make hopping to a vacant site unfavorable unless there is a another vacancy nearby. In this model, vacancy pairs stay bound together to lowest order in $c_v$. In the case of very strong repulsion a single vacancy cannot diffuse without a neighboring vacancy and vacancy pairs can only be broken up by another vacancy pair. It seems that in this model the formation of vacancy pairs is a highly favored event. Divacancies give rise to the following set of transitions. A divacancy changes over to another divacancy.
configuration with no change in $\epsilon g$ and $\eta$. This causes only a change in the orientation of the principal axis system of the EFG. A simple estimate indicates that the reorientation of the principal axis system leads to a relatively small change in the quadrupolar interaction energy and thus a relatively weak contribution to the relaxation process. If one of the vacancies jumps away this will give a divacancy to monovacancy transition which produces in most cases a change in the asymmetry parameter of the EFG, while $\epsilon g$ stays constant. Finally for a small number of jumps we can observe a divacancy to divacancy transition which involves a change in both $\epsilon g$ and the asymmetry parameter. In this case, in the starting or final divacancy configurations the vacancies sit at opposite ends of a cube body diagonal. This is the least probable of the above transitions involving divacancies. All these types of events produce only a fractional change of the quadrupolar interaction energy. In contrast, the creation of a single vacancy produces a large (100%) change in the quadrupolar interaction energy on the same scale. The motion of a single vacancy is therefore the most effective relaxation mechanism.

We will try now to obtain more quantitative results starting from a model proposed by Seymour. The transitions between divacancy configurations, where $\eta$ and $\epsilon g$ stay constant, can be compared with the case of a rotating molecule with an internal EFG at the site of some select nucleus in the
molecule. The EFG principle axis system is fixed with respect to the molecule. In a liquid the rapid rotational motion of the molecule will produce quadrupolar relaxation of the specific nucleus in the molecule. During the rotational motion the EFG components $e_q$ and $\eta$ remain constant while the angles, characterizing the principle axis system with respect to the laboratory frame, will change with the molecular reorientation. This picture is completely equivalent to the case of divacancy to divacancy transitions if we ignore the divacancy configuration with $\eta=0$. The later divacancy arrangement only occurs with a probability of 0.14.

Transitions between monovacancy configurations can be pictured in an analogous way. Quadrupolar relaxation of a molecule with internal EFG in a liquid through molecular reorientation has been treated by Abragam. An exponential relaxation process will only exist for this model in the case of extreme narrowing and/or for spin $I=1$. Under either of these circumstances it is found that

$$T_{1Q}^{-1} = \left(3/80\right) \left(1 + \eta^2/3\right) \left(e^{2qO/h}\right)^2 \left[J(\omega_o) + 4J(2\omega_o)\right].$$

Notice that the combination of spectral density functions $J(\omega_o)$ is the same as in the simpler monovacancy case using the BPP approximation. This latter equation covers the case of transition from monovacancies to an environment of cubic
symmetry and vice versa. For the case $I=7/2$ it had been shown before to be of the form

$$T_1Q^{-1} = c_v \left(3\pi^2/49\omega_o\right) (Z'e^2qQ/h)^2 \left[J(\omega_o) + 4J(2\omega_o)\right].$$

The only remaining events comprise transitions between monovacancies and divacancy configurations where $\eta$ changes between $\eta=1$ and $\eta=0$ occur. As a rough approximation we still use the model of molecular reorientation and take the average of the values 1 and 4/3 for the prefactor $(1 + \eta^2/3)$, say 7/6. We are effectively neglecting the change in $\eta$. If the motion has random character the correlation times $\tau_c$ will be identical for these different classes of transitions. We will now calculate the transition rates between the different configurations.

Each particle has a clock which randomly sets off a jump attempt. The distribution of waiting times between jump attempts is given by a Poisson distribution. When a particle attempts a jump to a nearest neighbor site, it will be successful if the site is not blocked by another particle. To make further progress we need to determine the conditional probabilities $P^1(j|i)$ of having $j$ vacancies on the 8 cube vertices, given $i$ vacancies before a jump attempt of a vacancy took place. As the two configurations with $i$ and $j$ vacancies respectively are connected by one jump attempt we must have
\( j = i, i+1 \). For \( j = i \) the jump attempt was unsuccessful or one vacancy just changes its position with a particle on the same cube. To determine the one-step transition probabilities we not only need to know the initial distribution of vacancies on the eight cube sites but also the configuration of vacancies on the surrounding next-nearest-neighbor sites which can be reached by one jump from the 8 nearest neighbor sites. The enormous number of possible configurations on this shell of 24 next-nearest neighbor (n.n.n.) sites complicates the problem considerably. For a given number \( i \) of vacancies on the 8 cube sites the total number of possible configurations is given by:

\[
B(8,i) \{ \sum_j B(24,j) \} ; \quad 0 \leq j \leq 24 .
\]

The function \( B(j,i) \) represents the binomial coefficient \( 8!/i!(8-i)! \). Eventually we want to take an average over these possible vacancy configurations of the outer n.n.n. shell to calculate \( P^1(j|i) \). Thus the only method of tackling this problem consists in accounting for the large number of n.n.n. configurations in an average way. For the conditional transition probabilities \( P^1(i|j) \) with \( i = j \) we would like to exclude those events which represent an unsuccessful jump attempt. They are of no importance to the spin relaxation process. For the sake of simplicity keep them in \( P^1(i|i) \) and thereby introduce an error on the order of \( P_8(i) \) for \( P^1(i|i) \),
where \( i \) gives the number of vacancies on the 8 cube sites. \( P_g(i) \) is the probability of finding \( i \) vacancies on the 8 vertices. As \( i > 1 \) this error will not be too serious. The one-step transition probability \( P^1(i \rightarrow j) \) of observing a transition from an \( i \)-vacancy to a \( j \)-vacancy configuration is defined as

\[
P^1(i \rightarrow j) = P_g(i) \ P^1(j|i).
\]

Consider all transition probabilities for transitions whose final configuration has \( i \) vacancies. We must have

\[
P^1(i-1 \rightarrow i) + P^1(i+1 \rightarrow i) + P^1(i \rightarrow i) = P_g(i).
\]

The right hand side of this equation just gives the probability of occurrence for the final configuration with \( i \) vacancies. We will only consider configurations with less than 3 vacancies and therefore neglect transitions such as \( 2 \rightarrow 3 \). Trivacancies occur only very seldom for the range of compositions considered.

\[
P_g(2) = P^1(1 \rightarrow 2) + P^1(2 \rightarrow 2)
\]

In this equation we neglected \( P^1(3 \rightarrow 2) \) as just explained. A jump attempt will be successful if the site the particle tries
to reach is vacant. The conditional probability $P^1(1|0)$
equals in a mean field approximation $c_v$, and

$$P^1(0\to1) = P_0(0)c_v$$

We treat the transitions $1\to2$, $2\to2$, $1\to1$ and $2\to1$ all as simple
reorientations of the EFG principal axis system and use an
average value of 1.1 for $(1+\eta^2/3)$. The change between $\eta=0$ and
$\eta=1$ for some of these transitions constitutes an additional
change of the EFG which is neglected. Finally the assumption
of a steady state, $P^1(i\to j) = P^1(j\to i)$, implies for $P^1(1\to0)$

$$P^1(1\to0) = P_0(0)c_v .$$

We shall use the following abbreviation in our equation for
the quadrupolar relaxation rate:

$$R_{1Q}^0 = (1/\omega_o) (Ze^2qQ/h)^2 \{ J(\omega_o) + 4J(2\omega_o) \}$$

The quadrupolar relaxation due to the different transitions
can then be written as

$$R_{1Q} = \{(3\pi^2/49) [P^1(0\to1) + P^1(1\to0)] +
3/80 (1 + \eta^2/3) [P^1(1\to1) + P^1(1\to2) + P^1(2\to2) + P^1(2\to1)]\} R_{1Q}^0.$$
Using the above approximations for the transition probabilities we finally obtain

\[ R_{1Q} = \{3\pi^2/49 \ 2 P_8(0)c_v + 3/80 \ 1.1 (P_8(1) + P_8(2) - \ P_8(0)c_v)\} R^0_{1Q}. \]

The curve in Fig. 15 illustrates the behavior of the above equation. The value of \( R^0_{1Q} \) was chosen to adjust the maximum of the curve appropriately to the largest experimental value of \( R_{1Q}\mid_{\text{max}} \). The prefactor of \( R^0_{1Q} \) in the above equation reaches 50% of its saturation value at a vacancy concentration of \( c_v = 0.03 \) and saturates rapidly afterwards. It shows a weak maximum around a vacancy concentration of \( c_v = 0.13 \). Our experimental values for \( R_{1\mid_{\text{max}}} \) saturate more rapidly than predicted by the above equation. This might be an indication, as mentioned earlier, that the occurrence of divacancies is favored. We estimate the compositions \( ^1H/^{45}\text{Sc} (^{2}D/^{45}\text{Sc}) \) of the hydrides (deuterides) as determined during sample preparation to be uncertain by as much as 2%. This means that vacancy concentrations might deviate from their nominal values by as much as 200%! It seems that under these circumstances the above approximation to \( R_{1\mid_{\text{max}}} \) is adequate. Our result has to be contrasted with the prediction for the monovacancy regime where \( R_{1\mid_{\text{max}}} \) varies linearly with vacancy concentration. According to our approximation we expect a
linear dependence for vacancy concentrations up to 3% while the experimental results limit this range to 1% vacancy concentration. For higher vacancy concentrations the monovacancy approximation seems to be in serious disagreement with the experimental results.

**Asymmetry of Sc-\(T_1\) Minimum**

One of the most apparent features of the \(T_1\) minimum is the asymmetry of the \(\ln(\text{Sc-}T_1)\) versus \(T^{-1}\) curve for high vacancy concentrations. For the asymmetric \(T_1\) minima we observe a steeper slope on the low temperature side of the \(T_1\) minimum than on the high temperature side. This effect is nearly absent for very low vacancy concentrations. For the deuterides and hydrides we obtain a 50% decrease in the activation energy in going from the low temperature side of the \(\ln(\text{Sc-}T_1)\) minimum to the high temperature side for vacancy concentrations from \(c_v=0.1\) to \(c_v=0.2\). A model which produces an asymmetric \(\ln(T_1)\) minimum has been presented by Walstedt et al.\(^{59}\) Introducing a distribution of activation energies produces an asymmetric \(\ln(T_1)\) versus \(T^{-1}\) minimum whose slope is steeper on the high temperature side of the minimum than on the low temperature side. Walstedt et al. used Gaussian and Lorentzian distributions of activation energy and the
asymmetry is very similar in both cases. Our observation of a smaller rather than larger activation energy on the high temperature side of the minimum is in contradiction to the results of Walstedt et al. for a distribution of barrier heights. For almost any type of distribution of activation energies we expect the larger activation energies to become more relevant at higher temperatures leading to a steeper slope on the high temperature side of the $T_1$ minimum. Let the distribution of barrier heights $U$ be given by $G(U)$ and its width be characterized by $\Delta U$. The effective activation energies derived from $T_1$ measurements would approximately be given by

$$E_a \propto \ln\left[ \int \frac{dU}{\Delta U} G(U) \exp(-U/kT) \right]$$

for the case of slow motion ($\omega_0\tau >> 1$), and

$$E_a \propto \ln\left[ \int \frac{dU}{\Delta U} G(U) \exp(U/kT) \right]$$

for the case of fast motion ($\omega_0\tau << 1$). On the low temperature side of the $T_1$ minimum the activation energy is weighted by $\exp(-U/kT)$ towards lower values of barrier height for a given temperature. On the high temperature side of the $T_1$ minimum ($\omega_0\tau << 1$) the effective activation energy will be larger than the average barrier height due to the exponential
factor $\exp(U/kT)$. The variations in barrier height observed by Walstedt et al. are attributed to a distribution of defects in the sample.

