1973

Thermal expansion of solid neon from 1 to 15 K

James Clifton Holste
Iowa State University

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James Clifton Holste

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CHAPTER I. INTRODUCTION

Molecular solids rank among the most elementary solids, and therefore they are natural subjects for detailed study. The electrons in the molecular solids generally are confined to a single molecule, and the molecular properties are similar in both the solid and gaseous states. In particular, the two-body molecular interactions in the gaseous phase are not appreciably different from the two-body interactions in the solid state, so molecular scattering results and gas phase data can be used to obtain empirical descriptions of these interactions. A completely successful theory of solids will derive these molecular interactions from basic physical laws, but such a theory does not exist as yet, and the empirical representations are quite useful for present solid state theoretical calculations. The monatomic rare gas solids form the simplest class of molecular solids, in which the atoms have completely-filled electron shells and spherically symmetric shapes. Most of the theoretical and experimental work on molecular solids has been carried out with these.

The bulk properties of all solids can be compared qualitatively by using various reduced representations such as that suggested by the Debye model of specific heats. Appropriate scaling factors for one such comparison are the $T=0$, $P=0$ bulk modulus $B_0$, volume $V_0$ and Debye temperature $\Theta_0$, with results expressed as reduced pressure $(P/B_0)$, volume $(V/V_0)$ and temperature $(T/\Theta_0)$. The rare gas solids have relatively small Debye temperatures and bulk moduli, so a wide range of reduced parameters is available to the experimentalist, but experimental work has lagged theoretical calculations until only recently because of difficulties
associated with measurements on substances with low triple point temperatures and high vapor pressures, to mention just a few of the troublesome properties.

The atoms in a solid may be regarded as a collection of oscillators which are located in asymmetric potential wells, and as such they have an energy (zero point energy) and amplitude (zero point amplitude) of oscillation even when in the ground state. This zero point energy can have a significant effect on the properties of the solid in cases such as the rare gas solids where the interatomic forces are rather weak.

In the classical limit, the zero point motions are sufficiently small that the portions of the potential well which the oscillator samples may be adequately described as a harmonic potential with a small anharmonic correction. In the quantum solid limit, the zero point vibrations become so large that neighboring atoms are affected and strong correlations exist between the motions of neighboring atoms. These short-range correlations essentially dominate the properties of the solid. In the intermediate region, the short-range correlations are not significant, but the zero point amplitudes are sufficiently large that the oscillator samples a very anharmonic portion of the potential.

Solid neon is of specific interest since it lies in the intermediate region where the zero point energy is important, but does not dominate the properties of the solid. Theoretical calculations on neon must be performed carefully, since neither the classical limit of small harmonic oscillations nor the quantum solid limit of short-range correlations is valid. Solid neon, therefore, should present an excellent test for
present theoretical techniques.

Thermodynamic relations between the macroscopic properties of solids were formulated long before reliable methods existed for relating macroscopic properties to the microscopic properties of the atoms which form the solid. All of the bulk thermodynamic properties of a solid are contained in the Helmholtz free energy \( F(T,V) \), which is defined as

\[
F = U - TS, \tag{1-1}
\]

where \( U \) is the internal energy, \( T \) is the absolute temperature, and \( S \) is the entropy. The various derivatives of \( F \) give the equation of state \( P(V,T) \), the entropy \( S(V,T) \), the specific heat at constant volume \( C_V(V,T) \), the isothermal bulk modulus \( B_T(V,T) \), and the volume thermal expansion \( \beta(V,T) \) as

\[
P = -\left( \frac{\partial F}{\partial V} \right)_T,
\]

\[
S = -\left( \frac{\partial F}{\partial T} \right)_V,
\]

\[
C_V = \left( \frac{\partial U}{\partial T} \right)_V = -T\left( \frac{\partial^2 F}{\partial T^2} \right)_V,
\]

\[
B_T = -V\left( \frac{\partial P}{\partial V} \right)_T = V\left( \frac{\partial^2 F}{\partial V^2} \right)_T,
\]

and

\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{B_T} \left( \frac{\partial^2 F}{\partial T \partial V} \right)_T.
\]