A rather simple minded interpretation would describe this lower activation energy on the high temperature side of the $T_1$ minimum as a precursor effect of the anomalous decrease of $\text{Sc-T}_1$ at very high temperatures. A new source of spin-lattice relaxation, dominant above 1000 K producing a second high temperature $\text{Sc-T}_1$ minimum causes a depression of the $\text{Sc-T}_1$ values on the high temperature side of the first minimum, while being negligible on its low temperature side. This raises the question as to why the asymmetry of the $\text{Sc-T}_1$ minimum is only observed for samples with higher vacancy concentrations, although the second high temperature $\text{Sc-T}_1$ minimum is observed to the same degree for all vacancy concentrations. We note here that the high temperature minimum of $T_1$ is not due to conduction electron relaxation, which is much too weak to produce this kind of behavior. We will assume that at high temperatures Frenkel pair defects increase the number of vacancies on the tetrahedral sublattice. A justification will be given later when we discuss the second $T_1$ minimum at high temperatures. The vacancy concentration will become temperature dependent, and a plausible choice for its temperature dependence would be a Boltzmann factor,
$c_V(T) = c_V + c_H \exp(-E_D/kT)$,

where $E_D$ is the energy necessary to create a Frenkel pair defect. On the high temperature side of the conventional $T_1$ minimum ($\omega_0 T_v << 1$) the spin-lattice relaxation follows the following asymptotic behavior

$$T_1^{-1} \propto c_V \exp(E_a/kT) + c_H \exp\left[-(E_D + E_a)/kT\right].$$

On the low temperature side ($\omega_0 T_v >> 1$) an equivalent expression can be written down

$$T_1^{-1} \propto \omega_0^{-2} \left[c_V + c_H \exp(-E_D/kT)\right] \exp(-E_a/kT).$$

As can be seen from these two equations the $T_1$ minimum should be asymmetric with a reduced slope on the high temperature side of the minimum. This corresponds to the behavior observed for the $Sc-T_1$ curves. The absence of asymmetry in the case of low vacancy concentration could simply be interpreted as a vacancy concentration dependence of the Frenkel pair formation energy. For the sake of consistency with our experimental results $E_D$ should increase with decreasing vacancy concentration meaning that it is easier to create a Frenkel pair defect in the presence of vacancies. The symmetry of the $T_1$ minimum at low vacancy concentration...
concentrations leads us to conclude that $E_D/kT \gg 1$ for these samples over the temperature range covered by the first $Sc-T_1$ minimum. The location of the site occupied by the Frenkel pair ion can only be guessed. We assume that the Frenkel pair vacancies are indistinguishable from the vacancies existing due to the nonstoichiometry of the sample and thus produce the same type of EFG at the site of the Sc nucleus. The absence of asymmetry for the $1H-T_1$ can be explained by the relative insensitivity of the dipolar relaxation rates to small changes in vacancy concentration for $c_v \ll c_H$. We attempted a nonlinear least squares fit of our $Sc-T_1$ data for $ScH_{1.64}$ using the above approximation for the temperature dependent vacancy concentration but obtained very small ($E_D=0.06$ eV for $ScH_{1.64}$) and unrealistic values for the Frenkel pair formation energy $E_D$. We are led to conclude that the exponential represents an incorrect choice of function describing the increase in vacancy concentration associated with the formation of Frenkel defects.

In summary we can say that there exists no experimental evidence for a distribution of activation energies. It would lead to the wrong kind of asymmetry. A plausible interpretation could possibly be given if we assume that the vacancy concentration increases with temperature due to the formation of Frenkel defects. This growth in the number of vacancies should be negligible for low vacancy concentrations.
as we observe a symmetric Sc-T\textsubscript{1} minimum for those compositions.

**Sc-T\textsubscript{1} Activation Energies**

To analyze the change of activation energy with composition we will concentrate on the low temperature side of the T\textsubscript{1} minimum. A decrease of activation energy occurs with decreasing vacancy concentration. The activation energy ranges from \( E_a = 0.8 \text{eV} \) at \( c_v = 0.095 \) to \( \approx 0.6 \text{eV} \) at \( c_v = 0.005 \) in the deuterides. For the hydrides \( E_a \) ranges from 0.7 eV to approximately 0.5 eV over the same range of compositions. It is evident from Figs. [16-17] that the decrease of activation energy becomes rather pronounced for very low vacancy concentrations \( (c_v \leq 0.02) \). The slightly lower activation energies for the hydrides can at least partially be accounted for by the difference in zero point vibration energies for hydrogen and deuterium atoms. The behavior of the activation energy for ScH\textsubscript{x} and ScD\textsubscript{x} is comparable with that observed for YH\textsubscript{2-x} and LaH\textsubscript{2+x}, where the decrease is even more pronounced. These hydrides form a trihydride phase and the lowering of the activation energy with increasing hydrogen concentration coincides with the increasing ability of the protons to occupy the octahedral sites of the fcc lattice. As indicated earlier
Fig. 16: Activation energies for scandium hydrides [The actual dihydride phase sample composition of ScH 1.64 is estimated at H/Sc=1.75.]
Fig. 17: Activation energies for scandium deuterides
Table 1. Activation energies $E_a$ and jump-attempt frequencies $\nu_o$ determined by a nonlinear least squares fit of BPP function and Korringa term to Sc-$T_1$ data

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample</th>
<th>$\nu_L$ [MHz]</th>
<th>$E_a$ [eV]</th>
<th>$\nu_o$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScD 1.99</td>
<td>#33</td>
<td>12.2</td>
<td>0.56</td>
<td>$3.4 \times 10^{14}$</td>
</tr>
<tr>
<td>ScD 1.98</td>
<td>#234</td>
<td>12.2</td>
<td>0.67</td>
<td>$1.9 \times 10^{14}$</td>
</tr>
<tr>
<td>ScD 1.95</td>
<td>#239</td>
<td>12.2</td>
<td>0.73</td>
<td>$8.8 \times 10^{14}$</td>
</tr>
<tr>
<td>ScD 1.91</td>
<td>#238</td>
<td>12.2</td>
<td>0.71</td>
<td>$6.0 \times 10^{14}$</td>
</tr>
<tr>
<td>ScD 1.88</td>
<td>#32</td>
<td>24.0</td>
<td>0.74</td>
<td>$8.2 \times 10^{14}$</td>
</tr>
<tr>
<td>ScD 1.88</td>
<td>#231</td>
<td>12.2</td>
<td>0.72</td>
<td>$4.6 \times 10^{14}$</td>
</tr>
<tr>
<td>ScD 1.82</td>
<td>#230</td>
<td>12.2</td>
<td>0.73</td>
<td>$4.7 \times 10^{14}$</td>
</tr>
<tr>
<td>ScD 1.81</td>
<td>'Neutron'</td>
<td>12.2</td>
<td>0.73</td>
<td>$2.1 \times 10^{16}$</td>
</tr>
<tr>
<td>ScD 1.81</td>
<td>'Neutron'</td>
<td>24.0</td>
<td>0.82</td>
<td>$6.8 \times 10^{15}$</td>
</tr>
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Table 2. Activation energies $E_a$ and jump-attempt frequencies determined by nonlinear least squares fit of BPP function and Korringa term to Sc-$T_1$ data

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample</th>
<th>$\nu_L$ [MHz]</th>
<th>$E_a$ [eV]</th>
<th>$\nu_0$ [s$^{-1}$]</th>
</tr>
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<tr>
<td>ScH = 2.0</td>
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<td>12.2</td>
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<td>5.7 $10^{14}$</td>
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<tr>
<td>ScH 1.98</td>
<td>#259</td>
<td>12.2</td>
<td>0.76</td>
<td>4.5 $10^{14}$</td>
</tr>
<tr>
<td>ScH 1.98</td>
<td>#259</td>
<td>24.0</td>
<td>0.76</td>
<td>4.3 $10^{14}$</td>
</tr>
<tr>
<td>ScH 1.94</td>
<td>#260</td>
<td>12.2</td>
<td>0.76</td>
<td>2.2 $10^{14}$</td>
</tr>
<tr>
<td>ScH 1.88</td>
<td>#268</td>
<td>12.2</td>
<td>0.74</td>
<td>1.8 $10^{14}$</td>
</tr>
<tr>
<td>ScH 1.88</td>
<td>#267</td>
<td>12.2</td>
<td>0.71</td>
<td>9.4 $10^{14}$</td>
</tr>
<tr>
<td>ScH 1.82</td>
<td>#266</td>
<td>12.2</td>
<td>0.7</td>
<td>7.2 $10^{14}$</td>
</tr>
<tr>
<td>ScH 1.82</td>
<td>#266</td>
<td>24.0</td>
<td>0.8</td>
<td>6.2 $10^{15}$</td>
</tr>
<tr>
<td>ScH = 1.75</td>
<td>#28</td>
<td>12.2</td>
<td>0.87</td>
<td>6.3 $10^{16}$</td>
</tr>
<tr>
<td>ScH = 1.75</td>
<td>#28</td>
<td>24.0</td>
<td>0.83</td>
<td>6.2 $10^{15}$</td>
</tr>
</tbody>
</table>
there exists no experimental evidence for occupancy of the octahedral sites beyond 0.5% in scandium hydrides. For ZrH$_x$ ($x \leq 2$) and TiH$_x$ ($x \leq 2$) the activation energy is essentially constant as a function of hydrogen concentration. The only deviation from this behavior has been reported by Bowman et al.\cite{60} for proton T$_1p$ measurements on ZrH$_x$. They observe a decrease of $E_a$ for decreasing vacancy concentration for compositions in the range 1.8 $\leq x \leq$ 2.0. Above $x \geq 1.95$ $E_a$ increases quite rapidly, and this change is due to a tetragonal distortion. The decrease in $E_a$ from 0.47 eV for $x=1.8$ to 0.45 eV for $x=1.9$ might be due to some change in the unit cell volume\cite{61} producing a decrease in barrier height.

For the scandium hydrides and deuterides there is no indication of a change in the unit cell volume with increasing hydrogen concentration. The comparison with the behavior of $E_a$ in LaH$_{2+x}$ and YH$_{2-x}$ thus suggests that, while there is no experimental evidence for noticeable octahedral site occupancy on the low temperature side of the T$_1$ minimum, the ability for large amplitude motion away from the tetrahedral site might be nonnegligible at high temperatures. Richards\cite{62} showed that particle repulsions and large amplitude vibrations might inhibit octahedral site occupancy. The octahedral site occupancy might increase for an intermediate temperature range in some fcc hydrides, but it will eventually become less favorable at higher temperatures due to large amplitude
vibrations. Richards concentrates on the relevance of his model to metal hydrides but also mentions superionics as a system where such behavior might be observed. And indeed for superionic conductors with the fluorite structure, such as SrCl₂, molecular dynamics calculations⁶³ and neutron scattering experiments seem to result in a similar picture. The anions execute large amplitude motion about their tetrahedral equilibrium sites near the transition temperature \( T_c \) to the superionic phase. The octahedral sites are said to be destabilized, meaning that the occupancy of these sites is insignificant. The analogy with superionic conductors and the relevance of large amplitude vibrations to the diffusion process will be of considerable interest when we analyze our high temperature \( T_1 \) results.

The lowering of the activation energy \( E_a \) in ScH\(_x\) and ScD\(_x\) with decreasing vacancy concentration might be interpreted as a strengthening of the attractive interaction between vacancies, leading to the formation of vacancy pairs. Vacancy pairs should have a smaller activation energy than single vacancies in the presence of particle interactions. The before mentioned model by Richards of interacting particles diffusing on a regular lattice predicts the form of the correlation functions for different interaction strengths. The form of the \( \ln(45\text{Sc}-T^1) \) versus inverse temperature functions shows only a weak resemblance with our experimental
results. The $\text{Sc}-T_1$ values were calculated for three values of repulsive particle interaction strength: $J = 0.1 \text{ eV}$, $0.2 \text{ eV}$ and $0.5 \text{ eV}$. The resulting curves of $\text{Sc}-T_1$ versus $T^{-1}$ are shown in Fig. 18. For the intermediate value of $J = 0.2 \text{ eV}$ the $\ln(\text{Sc}-T_1)$ versus $T^{-1}$ curve shows a series of secondary minima superimposed on a steady decrease of $T_1$ with temperature, but no BPP-type minimum as observed experimentally.

We feel that the $\ln(1^{-1}H-T_1)$ versus inverse temperature curves determined by Richards for the case of mean-field like motion of labeled particles show some interesting resemblance with our $\text{Sc}-T_1$ results. According to Richards' model the motion of the vacancies should be nonmean-field like and proceed on two different time scales for monovacancies and divacancies. We expect the attractive interaction between vacancies to become weaker with increasing vacancy concentration and therefore should see an increase in the activation energy for the vacancy motion. The repulsion between particles should increase with increasing particle density. Keeping in mind these assumptions we would like to summarize the main features of the $\ln(T_1)$ versus inverse temperature curves derived by Richards for mean-field-like labeled particle motion. The high temperature side of the $T_1$ minimum for the mean-field case shows a significantly weaker slope than the low temperature side for strong particle
repulsion. The asymmetry of the $T_1$ minimum becomes more pronounced with increasing interaction strength, being nearly absent for $J=0.2$ eV. Our experimental results show this same increase in asymmetry of the Sc-$T_1$ minimum with increasing vacancy concentration. The inverse temperature specifying the position of the $T_1$ minimum in the model moves to higher temperatures with increasing repulsion between the particles. We observe a much smaller shift in the temperature position but the same tendency for increasing vacancy concentration. One possible conclusion to be drawn from this smaller shift in position of the $T_1$ minimum is that the actual change in interaction strength with vacancy concentration is much smaller than the range of values chosen by Richards for the model calculation. We can say that the $T_1$ values calculated from the mean field model for labeled particle motion seem to show some of the same distinguishing features as our experimental Sc-$T_1$ results. To produce a nonmean-field type behavior for the vacancy motion the repulsive particle interaction has to be on the order of 0.1 eV or larger, which may not be the case.
Expected spin-lattice relaxation time $T_1$ for NMR of metal nucleus (solid curve) and proton (dashed curve). The relative magnitudes of solid and dashed curves have no significance.

(a) $J = 0.5 \text{ eV}$
(b) $J = 0.2 \text{ eV}$
(c) $J = 0.1 \text{ eV}$

Fig. 10 in 'Vacancy and labeled particle hopping with interactions' by Peter M. Richards, Sandia National Laboratories, published in Phys. Rev. B, 33, 5, 3064 (1986). Figure reproduced with permission of the author.

Fig. 18: Spin-lattice relaxation times for Richards' model of interacting particles
Fig. 19: Normalized hopping frequencies for interacting particles
[Particle concentration is \( c_H = 0.9 \); \( E_a = 0.5 \) eV; \( v_0 = 10^{14} \); \( v_L = 24 \) MHz]
Attempt Frequencies

One of the more surprising results of the present study are the values obtained for the attempt frequencies $v_0$ from the Sc-$T_1$ measurements. The values of $v_0$ are listed in tables 1 and 2 and were obtained from a nonlinear least squares fit of the Sc-$T_1$ data to a BPP function and Korringa term. Notice the unrealistically large values of $v_0$ for the low composition samples ($c_{H(D)} < 0.1$). For these samples we observe the highest degree of asymmetry of the $T_1$ minimum, and the BPP function is therefore slightly inadequate to describe the behavior of our Sc-$T_1$ data. With the exception of the low composition samples the values obtained for $v_0$ are in good agreement with results of neutron measurements. Recalling equation 3 we see that the attempt frequency is related to the vibration frequency of the particle in the potential well, which is on the order of an optical phonon frequency. The neutron measurements give $h\nu_0 = 126$ meV or $v_0 = 1.8 \times 10^{14}$ s. The motion of labeled particles and vacancies are related by

$$v_0(v) c_v = v_0(H) (1-c_v),$$

if we assume that the activation energies for vacancy and particle motion are equal. Use of this equation or the more general relation, $v_H c_H = v_C c_V$, to deduce from the $^{1}H$-$T_1$ data the
vacancy attempt frequency leads to serious inconsistencies with the $^{45}$Sc-$T_1$ results, especially for lower vacancy concentrations. The Sc-$T_1$ results reflect the motion of the vacancies which do not carry a spin label as in the case of dipolar relaxation. Relating the vacancy attempt frequencies obtained from the Sc-$T_1$ measurements and the attempt frequency of labeled particles determined from the H-$T_1$ results by the above equation is therefore not correct. We expect the disagreement to be on the order of $1-f$ where $f$ is the correlation factor for tracer diffusion. Neglect of this factor can certainly not account for the observed discrepancies. For $c_v=0.05$ the ratio of attempt frequencies reaches nearly a factor of $10^2$, with the proton derived vacancy attempt frequency showing an approximately linear decrease with decreasing vacancy concentration. The attempt frequencies derived from the Sc-$T_1$ results show a relatively negligible decrease.

This difference between the results obtained from the proton $T_1$ and the Sc-$T_1$ data may again be attributed to particle interactions. The hopping rate $\nu$ of a particle in the presence of particle interactions will depend on the distribution of particles on the 2 nearest neighbor sites

$$\nu(n) = \nu_0 \exp[-(E_0 + Jn)/kT] ,$$  \hspace{1cm} [84]
where $J$ is the interaction parameter and $E_Q$ is the activation energy when all $Z$ neighboring sites are vacant. The probability of finding $n$ particles among the $Z$ sites is

$$P(n) = B(Z', n) \left(1 - c_v\right)^n c_v^{Z-n} ,$$

and the average hopping rate for particles determined by using this probability distribution is

$$\langle v \rangle = v_0 \exp \left(-E_Q/kT\right) \left[\left(1-c_v\right) + c_v \exp(-J/kT)\right]^Z . \tag{85}$$

According to Richards it can be shown that the ratio of the jump prefactors can be as large as $c_v^Z$ for large values of $J$ when particles can only hop in the presence of a vacancy pair.

For the average vacancy hopping rate we simply exchange $c_v$ and $c_H$. It is rather interesting to try different parameter sets for Eq. 86 for the particle and vacancy hopping rates. We will concentrate on effects produced by a change in interaction strength, considering both repulsive interactions ($J>0$) for particles and attractive interactions ($J<0$) for vacancies. The values chosen for the remaining parameters in the above equation correspond to typical values for the scandium hydrides and deuterides. A change of $J$ for vacancies from $J = -0.05$ eV to $J = 0$ can produce a large change ($= 40\%$) in the apparent activation energy for the range of vacancy
concentrations present in our samples. For repulsive interactions between particles and particle concentrations in the neighborhood of \( c_H = 0.9 \), the change in slope with a change in \( J \) is of the same order. In Fig. 17 we show the particle hopping frequency calculated with the above equation normalized by the Larmor frequency as a function of reciprocal temperature. The position of the \( T_1 \) minimum is determined by \( \nu/\nu_L = 1 \). We chose the following parameter values for this figure: \( c_H = (1-c_v) = 0.9 \), \( \nu_0 = 10^{14} \) and \( E_0 = 0.5 \) ev. Equation 85 will still produce an Arrhenius type behavior over a wide temperature range. One problem which becomes apparent from Fig. 17 is that with the change in interaction strength there would also be a rather large change in the temperature value at which the \( T_1 \) minimum occurs. We assume that even with particle interactions the condition \( \omega \tau = 1 \) at the \( T_1 \) minimum is still approximately fulfilled. The Sc-\( T_1 \) minimum should therefore occur at lower temperatures as the attractive interaction becomes more pronounced. We claimed that the decrease in activation energy with decreasing vacancy concentration observed in our \( T_1 \) measurements reflects such an increase in the attractive interaction between vacancies. The predicted effects for the chosen values of \( J \) seem to be too large, which might indicate that the changes in interaction strength are rather weak, but nevertheless observable in the Sc-\( T_1 \) results.
Position of Sc-T<sub>1</sub> Minimum

The effects of three particle correlations and conduction electron screening discussed in an earlier section could partially account for the shift of the position of the T<sub>1</sub> minimum to lower temperatures for c<sub>v</sub> → 0. The model developed by Barton<sup>65</sup> applies to deuterium spin-lattice relaxation in transition metal deuterides, but we expect the same qualitative effects for the spin-lattice relaxation of the stationary Sc-nucleus due to diffusing vacancies. For monovacancy configurations three particle correlations will be absent. Divacancies will let the angular distribution of EFG sources and thereby three particle effects come into play. The function P<sub>3</sub>(r<sub>k</sub>,r<sub>j</sub>,t), entering into the three particle correlation function, is the conditional probability that a particle initially at r<sub>k</sub> moves to r<sub>j</sub> in a time t given that at t=0 there was a particle at position r<sub>i</sub>. The three particle function P<sub>3</sub>(r<sub>k</sub>,r<sub>j</sub>,t) contains the condition that a further particle is located at the origin during this jump process. We translate this condition to the case of quadrupolar relaxation of the Sc nucleus. The particle at the origin will be taken to be the Sc nucleus and during any change of vacancy configuration it will obviously remain fixed at that site. Possible contributions to the three particle conditional probabilities now come from transitions from monovacancies to
divacancies and vice versa and transitions between divacancy configurations. The relative importance of three particle terms is therefore expected to be on the same order as the probability of encountering two vacancies on the eight vertices of a cube centered on the Sc nucleus, $P_8(2)$. Having said that, we are led to conclude that 3 particle correlations have relevance for the Sc spin-lattice relaxation, although we are unable to predict the magnitude of the expected effect. For increasing vacancy concentration we expect according to the model of Barton and Seymour the $T_1$ minimum to move to higher temperatures. Electron screening will reduce the electric field gradients produced by vacancies at the site of the Sc-nucleus. Barton and Seymour predicted that the position of the $T_1$ minimum will move to higher temperatures for increasing vacancy concentration due to electron screening. Three particle correlations and electron screening will therefore produce a shift of the position of the $T_1$ minimum in the same direction. Barton and Seymour present tables of numerical values of $T_1Q^\beta c_D$ versus $\omega T$ to demonstrate the effects of 3 particle correlations on the $^2\text{D}-T_1$ values. The constant $\beta$ is defined as $\beta=eQ/2I(2I-1)$ and $c_D$ gives the deuterium concentration. The $^2\text{D}-T_1$ values plotted on a logarithmic scale versus inverse temperature produce an asymmetric minimum for $^2\text{D}$ concentrations $c_D$ above 0.2. The increased slope on the high temperature side compared with the
low temperature side of the $T_1$ minimum is inconsistent with the corresponding reduction in slope observed for the Sc-$T_1$ measurements. The degree of asymmetry depends on composition as in our case. No results of numerical calculations are presented to illustrate the changes of the relaxation rates produced by electron screening.

$^{45}$Sc Knight Shift

The temperature dependence of the Sc-Knight shift was measured in a temperature range from room temperature to 1100 K. To determine the Knight shift we recorded the pulse Fourier transform spectrum of $^{45}$Sc by digitizing the off-resonance FID at a rate of 1 MHz and transforming the discrete time FID from the time domain to the frequency domain with a fast discrete Fourier transform. We gathered the spectrum for several temperatures and measured the frequency shift of the Lorentzian type peak. This determined the relative change of the Knight shift with temperature. The recorded Fourier spectra at constant magnetic field and their shift with temperature are illustrated in Fig. 20. To obtain absolute values we measured the Knight shift at room temperature by determining the resonance frequency of $^{27}$Al for AlCl$_3$ in solution as reference. The ratio $\gamma(\text{^{45}Sc})/\gamma(\text{^{27}Al}) = 1.07257$
Scandium Fourier Transform Spectra

Sample: ScH 1.66 (928)

Frequency shift with respect to room temperature spectrum

$1000/T = 2.1$  
Frequency: 2.9 kHz

$1000/T = 1.6$  
Frequency: 5.7 kHz

$1000/T = 1.4$  
Frequency: 8.6 kHz

$1000/T = 1.2$  
Frequency: 10.7 kHz

$1000/T = 1.0$  
Frequency: 13.1 kHz

$1000/T = 0.9$  
Frequency: 17.2 kHz

Fig. 20: Scandium pulse Fourier transform spectra at constant magnetic field
Fig. 21: Knight shift as a function of temperature
for bare nuclei has been determined before with sufficient accuracy to be used here. The Sc-Knight shift (Fig. 21) shows a linear dependence on temperature, roughly doubling its value over a 500 K temperature interval for ScH 1.64 and ScH 1.88.

In a transition metal we expect the total magnetic susceptibility to be mainly composed of the following contributions:\[86\]

\[ X = X_s + X_d + X_{vV} + X_L + X_{dia} \]

The first two terms are the electron s- and d-spin susceptibilities which are proportional to the fractional densities of state in the s- and d-bands \( N_s(\varepsilon_F) \) and \( N_d(\varepsilon_F) \). The third term \( X_{vV} \) is a second order effect of the spin orbit interaction and is analogous to the temperature independent Van Vleck susceptibility. The last two terms are diamagnetic contributions due to the conduction electrons and the ion core. These diamagnetic terms are usually dominant in simple metals, but of little importance in transition metals.

We next discuss the temperature dependence of the different contributions to the magnetic susceptibility. The Pauli susceptibility of a free electron gas is temperature independent for temperatures which are small compared with the Fermi temperature \( T_F \). The paramagnetic susceptibility of the s-state electrons at the Fermi surface should be essentially
constant. The orbital angular momentum of the Sc-3d electrons is at least partially quenched in a solid. This means that

\[ \langle mk | L | mk \rangle = 0 \]

In the case of total quenching, first order effects of the interaction between nuclear spin and the electronic orbital angular momentum vanish. Second order effects involve the orbital moment induced by a magnetic field. Off-diagonal elements of the electronic angular momentum operator do not vanish. In the tight-binding approximation the resulting paramagnetic susceptibility can be shown to have the following form

\[ x_{\gamma\gamma} = \frac{2\pi \gamma_e}{(2\pi)^3} \int dk \sum_{m',m} \left[ f(\varepsilon_{mk}) - f(\varepsilon_{m'k}) \right] / \Delta \times \left| \langle m'k | L | mk \rangle \right|^2, \]

which is similar to the Van Vleck susceptibility. Due to the Fermi function \( f(\varepsilon) \), only terms in the above sum involving a matrix element of \( L \) between occupied and unoccupied states will make a nonzero contribution. The orbital term of the susceptibility is smallest when the d-band is nearly empty, as for Sc, or filled. It is expected to be temperature independent in analogy to Van Vleck paramagnetism of ionic salts.
The d-band electrons do not contribute directly to the contact hyperfine field. Nevertheless their presence can lead to a slight polarization of core s-state electrons through the exchange interaction. The contribution of d-band electrons will depend on their polarization which in turn is proportional to the d-band electronic susceptibility. The core polarization is negative if it originates from d- and f-shells\textsuperscript{71} which means the polarized electrons in the core have an orientation which is antiparallel to the unpaired spin inducing the polarization. In contrast the core polarization due to an unpaired s-electron is always positive and simply enhances the normal contact interaction. The d-band core polarization dominates the temperature dependence of the magnetic susceptibility in many transition metals.