In the special case where
\[ F = T \Phi \left( \frac{V}{T} \right), \quad (1-2) \]

with \( \Phi \) a function of volume only, the Mie-Grüneisen equation of state is obtained as:

\[ P = - \frac{d\Phi}{dV} + \frac{\gamma U}{V}. \quad (1-3) \]

Here \( U_0 \) represents the static energy of the lattice and

\[ \gamma(V) = - \frac{d \ln \Theta}{d \ln V} \quad (1-4) \]

is the Grüneisen parameter and is a function of volume only. Another version of Equation 1-3, which can be obtained by differentiation with respect to temperature, is given by

\[ \gamma = \frac{\beta B_T V}{C_V} \quad (1-5a) \]

The quantities measured experimentally in most cases are the heat capacity at constant pressure,

\[ C_P = T \left( \frac{\partial S}{\partial T} \right)_P, \]

and the adiabatic bulk modulus

\[ B_S = -V \left( \frac{\partial P}{\partial V} \right)_S. \]

The heat capacities at constant volume and at constant pressure are related by

\[ C_P = C_V (1 + \gamma T), \]

and the adiabatic and isothermal bulk moduli are related by
\[ B_S = B_T (1 + \beta \gamma T), \]

so that

\[ \frac{B_S}{B_T} = \frac{C_P}{C_V}. \]

Equation 1-5a then can be written as

\[ \gamma = \frac{\beta B_S V}{C_P} \quad (1-5b) \]

or, if heat capacity data at constant volume are available,

\[ \gamma = \frac{\beta B_S V}{C_V (1 + \beta \gamma T)}. \quad (1-5c) \]

While \( \beta \gamma T \) is small for most solids (~0.05 at 300 K for copper), it can be quite large (0.2 at 20 K for neon) for the rare gas solids. The initial assumptions of the Mie-Grüneisen equation of state are not exactly correct, but the Grüneisen parameter for most solids varies only slowly with temperature and provides a convenient means for examining the relationship between experimental data for \( C_p \) and \( \beta \), each of which may vary by several orders of magnitude even at low temperatures.

The free energy may be calculated from the microscopic or atomic properties of a solid using statistical mechanics. For a canonical ensemble, the free energy is given by:

\[ F = -\frac{1}{\beta} \ln \text{Tr}[\exp(-\beta H)]. \quad (1-6) \]

Here \( \beta = \frac{1}{k_B T} \), where \( k_B \) is Boltzmann's constant and \( H \) is the Hamiltonian.
for the system, so the problem becomes one of evaluating the characteristic energies of the crystal. The usual approximation (1) is to expand the potential energies of the individual particles about their equilibrium positions in a Taylor series, with the total potential energy operator assuming the form:

\[ V = \sum_{n=0}^{\infty} V_n, \]

where \( V_n \) contains \( n \)th derivatives of the potential function evaluated at the equilibrium positions and is of \( n \)th order in the atomic displacements. Since the derivatives are evaluated at the equilibrium positions, \( V_1 = 0 \) and

\[ V = V_0 + V_2 + V_3 + V_4 + \ldots \]

and the total energy is given by

\[ H = V_0 + (E_k + V_2) + (V_3 + V_4 + \ldots) \]

\[ = V_0 + H_{\text{harm}} + H_{\text{anh}}, \]

where \( E_k \) is the total kinetic energy operator. Here \( V_0 \) operates on the crystal to give the static lattice energy, \( H_{\text{harm}} \) is a solvable harmonic Hamiltonian, and \( H_{\text{anh}} \) contains the anharmonic contributions to the energy of the crystal. The free energy then assumes the form

\[ F = F_0 + F_{\text{harm}} + F_{\text{anh}}, \quad (1-7) \]

where \( F_0 \) is the static lattice energy (\( F_0 \) is equivalent to \( U_0 \) in Equation 1-3), \( F_{\text{anh}} \) is the anharmonic contribution to the free energy, and \( F_{\text{harm}} \) is the well-known harmonic result.
The sum over $\omega_i$ in Equation 1-8 is carried out over all the allowed harmonic normal mode frequencies of the crystal. These normal mode frequencies are calculated from the secular equation for the dynamical matrix, and they depend directly on the second derivatives of the interatomic potential function as evaluated at the equilibrium lattice positions. In a purely harmonic crystal, the normal modes have no volume dependence, so the mixed volume and temperature derivative is identically zero and such a crystal has no thermal expansion.