The conduction band diamagnetic contribution to the susceptibility for electrons weakly bound to a periodic lattice potential is given by

\[ X_{\text{dia}} = - \frac{8\pi}{3} \left( \chi_p / 3 \right) \left< \frac{m}{m^*} \right>^2, \]

where \( m^* \) denotes the effective mass of the electron and \( \chi_p \) the paramagnetic susceptibility of the conduction electrons.\textsuperscript{72} In transition metals with \( m/m^* \) very small the diamagnetic contribution to the electronic magnetic susceptibility is negligible compared to the paramagnetic contribution \( \chi_p \). We
can therefore approximate the magnetic susceptibility of the d- and s-band electrons by

\[ \chi_{d(s)} = \left( \gamma_e h \right)^2 / 2 \, N_{d(s)}(\varepsilon_F) \],

where \( N_{d(s)}(\varepsilon_F) \) represent the fractional densities of state of s- and d-band electrons at the Fermi level.

Knight shift and magnetic susceptibility are related through

\[ [87] \]

\[ K = K_s + K_d + K_{\text{orb}} = -(2/\gamma_e h) \left[ h(s) \chi_s + h(d) \chi_d + h(\text{orb}) \chi_{\text{VV}} \right] = -\gamma_e h \left[ h(s) N_s(\varepsilon_F) + h(d) N_d(\varepsilon_F) \right] - 2/\gamma_e h \, h(\text{orb}) \chi_{\text{VV}}, \]

where \( h \) is the hyperfine field. We neglected the diamagnetic contributions as they are relatively small in transition metals. A useful method of analysis introduced by Jaccarino consists in plotting the Knight shift versus the magnetic susceptibility with the temperature being an implicit parameter. If the temperature dependence of Knight shift and magnetic susceptibility are dominated by the same mechanism we should obtain a straight line.

The magnetic susceptibility of \(^{45}\text{Sc}\) was measured by Spedding and Croat from 4 K to 300 K and particular attention was given to possible effects of paramagnetic
impurities. The inverse susceptibility exhibits Curie-Weiss behavior above roughly 70 K. Dilute amounts of nonmagnetic impurities decrease the susceptibility of scandium at high temperatures. Blumberg et al.\textsuperscript{74} report that the Sc Knight shift in scandium shows a linear decline with temperature. The measurements covered a temperature range from 4 K to 300 K. They failed to observe the Knight shift anisotropy as pointed out by Barnes et al.\textsuperscript{75} The values of the isotropic Knight shift reported by Barnes et al. agree fairly well with the values obtained by Blumberg et al. A plot of the Knight shift versus susceptibility reveals an approximately straight line behavior with positive slope. This indicates that d-band core polarization, which produces a positive dK/dx slope, dominates the temperature dependence of the Knight shift in scandium. A similar analysis was made for \textsuperscript{195}Pt by Clogston, Jaccarino and Yafet.\textsuperscript{76} Spin orbit coupling which might be thought to be important for the heavy transition metals has only a minor effect on the susceptibility of Pt. The behavior of Knight shift and susceptibility for scandium is similar to other transition metals.

Unfortunately it is difficult to find susceptibility data for ScH\textsubscript{x} in the literature in which the effects of impurities can be ruled out as negligible. Savin et al.\textsuperscript{77} observe a weak linear decrease of the susceptibility for ScH\textsubscript{x} (1.7 \leq x \leq 2.0) over a temperature region from 70K to 900 K.
A negative $d\kappa/d\chi$ slope for $\text{ScH}_x$ could be explained by an s-state admixture into the d-band. Such a mixing of the metal s- and d-bands has been inferred from band structure calculations for $\text{ScH}_2$ and many other fcc dihydrides. Equivalently we can say that the s-state density of states at the Fermi level increases while $N_d(e_F)$ decreases. The $\text{ScH}_x$ samples used by Savin were contaminated by substantial amounts of impurities and although his data seem to support our hypothesis of s-state admixture to the d-band we do not want to draw any definite conclusions based on them.

This lack of susceptibility data for scandium hydride samples with low impurity levels on the order of a few parts per million provided the motivation for the recent susceptibility measurements by Shelton. The measurements were performed for one of the hydride samples used in the NMR study ($\text{ScH} 1.88$, sample # 267) over a temperature range from 2.6 K to 350 K. The automated susceptometer manufactured by 'Quantum Design' uses a superconducting quantum interference detector (SQUID). Above 25 K the susceptibility shows a weak linear decrease with temperature ranging from $5.4\times10^{-6}$ emu/g at 25 K to $5.28\times10^{-6}$ emu/g at 320 K. The decrease of the susceptibility is rather pronounced in the temperature region from 2.6 K to 20 K, and this is probably due to residual amounts of paramagnetic impurities. Although the temperature ranges of our measurements of the Knight shift and Shelton's
results of the magnetic susceptibility overlap only over a small common temperature region we can claim with reasonable confidence that $d\kappa/d\chi$ is indeed negative as hinted at by Savin's results.

The Knight shift term $k_d$ is proportional to the density of states in the d-band $N_d(\varepsilon_F)$. As mentioned before, the d-band core polarization is negative and an increase in the Knight shift with temperature therefore corresponds to a decrease of $N_d(\varepsilon_F)$ if the remaining contributions to the Knight shift are essentially temperature independent. For the case of cubic symmetry the NMR relaxation rate due to conduction electrons is given by

$$
\frac{1}{T_{1e}} = \frac{4\pi \gamma_n^2 kT}{\hbar} \left\{ \left[ (N_d(\varepsilon_F)\hbar(\varepsilon))^2 + (N_s(\varepsilon_F)\hbar(\varepsilon))^2 \right] q + (N_d(\varepsilon_F)\hbar(\varepsilon))^2 p \right\},
$$  \[88\]

where $q$ and $p$ are reduction factors giving the relative weights of the irreducible representations of the atomic d-function at the Fermi level. The Knight shift increase for $\text{ScH}_x$, if due to a decrease of $N_d(\varepsilon_F)$, should therefore be accompanied by an increase of the Korringa product $T_{1e}T$. The $^{51}\text{V}-T_1$ measurements by Guenther and Kanert provide an example. In vanadium the temperature dependence of the Knight shift is dominated by d-band core polarization, and the Knight shift increases with temperature. This can be interpreted as
a decrease of $N_d(e_F)$ as the hyperfine field $h^{(d)}$ is negative. Only the square of the hyperfine field enters into the above equation 88 for $T_{1e}^{-1}$, and we should therefore observe an increase in the Korringa product with temperature. The measurements of $T_{1e}T$ for $^{51}$V by Guenther and Kanert support this interpretation. We would like to point out that the high temperature (above 800 K) decrease of Sc-$T_1$ might at first sight appear to be due to a decrease of $T_{1e}T$. Our above analysis of the Knight shift data suggesting a increase in $T_{1e}T$ seems to contradict this interpretation.

Conclusions on $^{45}$Sc Results

We can say that the Sc-$T_1$ results display some unique features not discernible through the H-$T_1$ results, as we will see. The asymmetry of the $T_1$ minimum is absent in the proton results. The Sc-$T_1$ measurements prove that a simple interpretation based on a BPP-type spectral density function is inadequate. The vacancy motion observed through quadrupolar relaxation of the Sc nucleus suggests a more complex picture. The formation of vacancy pairs, the interaction between particles, three particle correlations and electron screening might possibly account for some of the features observed. The measurements of the Knight shift as a
function of temperature provided evidence for s-state admixture to the d-band as predicted by band structure calculations. The accompanying reduction of \( N_d(\varepsilon_F) \) will lead to an increase of the Korringa product \( T_{1e}T \).

\( ^1H-T_1 \) Results

\( ^1H-T_1 \) data were taken for a limited number of scandium hydride samples. Fig. 22 shows an example of the \( ^1H \) data for ScH 1.82 taken at two different Larmor frequencies. The results can be reasonably well accounted for with dipolar and conduction electron contributions to the total relaxation rate. In some cases, residual amounts of paramagnetic impurities on the order of a few parts per million produce a weak secondary minimum on the low temperature side of the \( T_1 \) minimum. These samples belong to a batch labeled with double digit numbers. All samples prepared by B. Beaudry were made from high purity scandium metal labeled with three digit numbers. Proton \( T_1 \) measurements for these latter samples did not provide any evidence for the presence of paramagnetic impurities with the exception of samples which were intentionally doped with a controlled amount of paramagnetic impurity. We obtained for the pure samples symmetric \( \ln(\frac{1}{^1H-T_1}) \) versus \( T^{-1} \) minima. On a logarithmic scale the slopes
showed no visible deviation from straight line behavior. In comparison with the Sc-T₁ minima the H-T₁ minima are generally narrower. The depth of the T₁ minima is less sensitive to the hydrogen concentration than the minimum quadrupolar relaxation time for the Sc-T₁ measurements. One reason for this behavior is that for the composition range studied we change the vacancy concentration over one order of magnitude while the maximum change in hydrogen concentration amounts to approximately 15%. The depth of the quadrupolar Sc-T₁ minimum also attests to the relatively greater strength of the quadrupolar interaction relative to the dipolar interaction in scandium hydrides. An important contribution to the H spin-lattice relaxation arises from the metal-hydrogen dipolar interaction and this contribution to the total relaxation rate will be insensitive to a change in hydrogen concentration of the sample.

Table 3 shows the values obtained for the activation energies and jump-attempt frequencies from the H-T₁ data. A BPP type spectral density function was used for the fitting procedure and we accounted for the H-H and dipolar interactions. The dipolar relaxation rate is given by

\[ R\text{ld} = 1.5 \gamma_I^2 c_I \left[ J^{(1)}(\omega_I) + J^{(2)}(2\omega_I) \right] + \gamma_I^2 c_S \left[ (1/12)J^{(0)}(\omega_I - \omega_S) + 1.5J^{(1)}(\omega_I) + (3/4)J^{(2)}(\omega_I + \omega_S) \right], \]
Fig. 22: $^1H$ spin-lattice relaxation times for Sch 1.82
Table 3: Activation energies $E_a$ and jump frequency prefactors $\nu_0$ determined by nonlinear least squares fit from $^1H-T_1$ data [Korringa constant $T_1gT$ was a fixed parameter. For samples with very low levels of paramagnetic impurities on the order of a few parts per million $H-T_1$ measurements from 77 K to room temperature yielded a value of $T_1gT$ of $=340$ sK for $T_1gT$ and this value was used for the nonlinear least squares fit. We estimate the uncertainty in the attempt frequency $\nu_0$ to be on the order of 40%. The error margin for $E_a$ is roughly 10%.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Larmor Freq. [MHz]</th>
<th>$E_a$ [eV]</th>
<th>$\nu_0$ [$s^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sch 1.98 (#261)</td>
<td>12.2</td>
<td>0.52</td>
<td>$2.0 \times 10^{11}$</td>
</tr>
<tr>
<td>Sch 1.94 (#260)</td>
<td>12.2</td>
<td>0.63</td>
<td>$3.4 \times 10^{12}$</td>
</tr>
<tr>
<td>Sch 1.88 (#267)</td>
<td>12.2</td>
<td>0.53</td>
<td>$9.1 \times 10^{11}$</td>
</tr>
<tr>
<td>Sch 1.83 (#25)</td>
<td>12.2</td>
<td>0.56</td>
<td>$7.7 \times 10^{11}$</td>
</tr>
<tr>
<td>Sch 1.83 (#25)</td>
<td>24.0</td>
<td>0.58</td>
<td>$1.4 \times 10^{12}$</td>
</tr>
<tr>
<td>Sch 1.82 (#266)</td>
<td>12.2</td>
<td>0.73</td>
<td>$2.8 \times 10^{13}$</td>
</tr>
<tr>
<td>Sch 1.82 (#266)</td>
<td>24.0</td>
<td>0.68</td>
<td>$1.6 \times 10^{13}$</td>
</tr>
<tr>
<td>Sch 1.64 (#28)</td>
<td>12.2</td>
<td>0.73</td>
<td>$3.8 \times 10^{13}$</td>
</tr>
<tr>
<td>Sch 1.64 (#28)</td>
<td>24.0</td>
<td>0.80</td>
<td>$1.1 \times 10^{14}$</td>
</tr>
</tbody>
</table>
with $C_I = \gamma_I^2 h^2 I(I+1)(2/15) E_i r_i^{-6}$ and $C_S = \gamma_S^2 h^2 S(S+1)(2/15) E_S r_S^{-6}$. To calculate the lattice sums we choose an arbitrary tetrahedral site as origin. The sum $E_i$ extends over all tetrahedral sites and the sum $E_S$ includes all sites of the Sc host lattice. For a polycrystalline sample and after determining the lattice sums we obtain

$$R_{1d} = C_H \cdot 4.07 \times 10^9 \frac{\omega_I^{-1}}{4y/(4+y^2) + 4y/(1+y^2)} +$$
$$8.25 \times 10^9 \frac{\omega_I^{-1}}{0.5y/(1+0.573y^2) + 1.5y/(1+y^2) + 3y/(1+1.545y^2)} ,$$

with $y$ defined as $y = \omega_I \tau_H$. The hydrogen concentration is given by $C_H = x/2$ for ScH$_x$. We assumed that the hydrogen hopping frequency follows an Arrhenius type relationship

$$\tau_H^{-1} = v_0^H \exp(-E_a/kT) .$$

The above expression for the dipolar relaxation rate plus a term accounting for the conduction electron relaxation were fit the the experimental $H-T_1$ results. The nonlinear least squares fits give rather accurate values for the activation energies. We estimate the uncertainty for the jump-attempt frequencies to be on the order of 80%.

The activation energies obtained from the $^1H-T_1$ data are in poor agreement with the values obtained from the Sc-$T_1$ measurements. The values of $E_a$ derived from the proton $T_1$
results fall consistently below the values obtained from the Sc-$T_1$ data. The difference in the $E_a$ values for a particular composition amounts to nearly 20% of the Sc-$T_1$ activation energy. $E_a$ for the $^1H-T_1$ data nevertheless shows the same tendency of decreasing with increasing hydrogen concentration.

The position of the $T_1$ minimum on a reciprocal temperature scale shows a shift to higher temperatures for increasing hydrogen concentration. This shift in position is opposite to the one observed for the Sc-$T_1$ minimum. For the motion of labeled particles and vacancies the principle of detailed balance relates vacancy and particle hopping rates through their concentrations. If the $^1H-T_1$ and Sc-$T_1$ minima occur when the hopping frequency is approximately equal to the Larmor frequency ($\omega_0 \tau = 1$) we would expect with changing composition a shift of the temperature at which the $T_1$ minimum occurs to be in the same direction for both Sc- and $H$-resonances. Our results show that the position of the $H-T_1$ minimum shifts to higher temperatures while the Sc-$T_1$ minimum moves in the opposite direction for increasing hydrogen concentration. For hydrogen diffusion the motion of the interstitials is constrained by the number of nearest neighbor vacancies to which an atom can hop. We expect a slowdown of hydrogen motion with decreasing vacancy concentration. We should also recall that particle correlations will reduce the tracer diffusion coefficient. According to the computer
simulations of Kehr, Kutner and Binder\textsuperscript{81} for diffusion in concentrated lattice gases the correlation factor $f$ is 0.8 and 0.85 for hydrogen concentrations of $c_H=1.0$ and $c_H=0.8$ respectively. These values differ somewhat from the result $f=0.65$ obtained by Sholl\textsuperscript{82} for the monovacancy limit. Nevertheless, the correlation effects will be more pronounced for higher particle concentrations and thus lengthen the decay of the dipolar correlation functions. The position of the $T_1$ minimum should move to higher temperatures due to increased correlation of the particle motion. The magnitude of this effect is probably small. For vacancies, correlation effects are presumably negligible and most likely do not provide an explanation for the shift of the position of the Sc-$T_1$ minimum to higher temperatures with increasing vacancy concentration. We think, as explained earlier, that three particle correlations, conduction electron screening and particle interactions are more plausible reasons for this behavior.

The Korringa constant determined from the Sc-$T_1$ measurements below room temperature showed no systematic variation with composition over the range $H/Sc=2.0$ to $H/Sc=1.64$. Measurements by Lu\textsuperscript{83} and the author indicate that the $^1H-T_1$ Korringa constant is on the order of 300-400 sK for $H/Sc = 1.75$ to 1.97. The Korringa constant increases over this range with increasing hydrogen concentration. This indicates an increase in the density of states at the Fermi
level around the proton site. Calculations of the electronic band structure by Papaconstantopoulos and Switendick\textsuperscript{84} indicate such an increase in $N(\varepsilon_F)$ with increasing hydrogen concentration for TiH$_x$, ZrH$_x$ and HfH$_x$. The calculations for $x=2.0$ were performed using a self-consistent augmented plane wave method, and for $x=1.9$ the value of $N(\varepsilon_F)$ was derived from a coherent potential approximation.

$^2\text{D}-T_1$ Results

$^2\text{D}-T_1$ data were taken at 12.2 MHz for samples with composition D/Sc = 1.98, 1.88 and 1.82. When plotted on a logarithmic scale versus reciprocal temperature the $^2\text{D}-T_1$ minima show symmetric behavior. The activation energy determined from the straight line slopes of the ln($T_1$) versus $T^{-1}$ minimum is approximately 0.5 eV for all samples investigated and these values do not reveal any change with sample composition. We feel that the compositions of these three samples cover a sufficiently wide range for this result to be of general validity for scandium dideuterides.

The Korringa constant $T_{1e}T$ was not determined accurately by low temperature $T_1$ measurements. The NMR signal was difficult to detect outside the region of motional narrowing. We estimate the Korringa constant to be on the order of at
least 4000 sK. The position of the $D-T_1$ minimum on the reciprocal temperature scale is always close to the $H-T_1$ minimum and at a slightly lower temperature. The temperature difference in the position of the two minima is on the order of 60 K. If we assume that the jump attempt frequency of the two hydrogen isotopes follows the $m^{-1/2}$ mass dependence characteristic of the eigenfrequency of a harmonic oscillator, we can calculate the temperature difference of the position of the $^1H$- and $^2D-T_1$ minima. We assume in both cases that the position of the minimum is determined by $\omega_0 T_D(H)^{-1}$. The isotope effect will produce a shift of the $^2D-T_1$ minimum with respect to the $^1H-T_1$ minimum to lower temperatures which for ScD 1.98 should be roughly 30 K. The observed temperature difference for scandium hydrides and deuterides exceeds our estimate by 100%. This larger than expected temperature difference has been observed and discussed by Barton and Seymour for a series of transition metal deuterides. It can be ascribed to conduction electron screening and three particle correlations both of which influence the quadrupolar relaxation rate of the $^2D$ nucleus. Three particle correlations are of no importance for the $^1H$ spin-lattice relaxation, and conduction electron screening is irrelevant for dipolar relaxation. Barton and Seymour evaluate the mean field quadrupolar relaxation rates using an unscreened Coulomb potential and taking into account three particle
correlations for several compositions. The results are presented in the form of $(T_1\beta c_p)^{-1}$ versus $y$ with $\beta = eQ/2I(2I-1)$ and $y = \omega_0 \tau$. According to these calculations the low temperature side of the $T_1$ minimum shows no change in activation energy with composition, consistent with our experimental results. However the $T_1$ curves presented by Barton and Seymour are characterized by an asymmetry of the $T_1$ minimum, the high temperature side of the $T_1$ minimum having a steeper slope than the low temperature side. The asymmetry is substantial with the slope on the low temperature side being three to four times larger than on the high temperature side of the $^2$D$_1$-$T_1$ minimum for a deuterium concentration of $c_D = 0.8$. Such asymmetry is not observed in our experimental $^2$D$_1$-$T_1$ results. For the Sc-$T_1$ results we observed a decrease in activation energy on the high temperature side in comparison with the low temperature side of the $T_1$ minimum. We think that in the case of the Sc-$T_1$ the reduction in activation energy is related to the creation of Frenkel defects at high temperatures and probably not related to three particle correlations. While the three particle correlation effects on the quadrupolar relaxation rates can be estimated accurately from rather general computer simulation models of deuterium diffusion, the effects of conduction electron screening for a transition metal deuteride will depend in their magnitude on the specific features of the band structure. One can
nevertheless say in general that conduction electron screening will push the position of the $T_1$ minimum to lower temperatures for decreasing vacancy concentration thereby reinforcing the temperature shift of the $T_1$ minimum position produced by three particle correlations.
Fig. 23: $^2$D spin-lattice relaxation times for ScH 1.82
**Figure 24:** H spin-lattice relaxation times for ScH 1.64
Fig. 25: $^{45}$Sc spin-lattice relaxation times for ScD 1.99
SC-T1

SAMPLE: SCH 1.98 + 100 PPM GD;

Fig. 26: $^{45}$Sc spin-lattice relaxation times for sample doped with Gd
HIGH TEMPERATURE NMR RESULTS AND DISCUSSION

At high temperatures, when $\omega_0 \tau << 1$, we observe for $^{45}\text{Sc}$, $^{2}\text{D}$ and $^{1}\text{H}$ a substantial decrease of the $T_1$ and $T_2$ values. This clearly contradicted our expectations and was a rather serendipitous discovery. We expected the $\ln(T_1)$ values to increase linearly with inverse temperature after they had reached their minimal value in the region $\omega_0 \tau = 1$. This linear increase should cease when relaxation by conduction electrons again becomes the dominant mechanism leading to behavior described by the Korringa relation

$$T_1 T = \text{constant}$$

The striking decrease of $T_1$ can clearly not be accounted for by the conduction electron contribution. This becomes particularly evident after subtracting the conduction electron contribution from the relaxation rates. The decrease of $T_1$ with temperature $T$ occurs at a much faster rate than $T^{-1}$, and indeed $\ln(T_1)$ versus $T^{-1}$ displays straight line behavior. The measurements of the Sc-Knight shift indicated that the conduction electron density of states shows no abnormal behavior in the region of the $T_1$ decrease. The Knight shift
continues to increase linearly with temperature as at lower temperatures. The decrease in $T_1$ was not accompanied by any major observable shift in resonance frequency, consistent with the Knight shift results. We should have been able to detect any shift in resonance larger than 2-3 Gauss over the region of the $T_1$ decrease. We will denote the temperature at which $T_1$ turns down and starts decreasing by $T_c$. For the samples with high hydrogen (deuterium) concentrations within one to two percent of the dihydride composition, such a temperature cannot be defined with high accuracy as the region in which $T_1$ turns around is rather broad, and the onset of the $T_1$ decrease is gradual. This is well illustrated by the Sc-$T_1$ data for ScD 1.99 shown in Fig. 25. The jump frequency of the mobile interstitials reaches $10^{10}$ s$^{-1}$ around $T_c$. Our experimental results suggest that for a particular nuclear species $T_c$ is essentially insensitive to the composition of the sample. The reciprocal temperature spacing of the local $T_1$ maximum for different nuclear species is roughly the same as for the lower temperature $T_1$ minimum. This means that the decrease in $T_1$ values is observed first for the $^{45}$Sc-$T_1$ values, and we were in some cases able to reach the bottom of the Sc-$T_1$ minimum. The minimum Sc-$T_1$ value, which was on the order of 4 ms, seemed to be independent of sample composition. We realize that strictly speaking our experimental results do not allow us to characterize the decrease in $T_1$ as a $T_1$ minimum.
Nevertheless, keeping this reservation in mind, we will use this expression.

The hydrogen pressures in the sample tubes reached at the highest temperatures of our measurements were a barrier to investigating the $T_1$ behavior at even higher temperatures. For the lower composition scandium hydrides and deuterides the softening temperature of quartz was reached in the course of our measurements. The high hydrogen pressures in the sample tubes caused the explosion of several high composition samples. A simple calculation using the diagram of pressure-composition isotherms (fig. 1) shows that the composition of the samples at these high temperatures is nearly unchanged in comparison to room temperature in spite of the high hydrogen pressures. We repeated for a ScD$_{1.99}$ sample the Sc-$T_1$ measurements after resealing the sample in a quartz tube of one third the original volume. The low temperature $T_1$ minimum is slightly deeper than for the first run ($T_1|_{\text{min}}$ decreased from 10 msec. to 6 msec.), meaning that minute amounts of hydrogen escaped during the process of changing the sample tubes. The high temperature $T_1$ values are identical for the two $T_1$ measurements. The reduction in the volume of the quartz tubes will limit the change in composition with increasing temperature by a corresponding factor. The observation of no change whatsoever in the high temperature $T_1$ results shows that the escape of hydrogen with increasing temperature from the hydride grains is completely negligible.
A sample of scandium hydride was prepared from Sc doped with 100 parts per million of Gd. No change in behavior of the Sc-$T_1$ values at high temperatures was observed. A secondary minimum on the low temperature side of the conventional $^1H-T_1$ minimum reflected the presence of the paramagnetic impurities, but in contrast the high temperature $^1H-T_1$ decrease remained unaltered.