The quasi-harmonic approximation provides a simple method for including a first order anharmonic contribution to the free energy. Contributions from the third derivative are used to calculate the normal mode frequencies so that the frequencies $\omega_i(V)$ are volume-dependent. At any given temperature, the $\omega_i(V)$'s are determined by the lattice spacings which result in the minimum total free energy for the crystal at that temperature. The quasi-harmonic frequencies $\omega_i(V)$ replace the harmonic frequencies $\omega_i$ in Equation 1-8 in the calculation of the free energy, and hence the bulk properties, of the solid. Equation 1-8 also may be written in the form

$$F_{\text{harm}} = \sum_i \left( \frac{\hbar^2}{2 \omega_i} + kT \ln \left[ 1 - \exp(-\frac{\hbar \omega_i}{kT}) \right] \right) \quad (1-8)$$

$$= F_{zp} + F_{\text{thermal}} \quad (1-9)$$

where $(F_{\text{harm}})_i$ represents the free energy associated with each normal
mode of the crystal. Each \( F_{\text{harm}} \) has the functional dependence assumed in Equation 1-2 if \( \Theta(V) \) is replaced by

\[
\frac{\hbar \omega_i(V)}{k_B},
\]

so it is reasonable to define a Grüneisen parameter for each normal mode by

\[
\gamma_i = \frac{\frac{d \ln \omega_i}{d \ln V}}{k_B T}.
\]

The bulk Grüneisen parameter then is given in terms of the \( \gamma_i \)'s by:

\[
\gamma = \frac{\sum \gamma_i C_{vi}}{\sum C_{vi}}.
\]

Furthermore, this procedure is reasonable for any solid where the anharmonic contributions to the free energy can be written as:

\[
F_{\text{anh}} = \sum_i (F_{\text{anh}})_i
\]

where \( (F_{\text{anh}})_i \) is a function of

\[
\frac{\hbar \omega_i(V)}{k_B T}.
\]

A more exact computation of the anharmonic contribution to the free energy is difficult and tedious, but unfortunately quite necessary for solids such as neon where the zero point energy is important. Considerable attention has been devoted to the self-consistent phonon theory, where \( F_{\text{harm}} \) and the leading terms of \( F_{\text{anh}} \) are evaluated by considering the
motions of the atoms in a self-consistent fashion when the normal mode frequencies for the system are calculated. A brief history of the evolution of the self-consistent theory is offered by Klein and Horton (1), and a review of the application of the theory to quantum solids is given by Werthamer (2). Goldman, Horton, and Klein (3) have used the self-consistent theory of Choquard (4) to obtain an expression for the first order anharmonic contribution to the free energy of solid neon:

$$ F^{(1)}_{\text{anh}} = -\frac{1}{4} \sum_\omega \hbar \omega \coth(\frac{\hbar}{2} \beta \omega), \quad (1-14) $$

and Gillis, Werthamer, and Koehler (5) have used a variational approach to obtain the same result. Goldman et al. (3) also have calculated a second order anharmonic correction $F^{(2)}_{\text{anh}}$ which contains products of the normal mode frequencies. Only $F^{(2)}_{\text{anh}}$ shows departures from the functional form leading to the microscopic Grüneisen parameters in Equations 1-11 and 1-12; this suggests that the Mie-Grüneisen equation of state should be useful in a description of the equation of state for solid neon. Monte Carlo calculations (6) and calculations using the harmonic approximation at high densities (7) have obtained equivalent results for the solid properties of neon when the same potential function is used. A number of earlier calculations for neon also exist, but these generally were inadequate in one or more respects, and references to them may be found in any of several recent reviews of the properties of the rare gas solids (8,9,10).