One of the more striking aspects of the high temperature $T_1$ minimum is the near absence of frequency dependence of the $T_1$ values. The only exception occurs for the scandium resonance in the samples with low vacancy concentration, which show a very weak but discernable frequency dependence in the region of the local Sc-$T_1$ maximum. We are not able to observe any frequency dependence in the high temperature region where $\ln(T_1)$ versus $T^{-1}$ shows straight line behavior. We are reminded of the fact that for a BPP type $T_1$ minimum frequency independence of the $T_1$ values is only observed in the region $\omega_0 \tau \ll 1$, where $\tau$ represents the correlation time of the fluctuations in the local environment. For the limited subset of low composition samples in which the bottom of the $T_1$ minimum was reached, the values of $T_1$ in this region again show no dependence on frequency (and composition as mentioned earlier).
Fig. 27: $^1$H spin-spin and spin-lattice relaxation times for ScH 1.82
H-T$_2$ Results

We measured the spin-spin relaxation time $^1$H-T$_2$ at 12.2 MHz in ScH 1.82 using a Hahn echo or the CPMG pulse sequence. Fig. 27 shows the results of these measurements and allows a comparison with the $^1$H-T$_1$ data for the same Larmor frequency. The H-T$_2$ values obtained with the CPMG method are, in the region where ln(T$_2$) versus T$^{-1}$ follows linear behavior, in approximate agreement with the corresponding T$_1$ values. The H-T$_2$ values obtained with a Hahn echo fall substantially (40%) below the values obtained with the CPMG pulse sequence. We feel that the T$_2$ results obtained with the CPMG sequence are more reliable. At roughly a 1000 K we observe a turndown of the T$_2$ data analogous to the behavior of the T$_1$ results. Some datapoints in the region of the T$_2$ turndown were corrected for the effects of echo attenuation due to magnetic field gradients. The magnetic field gradients are produced by the inhomogeneity of the magnetic susceptibility in a polycrystalline sample. The relaxation rate related to the loss of phase coherence among the spins in a magnetic field gradient is given by

$$\frac{1}{T_2^+} = \frac{1}{3} D v^2 G^2 \Delta t^2,$$
where $D$ is the diffusion constant, $G$ the average magnetic field gradient produced by the inhomogeneities of the magnetic susceptibility and $\Delta t$ the time interval between consecutive 180° pulses of the CPMG pulse sequence. Notice that this contribution vanishes for $\Delta t=0$. As the mean value of the gradient $G$ is unknown we extrapolated the total spin-spin relaxation rate $1/T_2$ to $\Delta t=0$ by measuring $T_2$ for different $\Delta t$. The corrected $T_2$ data still show a high temperature turndown. The $T_2$ value at the $T_2$ maximum is $T_2=35$ ms, while the corresponding $T_1$ value reaches 90 ms near its local high temperature maximum. For the case of extreme motional narrowing ($\omega_0 \tau \ll 1$) we would expect $T_1$ and $T_2$ to be roughly equal and this departure from equality of $T_1$ and $T_2$ in the region where the relaxation times turn down could mean that the extreme narrowing criterion, $\omega_0 \tau \ll 1$, is no longer fulfilled. In other words, the dipolar correlation time increased at high temperatures to the point where $\omega_0 \tau \leq 1$. Such an increase in dipolar correlation time at high temperatures could be interpreted in terms of highly correlated modes of motion and/or some slowdown of the $^1H$ motion.
There exist several conceivable relaxation mechanisms which could reproduce some of the features observed in our experimental $T_1$ results. We begin with a discussion of spin-lattice relaxation due to $^{45}$Sc self-diffusion. The melting point of Sc-metal lies at 1812 K, which is considerably above the temperature region of the anomalous $T_1$ behavior. Guenther and Kanert studied the atomic motion of $^{51}$V in vanadium metal by means of NMR. The results for the spin-lattice relaxation time in the rotating frame, $T_{1p}$, show a minimum due to $^{51}$V self diffusion at 1600 K for a locking field of 8 G. Guenther and Kanert obtain for the $^{51}$V average dwell time

$$\tau = 10^{-15} \exp(3.1 \text{ eV}/kT)$$

For a Larmor frequency of 12 MHz, which corresponds to one of the frequencies at which we carried out $T_1$ measurements, the $^{51}$V-$T_1$ minimum due to self-diffusion should occur at approximately 2000 K. The reason that a $T_1$ minimum due to self-diffusion is not observed around this temperature lies in the strong conduction electron relaxation, which masks the other contributions to the spin-lattice-relaxation rate. This should be of no concern to us, and the $T_{1p}$ results, being relatively insensitive to conduction electron relaxation, show
the normal diffusion induced relaxation time minimum.
Although the melting temperature of vanadium occurs at 2175 K, which is higher than for scandium metal, we can infer from these order of magnitude estimates that self-diffusion of $^{45}$Sc in scandium hydrides is too slow to give rise to the observed high temperature $T_1$ minimum. Furthermore we would expect Sc self-diffusion to produce the normal type of frequency dependence of the relaxation times which is exemplified by the V-$T_1$ results. The anomalous $^1$H-$T_1$ behavior for ScH$_x$ at high temperatures has more recently also been observed in Ti-, Zr- and Y-dihydrides. Let us for a moment assume that self diffusion of the metal nuclei could account for the observed behavior. This would mean that all these metal nuclei would have to diffuse rapidly, which seems very improbable. In addition $^{47}$Ti and $^{91}$Zr have low abundance and $^{89}$Y has a relatively weak moment so that we do not expect significant dipolar relaxation of the protons. We therefore abandon this hypothesis and turn now towards the possible effects of impurities on the high temperature $T_1$ behavior.

**Impurity Diffusion**

The measurements by Guenther and Kanert showed that the migration of oxygen impurities contribute to spin-lattice relaxation. For a Larmor frequency of 48 MHz they observe a
weak $T_1$ minimum at approximately 900 K due to oxygen diffusion in vanadium. The equilibrium oxygen concentration in the vanadium samples was estimated at 1600 parts per million. To observe a quadrupolar Sc-$T_1$ minimum in Sc$H_x$ and Sc$D_x$ whose origin lies in oxygen self diffusion would therefore require substantial amounts of oxygen in all samples. The O-diffusion induced $T_1$ minimum should also show some frequency dependence. For the H-$T_1$ results we should notice that $^{17}O$ ($^{16}O$ has no nuclear moment) has an extremely low nuclear abundance. Similar arguments against the idea of a high temperature $T_1$ minimum induced by nonmagnetic impurities apply to other impurity interstitials such as C and N.

**Surface Effects**

Another possible relaxation mechanism would be relaxation at the hydride grain surface by ortho-hydrogen molecules or some impurity. The relaxation rate would depend on the rate at which ions reach the surface of the hydride grains. Assuming that the ions perform a random walk and using an average jump time of $10^{-11}$ s the mean time to reach the surface of a grain of 50 $\mu$m diameter would be on the order of $10^4$ s for a step length of 2.5 $10^{-10}$ m. This is much too slow as this time has to be considerably shorter than the
observed spin-lattice relaxation time. While spin diffusion is clearly possible for spins larger than 1/2 it can certainly not explain the Sc-\(T_1\) values observed. If we calculated the spin diffusion constant \(D_S\) using an expression derived by Lowe and Gade\(^{89}\) we obtain \(D_S = 2 \times 10^{-17} \text{ m}^2\text{s}^{-1}\), which would give rise to exceedingly long relaxation times.

**Paramagnetic Impurities**

Relaxation through paramagnetic impurities can occur through atom or spin diffusion. We already saw that spin diffusion is several orders of magnitude too slow to effectively transport magnetization to the paramagnetic impurities. In this slow spin diffusion regime the bottleneck for relaxation is given by the rate at which spins reach the impurity. When atom diffusion reaches the same magnitude as spin diffusion we expect the relaxation rate due to paramagnetic impurities to start increasing. When \(D_a = D_S = 10^{-17} \text{ m}^2\text{s}^{-1}\) we obtain a value for \(\tau_{SC}\) of \(4 \times 10^{-3}\) s. We define \(\tau^{-1}(d)\) as the relaxation rate of a single Sc nucleus which is held at distance \(d\) from the paramagnetic ion. With further increase in temperature we reach the region of fast atomic diffusion where \(R_{IP}\) reaches a maximum when \(\tau_{SC} = \tau(d)\). It has been shown by Bloembergen\(^{90}\) that \(\tau^{-1}(d)\) is given by:
\[
\tau^{-1}(d) = \frac{C}{d^6},
\]

The term \( C \) measures the interaction strength between the ion and nucleus and is related to the gyromagnetic ratios of impurity ion \( \gamma_p \) and nucleus \( \gamma_n \) by:

\[
C \propto \gamma_p^2 \gamma_n^2 \tau_i,
\]

for \( \omega_e \tau_i \gg 1 \) and \( \omega_0 \tau_i \gg 1 \), where \( \tau_i \) is the spin-lattice relaxation time of the ion. For s-state ions such as \( \text{Gd}^{3+} \) it will follow a Korringa type behavior. The Larmor frequencies of nucleus and unpaired electron are given by \( \omega_0 \) and \( \omega_e \) respectively. We can now calculate the approximate relaxation rate of \(^{45}\text{Sc}\) due to paramagnetic impurities based on the results for \(^1\text{H}-T_1\text{p}\) in \(\text{ScH}_x\). Using the facts that \( \gamma_{\text{Sc}}^2/\gamma_{\text{H}}^2 = 4^{-2} \), \( r_{nn}^6(\text{Sc}) = 8r_{nn}^6(\text{H}) \) we obtain

\[
\frac{R_{1p/\text{max}}(\text{Sc})}{R_{1p/\text{max}}(\text{H})} = 256^{-1}.
\]

For protons in \(\text{ScH}_x\) the maximum relaxation rate due to paramagnetic impurities was determined to be on the order of 5 s\(^{-1}\) at 570 K. These estimates seem to exclude the possibility of paramagnetic impurities being the source of the high temperature \( T_1 \) decrease. Furthermore, the level of paramagnetic impurities would have to be substantial. An
additional decisive argument against this hypothesis comes from the observation that samples doped with 100 parts per million of Gd showed no change in high temperature $T_1$ behavior for either the $^{45}\text{Sc}$, $^1\text{H}$ or $^2\text{D}$ resonances in comparison with clean samples.

The full expression for the quantity $C$ defined in Eq. 90 is given by

$$C = \frac{2}{5} \gamma_p^2 \gamma_n^2 \hbar^2 J(J+1)\left[\frac{\tau_i}{(1+\omega_0^2 \tau_i^2)} + \frac{7\tau_i}{3(1+\omega_e^2 \tau_i^2)}\right]. \quad \text{[91]}$$

A derivation can be found in the above mentioned paper of Bloembergen. As can be seen from this expression we could in principle obtain a $T_1$ minimum when $\omega_e \tau_i = 1$. This $T_1$ minimum would be independent of the Larmor frequency of the nucleus, $\omega_0$. The low temperature secondary $^1\text{H}$-$T_1$ minimum produced by the paramagnetic impurities allows us to assert for the relaxation time of the paramagnetic ion $\tau_i$ that $\omega_e \tau_i >> 1$. We expect this condition still to hold in the region of the second high temperature $T_1$ minimum as $\tau_i$ follows a $T \tau_i = \text{constant}$ behavior and therefore does not reach the regime where $\omega_e \tau_i = 1$. 
Electronic Structure Transition

A change in the electronic density of states at the Fermi level, $N(\varepsilon_F)$, produced by some phase transition could cause a abrupt decrease of $T_1$ if $N(\varepsilon_F)$ decreases. The decrease should in this case be frequency independent and occur for all nuclei at the same temperature. The change in $N(\varepsilon_F)$ should also affect the Knight shift. The last two predictions are contradicted by the experimental observations. The turndown of the $^1H-T_1$ data occurs at a higher temperature than for the $^{45}Sc-T_1$ values. The Knight shift proceeds to increase linearly with temperature in the region of the anomalous $T_1$ behavior and we argued earlier that this would lead to a increase of $T_{1e}T$, which is in the wrong direction to explain the $T_1$ decrease.

Superionic Conductors

At temperatures near the second, high temperature $T_1$ minimum the jump frequency for the vacancies reaches $10^{12}$ s$^{-1}$ which is within two orders of magnitude of an optical phonon frequency ($10^{-14}$s$^{-1}$) and the time of flight between tetrahedral sites. The particles will therefore eventually enter a regime in which the jump diffusion model becomes
inadequate. The motion might be better described as fluidlike and has a more continuous character than envisioned by simple hopping. Furthermore, the correlation time for the dipolar and quadrupolar fluctuations is no longer on the same order as the mean residence time $\tau$ deduced from a simple hopping model. In a fluidlike regime we would not be able to define such a mean residence time in a physically meaningful way. The collective fluidlike motion of the interstitials in the metal crystalline cage could provide relatively long correlation times compared with the normal vacancy hopping times extrapolated to the high temperature region. The decrease of the $\text{Sc}-T_1$ values at high temperatures also hints at an increase in the number of entities which produce an EFG at the site of the Sc nucleus. The creation of Frenkel pair defects associated with a disordering of the hydrogen sublattice could certainly provide such an enhancement of the quadrupolar relaxation. As we approach a critical temperature $T_C$ the number of Frenkel pair defects would rise dramatically and we would observe a frequency independent $T_1$ decrease if $\omega_0 \tau << 1$. In this limit the quadrupolar relaxation due to the Frenkel pair defects would be given by

$$T_1^{-1} \propto \eta \tau,$$
where \( \eta \) represents the concentration of Frenkel pair defects and \( \tau \) the Frenkel pair vacancy hopping time. For the \(^1\!H\) relaxation rates the increase in defect concentration will not produce much of an increase in the dipolar relaxation rates, and the \( T_1 \) decrease must originate from a slowing down of the decay of the dipolar pair correlation functions. The formation of defect clusters could possibly give rise to some highly correlated motion of the interstitials.

These tentative ideas resemble various models proposed for superionic conductors. A good review of the physics of superionic conductors has been given by Boyce and Huberman.\(^{92}\) Superionic conductors show a disordering of one of the ion sublattices of the material near a critical temperature \( T_c \), leading in many cases to diffusion coefficients typical of those found in liquids. The superionic phase is characterized by mobile and immobile sublattices and in some instances the term sublattice melting has been employed to describe the rapid rise in ionic mobility for one of the sublattices. In the superionic phase the fluorides exhibit diffusion rates comparable to those of \(^1\!H\) and \(^2\!D\) in scandium hydrides and deuterides in the region of the high temperature \( T_1 \) minimum. The mean residence time \( \tau \) reaches \( 10^{-10} \) s at the turndown of \( T_1 \) at \( T_c \) and approaches \( 11^{-12} \) s in the vicinity of the high temperature minimum. These values agree well with the hopping times of the mobile species in PbF\(_2\), CaF\(_2\) and SrCl\(_2\) reported
by Hutchings et al.\textsuperscript{93} from neutron scattering measurements. Boyce, Mikkelsen and O'Keeffe\textsuperscript{94} measured the $^{19}\text{F}$ spin-lattice relaxation rates in PbF$_2$ over a wide temperature region including the transition to the superionic phase. Between $250^\circ\text{C}$ and $450^\circ\text{C}$ the spin-lattice relaxation rate follows the BPP model showing an apparent increase in activation energy. This increase can be accounted for by an increase in the number of defects as the fluorine sublattice begins to disorder giving rise to a distribution of activation energies. Boyce et al. point out that above $450^\circ\text{C}$ the behavior of $T_1$ cannot be explained by a simple jump diffusion model. $T_1^{-1}$ and the inferred correlation time ($T_1 \propto \tau^{-1}$ for $\omega_0 \tau \ll 1$) begin to increase rather than decrease. The fluorine hopping rate is very rapid in this region, and there must exist long lived correlations in the local environment associated with low frequency correlated modes of motion.

The similarity of this anomalous $^{19}\text{F}-T_1$ behavior in PbF$_2$ above $450^\circ\text{C}$ with our own $T_1$ results for ScH$_x$ and ScD$_x$ is remarkable. In the region where the F-$T_1$ turndown is observed the $T_1$ values are frequency independent as in our case. The dipolar pair correlation function for the presumably highly correlated motion of the fluorine ions now decays with a time constant $\tau_L$ characteristic of the associated long lived fluctuations in the dipolar interaction. This time $\tau_L$ has to be considerably longer than the normal mean residence time $\tau$. 
of the ions. In this regime of extreme motional narrowing, Boyce et al. write for the spin-lattice relaxation rate $T_1^{-1}$,

$$T_1^{-1} \propto (1-f_C)\tau + f_C\tau_L \quad \text{[92]}$$

with $\omega_0\tau < \omega_0\tau_L << 1$, where $\tau$ is the particle hopping time.

The fraction of fluorine atoms taking part in the cooperative motion is given by $f_C$. At very high temperatures we expect $\tau$ to be very small ($\tau = 10^{-12}s^{-1}$), and we can approximate $T_1^{-1}$ by $T_1^{-1} \propto f_C\tau_L$. We tried to reproduce our $T_1$ data using a sum of a BPP function for the low temperature $T_1$ minimum and an expression of the form,

$$T_1 = C f_C \omega_0 \tau_L$$

for the high temperature $T_1$ decrease. The increase with temperature of the fraction of Frenkel pair defects or interstitials associated with the highly correlated motion $f_C$ was assumed to be described by a Boltzmann factor $\exp(E_D/kT)$, and $\tau_L$ was chosen to have the familiar form

$$\tau_L = \tau_L \exp(E_a'/kT)$$

A nonlinear least squares fit of the Sc-$T_1$ data for a representative scandium hydride to this functional form was
not possible without substantial deviations of the function
curve from our high temperature data points. The reason for
this could be an increased growth of the number of defects in
the region of the T₁ decrease. Huberman, in an attempt to
model the cooperative phenomena associated with the transition
to the superionic phase assumed the Helmholtz free energy to
be of the following form

\[ F = U₁f_c + U_jf_c^2 - 2kT[f_c\ln f_c + \]
\[ (1-f_c)\ln(1-f_c) + 3/2f_c\ln\Gamma]. \]  

The first two terms with prefactors U₁ and U_j correspond to a
Taylor expansion of the energy contribution U of a Frenkel
pair. U₁ is related to the energy of formation of a Frenkel
pair. The term U_jf_c^2 accounts for interactions between
Frenkel defects. The remaining terms are contributions to the
entropy of the system: a configurational part and a phonon
term with \( \Gamma = \omega_i/\omega \) where \( \omega_i \) and \( \omega \) are the average
phonon frequencies of the ion at the interstitial sites
occupied in the disordered phase and its regular lattice site
respectively. Minimizing the free energy functional with
respect to \( f_c \) one obtains

\[ f_c = \{r^{3/2} \exp[1/2 \beta (U₁ - 2f_cU_j) + 1] \}^{-1}, \]  

[94]
FRACTION OF FRENKEL PAIR DEFECTS

reaches 1 when sublattice melts

Fig. 28: Fraction of Frenkel pair defects on hydrogen sublattice
which is a transcendental equation. The behavior of this equation for various choices of $U_i$ and $U_j$ is shown in Fig. 28. We chose for this the parameter $\Gamma$ rather judiciously to be 0.2. It determines the temperature of transition to the superionic phase. For very weak interactions ($U_j \ll U_i$) $f_c$ shows an Arrhenius type behavior. As explained earlier this will not give satisfactory agreement with our experimental $T_1$ values at high temperatures. For $U_i = 3U_j$ one observes a deviation from an exponential increase above a certain temperature threshold which defines $T_c$. The number of defect interstitials and associated vacancies on the mobile sublattice will show a faster than exponential growth above $T_c$ while following an Arrhenius type behavior below $T_c$.

Superionic fluorides are thought to show such behavior, leading to a Schottky type specific heat anomaly at $T_c$. $U_i = 1.15U_j$ will give rise to a first order phase transition. $T_c$ denotes the temperature where the defect growth will diverge.

Boyce and Huberman\textsuperscript{96} also undertook a NMR study of CuI and interpreted the insulator to superionic phase transition as a process of sublattice melting. This model of a liquid of mobile ions coupled to the crystalline cage has been treated by Huberman and Martin.\textsuperscript{97} Light scattering constitutes another experimental tool which is useful in studying the dynamics of such ionic fluctuations.\textsuperscript{98} The light scattering
intensity at frequency shift $\omega$ and wave vector change $k$ with respect to the incident light can be expressed in terms of local fluctuations of the dielectric constant, \[ I(k,\omega) \propto \int_{-\infty}^{\infty} dt \int d^3r \int d^3r' e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \langle \delta \varepsilon(r',0) \delta \varepsilon(r,t) \rangle. \]

The angular brackets denote an ensemble average. In monatomic liquids where molecular rotations and vibrations are absent, the change in dielectric constant is caused by density fluctuations. Nemanich et al.\(^9\) report the results of light scattering on CuI and AgI in the $\alpha$ and melt phases. In the $\alpha$ phase, which corresponds to the superionic phase, CuI has an fcc lattice of I ions, and the Cu ions occupy predominantly the tetrahedral interstitial sites. The low frequency inelastic light scattering spectra for CuI have narrow and broad spectral components. The broad spectral component can be related to jump diffusion, and its width is proportional to the inverse hopping time. The main features of the narrow spectral component cannot be explained in terms of ions diffusing in a continuum even if interactions are included or in terms of a simple hopping model. Instead, it seems that the ions form highly correlated configurations, where an ion is screened by neighboring ions as in a fluid, but the motion of these ionic quasiparticles still reflects the periodic potential of the lattice structure. Due to interactions the
ions are displaced from the tetrahedral sites and form lower symmetry configurations.

Catlow et al.\textsuperscript{100} report Brillouin scattering experiments (light scattering from acoustical phonons) in the superionic fluorides. These measurements reveal the temperature dependence of the elastic constants. It seems that the symmetry of the fluorine sublattice is strongly affected by the formation of Frenkel pair defects around the transition temperature $T_C$. Lattice anharmonicity should produce a linear decrease of the elastic constants with temperature. The elastic constant $C_{11}$ shows a considerably larger nonlinear decrease which can only be explained by the formation of defects and the disordering of the fluorine sublattice. The elastic constant $c_{11}$ appears to couple to the order parameter of the second order transition while $c_{12}$ and $c_{44}$ decrease only linearly. The authors do not clarify the question of the nature of the order parameter and this seems to be a general difficulty for the superionic phase transition. Intuitively it seems that the mean square displacement of the mobile ions could constitute a useful order parameter. Neutron diffraction measurements which allow the determination of the mean square displacement indeed show an anomalous and rather abrupt increase of the mean square displacement as a function of temperature near $T_C$. 

Before discussing any neutron scattering results for superionic fluorides we would like to clarify the terminology used. It is customary to separate the differential scattering cross section into coherent and incoherent parts. The coherent part is related by a Fourier transform to the time dependent pair correlation function $G(r_{\alpha}, r_{\beta}, t)$, where the position of the pair constituents is given by $r_{\alpha}$ and $r_{\beta}$. If we integrate this term over all energy transfers for a certain value of wave vector the result is a picture of the average nuclear density. If we exclude from the coherent part the contribution from elastic or Bragg scattering we obtain the dynamical contribution which allows measurement of the phonon dispersion curves. The incoherent part of the scattering function is related to the self correlation function of the particles. If an atom diffuses randomly its motion will increase the energy width of the scattered neutron beam and we will measure the quasielastic scattering cross section. Both NMR and neutron scattering allow a determination of the pair correlation function. The spectral density functions determining the NMR relaxation rates give only the frequency spectrum of the pair correlation. The wave vector dependence is averaged and limited by the range of the interactions contributing to the spin relaxation.

Superionic conductors with the fluoride structure such as $\text{SrCl}_2$, $\text{CaF}_2$ and $\text{PbF}_2$ have been studied extensively by
neutron scattering. Hutchings et al. (see earlier reference 93) carried out such measurements and present a model involving short lived clusters of interstitials to interpret the diffusive coherent quasielastic scattering results. The clusters (Fig. 29) are formed around Frenkel pair anions located close to the mid-anion position but displaced along the $<110>$ direction into an empty cube in the simple anion sublattice. In the presence of such a Frenkel pair anion the neighboring anions on regular tetrahedral sites are slightly displaced from their positions in the $<111>$ direction away from the Frenkel anion toward the adjacent empty cube center. The best agreement with the neutron scattering results is reached for clusters with one Frenkel pair anion at the center and 8 relaxed anions on nearest neighbor and next nearest neighbor sites. Fig. 29 shows a simpler cluster configuration involving only two relaxed hydrogen atoms. The Frenkel pair vacancy will in most cases be located one lattice spacing away from the relaxed anions. Catlow and Hayes$^{101}$ employed static energy calculations and suggest that the Frenkel pair vacancy stabilizes the cluster.

The energy of the diffusive coherent scattering function $S_D(Q, \omega)$ is inversely proportional to the cluster lifetime $\tau_{coh}$. The cluster lifetime obtained from the observed energy widths is on the order of $10^{-12}$ s. It seems that the cluster lifetime is roughly equal to the hopping time of interstitials
which are not members of a cluster. A cluster lifetime of $10^{-12}$ s corresponds approximately to the mean interstitial residence time in ScH$_x$ and ScD$_x$ at the high temperature $T_1$ minimum. We argued before that the proton $T_1$ results should be interpreted as an increase in the correlation time for the dipolar fluctuations in the local environment of the relaxing proton. This explanation was similar to one put forward by Boyce and Huberman for PbF$_2$ in their interpretation of the $^{19}$F-$T_1$ behavior near the transition to the superionic phase.

The neutron scattering results of Catlow and Hayes do not seem to support such a conclusion and it is not immediately apparent how one could resolve this contradiction between the NMR and neutron scattering results. It is easier to reconcile the short cluster lifetimes with our Sc-$T_1$ data and to a lesser degree with our $^2$D-$T_1$ results. In the first place, the effect of the clusters on the Sc spin-lattice relaxation would be the creation of additional EFG-sources and not a noticeable increase of the quadrupolar correlation time.

The creation of clusters gives rise to additional sources of electric field gradients. To estimate this additional contribution to the quadrupolar relaxation rate we assume the clusters to be essentially static over their lifetime $\tau_{c1}$. The frequency independence of the high temperature $T_1$ data requires that $\omega_0 \tau_{c1} < 1$. In this region of extreme motional narrowing we can approximate the quadrupolar relaxation rate due to the clusters by
where \( n_{c1} \) gives the concentration of cluster interstitials. The rapid decrease of \( T_1 \) at high temperatures is due to an increase of \( n_{c1} \). To obtain an estimate of the cluster lifetime from our Sc-\( T_1 \) measurements we compare the quadrupolar relaxation rate at the lower temperature Sc-\( T_1 \) minimum with the rate at the high temperature minimum. At the lower temperature Sc-\( T_1 \) minimum we have \( \omega_0 = 1 \). We can therefore write for the ratio of the relaxation rates at the two minima

\[
(T_{1q})^{-1}/(T_{1q})^{-1} = [(e^2qQ)^2_{c1} n_{c1} \tau_{c1}]/[(e^2qQ)^2_v c_v \tau_v/2].
\]

For Sc\( _x \) an average value for the vacancy concentration \( c_v \) is 0.05 \((x=1.9)\) and neutron scattering experiments on the superionic fluorides yield an estimate of the maximum concentration of interstitials \( n_{c1} = 0.25 \). Estimates of the ratio of interaction strengths \((e^2qQ)^2_{c1}/(e^2qQ)^2_v\) indicate that the electric field gradient created by the relaxed anions at the site of a Sc-nucleus is canceled by the vacancy left behind at the tetrahedral site by the relaxed anion. The Frenkel interstitial ion at the center of the cluster produces a rather large EFG at the site of a nearby Sc nucleus. If one neglects conduction electron screening and antishielding...
effects the ratio of interaction strengths is roughly 2.5. Using these estimates in the above equation for the ratio of relaxation rates we obtain

\[
\frac{(T_{1q})^{-1}_{cl}}{(T_{1q})^{-1}_{v}} = 25\omega_0\tau_{cl}.
\]

For the cluster model the high temperature Sc-T₁ decrease implies the validity of following two conditions: (a) \(\tau_{cl} > \tau_v\) and (b) \(\omega_0\tau_{cl} < 1\). At the temperature of the cluster induced minimum, \(\omega_0\tau_v = 10^{-3}\), so that we need to have \(\omega_0\tau_{cl} > 10^{-3}\). Condition (b) gives an upper limit for \(\omega_0\tau_{cl}\). These limits mean that the ratio of relaxation rates \(\frac{(T_{1q})^{-1}_{cl}}{(T_{1q})^{-1}_{v}}\) should fall in the range of 0.25 to 2.5. The picture emerging from the experiments of Catlow and Hayes indicates that sublattice melting does not take place. A single crystal diffraction study of PbF₂ by Dickens et al. leads to a similar model of short lived clusters. The measured intensities of the Bragg reflections corrected for systematic errors were compared with the intensities calculated from a model of average anion positions in the presence of Frenkel pairs. In addition to the usual Debye-Waller factor an anharmonic component of the thermal vibrations of the fluorine lattice was included in the analysis of the Bragg peak intensities. Least squares fits of the various models of anion disordering to the data led to the following
conclusions: The number of interstitial Frenkel pairs and relaxed anions grows rapidly near $T_c = 711 \text{ K}$, the transition temperature to the superionic phase. A cluster model very similar to the one described above reproduces the experimental results quite well.

The results of a powder neutron diffraction study\(^{103}\) of ScD\(_{1.8}\) show none of the distinctive features observed in superionics with the fluoride structure. The mean square displacement shows a linear dependence on temperature up to 1250 K. It ranges from roughly 0.01 A\(^2\) at 350 K to 0.04 A\(^2\) at 1250 K. The scandium mean square displacement increases from 0.005 A\(^2\) to 0.023 A\(^2\) over the same temperature range. This is in contrast to the results for superionic fluorides which show an anomalous increase in the anion mean square displacement near $T_c$.\(^{104}\) The neutron diffraction data for ScD\(_{1.8}\) allow only for a gradual increase in the number of Frenkel defects. Cooperative effects would produce a large increase in the number of defects, and this would be reflected in a nonlinear increase of the mean square displacement as a function of temperature in the region of the phase transition. Having to work with a polycrystalline instead of a single crystal sample, the observation of only seven Bragg peaks and poor energy resolution limited the precision of the measurements. The results nevertheless totally exclude the possibility of substantial sublattice disordering or melting. They do not
rule out the existence of clusters, but the number of clusters would have to grow gradually. The results for the superionic fluorides showed that the displacement of the relaxed anions is relatively small.

Gillan\textsuperscript{105} undertook molecular dynamics simulations for the superionic fluorides \( \text{PbF}_2 \) and \( \text{CaF}_2 \). A computer generated graphical representation of the anion trajectories reveals that above \( T_C \) the anions execute large amplitude vibrations about their equilibrium sites and for large enough displacements this leads to jumps between equilibrium sites. The anion sublattice is still very well defined. These computer simulations suggesting the importance of large amplitude anion vibrations in the superionic phase led to a rather elegant model to explain the high temperature \( T_1 \) decrease observed for the scandium hydrides and deuterides.

\textbf{Richards' Model}

Richards\textsuperscript{106} studied the effects of large amplitude vibrations on the motion of hydrogen and deuterium in scandium hydrides and deuterides. The nearest neighbor jumps between tetrahedral sites can proceed over the direct path connecting the two sites or through the octahedral interstitial site. The two jump paths have different activation energies
associated with them. The saddle point energy is lower for a jump of an atom through the octahedral site. Jumps through the octahedral interstitial site presumably dominate at temperatures below the high temperature $T_1$ minimum. Large amplitude vibrations of surrounding interstitials towards the octahedral site increase the saddle point energy which must be overcome by a hopping particle. According to Richards we can write for the saddle point energy

$$E_s = E_a + n^* J,$$  

[96]

where $n^*$ gives the number of interstitials competing for the octahedral site during large amplitude displacements in the direction of that site. The repulsion between interstitials as they approach the octahedral site raises the saddle point energy by an amount $J$ per interstitial. The energy levels of the interstitials are described by harmonic oscillator levels below some energy $U$ and "particle in a box" levels above $U$.\(^{107}\) The box volume is given by the space available per hydrogen atom after excluding the volume occupied by the Sc atoms. Only nearest neighbor interstitials with an energy larger than $U$ contribute to a rise in the saddle point energy at the octahedral site. The excited particle states are extended states. The probability of finding the particle in an excited "particle in box" state can be expressed as
where $Z_{\text{box}}$ is the partition function $\text{Tr}_S\{\exp(-\beta E_S)\}$ and the trace extends over all "particle in a box" states $s$. $Z_{\text{vib}}$ is defined similarly. It has been shown by Richards that the average hopping rate is, using this model, given by

$$
\nu = \nu_0 \exp(-E_a/kT) \left[ 1 + (\exp(-J/kT) - 1)P^*(1-c) \right]^6 + \nu_0'\exp(-E_a'/kT).
$$

The first term of this equation is nearly identical to Eq. 85 for the model of interacting particles except for the factor $P^*$. The exponent 6 reflects the fact that we excluded the hopping particle and the vacant site the atom tries to reach from the count of nearest neighbor atoms of the octahedral site which could increase the saddle point energy if they were in an excited state. The last term of the above equation gives the hopping rate for direct jumps between tetrahedral sites. As has been shown by Richards it possible to fit the Sc-Ti data quite well with this equation for the hopping frequency and a Lorentzian spectral density (BPP model). $E_a$ and $\nu_0$ were chosen to give good agreement with the low temperature $T_1$ minimum. The repulsion strength was set to $J=0.5$ eV. For ScH 1.83 and ScD 1.98 U falls into the region of 0.4 to 0.5 eV, while one obtains values for $E_a'$ on the order of 1.4 eV.
The high temperature T\textsubscript{1} minimum can with this model be explained as a slowdown of the particle motion. Large amplitude displacements towards the octahedral site block particles attempting to hop through that site. Direct jumps between tetrahedral sites will become dominant but the high activation energy associated with this channel of motion leads to an overall reduction of the average particle and vacancy hopping rates. The lifetime of an excited "particle in a box" state is presumably on the order of 10\textsuperscript{-12} s or smaller. This corresponds roughly to the lifetime of a cluster in the superionic fluorides as determined by Dickens et al.\textsuperscript{102} In scandium hydrides the relaxed hydrogen atoms within a cluster could be responsible for a rise of the saddle point energy at the octahedral site and the lifetime of the cluster would in Richards' model correspond approximately to the vibration period for a large amplitude displacement. We would for Richards' model expect a T\textsubscript{1} decrease for all three nuclear species but it is not obvious why the decrease of the \textsuperscript{1}H-T\textsubscript{1} values occurs at a higher temperature than for the \textsuperscript{45}Sc-T\textsubscript{1} data. It was not possible to reach with the above equation the bottom of the high temperature Sc-T\textsubscript{1} minimum for ScD\textsubscript{1.98}. The fact that for ScD\textsubscript{1.99} (Fig. 25) the second high temperature Sc-T\textsubscript{1} minimum is actually deeper than the first minimum indicates either the presence of an additional source of spin-lattice relaxation or that the number of vacancies
increased slightly with temperature. The change in vacancy concentration could be attributed to the formation of Frenkel defects. The escape of hydrogen from hydride grains is presumably negligible. The apparent invariance of the depth of the high temperature Sc-\( T_1 \) minimum with a change in vacancy concentration seems to support this assertion.

Conclusions on High Temperature Results

The jump frequencies observed in scandium hydrides and deuterides in the region of the \( T_1 \) decrease are on the same order as for the superionics with the fluoride structure near the transition temperature to the superionic phase. The \( T_1 \) decrease (and \( T_2 \) decrease for \(^1\)H-resonance) for the three nuclear species \(^{45}\)Sc, \(^2\)D and \(^1\)H suggest a slowdown of the particle diffusion and/or the existence of highly correlated modes of motion. Molecular dynamics calculations for the superionic fluorides indicate that the anions execute large amplitude vibrations about their equilibrium sites above \( T_c \) and exclude the possibility of sublattice melting. In scandium hydrides and deuterides large amplitude motion towards the octahedral site would cut off the motion between nearest neighbor sites through the octahedral interstitial site. This and the high activation energy for direct jumps
between tetrahedral sites would lead to the required slowdown of the hydrogen diffusion. The hydrogen motion would still have to be fast enough to ensure \( \omega_0 \tau \ll 1 \), which is necessary to observe frequency independent \( T_1 \) values. The creation of Frenkel defects at high temperatures gives rise to the formation of short-lived clusters of interstitials and additional sources of electric field gradients at the site of the Sc nucleus. The existence of such clusters above a critical temperature \( T_c \) has been ascertained for the superionic fluorides. There is at the time of this writing no experimental evidence for a second order phase transition in scandium hydrides and deuterides at high temperatures analogous to the cooperative phenomena seen in superionic fluorides at their transition temperature \( T_c \).
Fig. 29: Cluster of Frenkel defect and relaxed anions
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