All statistical mechanics calculations of the free energy require a description of the interatomic potentials as input data. Such potentials cannot be calculated from the first principles as yet, so several.
empirically derived but qualitatively justifiable representations have been used. The general characteristics of the interactions between two rare gas atoms are a repulsive force which exists when the interatomic spacing is so small that the electron clouds begin to overlap, and a long range attractive force which arises because of van der Waal's interactions between the electron clouds. The most common form of two-body potential is the Lennard-Jones (LJ) potential

\[ V(r) = \frac{mne}{m-n} \left\{ \frac{1}{m} \left( \frac{a}{r} \right)^m - \frac{1}{n} \left( \frac{a}{r} \right)^n \right\} \]

where \( n \) is usually chosen as 6 to correspond to the van der Waal's interaction, \( m \) is either 12 or 13, \( e \) is the depth of the potential minimum and \( a \) is the atomic separation for which the potential minimum occurs. The Buckingham potential describes the repulsive interaction with an exponential:

\[ V(r) = \frac{6me}{m-6} \left\{ \frac{1}{m} \exp[-m(a/r) - 1)] - \frac{1}{6} \left( \frac{a}{r} \right)^6 \right\} \]

where the parameters \( m \), \( e \) and \( a \) are defined as in the case of the LJ potential. The Morse potential contains only exponential terms and has the form:

\[ V(r) = e\{\exp[-2C\left( \frac{r}{a} - 1\right)] - 2 \exp[-C\left( \frac{r}{a} - 1\right)]\}. \]

Other forms for the interatomic potentials have been used historically but are of little importance at present. These are summarized by Horton (8) and will not be discussed here. In all cases, these \textit{ad hoc} potentials were matched to gas phase data or to the cohesive energy and 0 K molar volume for the solid to determine the adjustable parameters. The
potentials then were used to calculate the bulk properties of the solids, with reasonable results in the first approximation.

The theory of lattice dynamics only recently has become sufficiently developed that the disagreements between theory and experiment may be attributed to inadequacies in the form of the potential functions as well as in the implicit assumption that only two-body interactions are important. Interest in interatomic potentials has been revived by the improvements in the theory of solids, and specific two-body potentials have been developed for argon (11,12,13) and krypton (14) which are based on single particle scattering results and selected solid state properties. These potentials produce excellent agreement with experiment, but only if three-body interactions also are included. Zucker and Doran (15) have extended three-body interaction calculations through the triple-quadrupole interaction, and they give results for the three-body contributions to the cohesive energies and the bulk moduli for Ne, Ar, Kr, and Xe. The three-body interactions for neon are not as large as those for the heavier gases, but they still contribute 4% to the cohesive energy and 8% to the bulk modulus and so they are not negligible.

Recent interatomic scattering experiments (16) have been used to generate a two-body potential function for neon which gives a good description of the gas phase properties (17), but which does not adequately describe the solid state properties (18). The scattering experiments were repeated at lower energies (19), and a new set of potential parameters has been obtained. These parameters produce reasonable results for the cohesive energies and for the temperature dependence of the bulk modulus.
at zero pressure, but they do not give good agreement for the pressure
dependence of the bulk modulus (19). An adequate two-body potential has
not been found as yet for neon, but the recent work definitely has shown
that the LJ 6-12 potential is not correct (16,19). Unfortunately, the
prospective new potentials are considerably less convenient to use than
the previous descriptions, since they are formed from a combination of
exponential functions for very small atomic separations, Morse potentials
in the intermediate regions, and van der Waal's dependences for large
separations, with the separate potentials joined smoothly using cubic
spline interpolating polynomials. The lack of success in predicting the
pressure dependence of the bulk modulus implies that even more pathological
forms may be required to obtain an adequate description of the two-body
interaction in neon.

Considerable thermodynamic data for solid neon have been reported
recently and most of the bulk properties have been determined. Heat
capacity measurements on natural neon have been made at both constant
pressure (20,21) and constant volume (22,23), and several measurements
have been reported for the separated isotopes $^{20}\text{Ne}$ and $^{22}\text{Ne}$ (22-25).
Figure 1 compares direct measurements of $C_p(T,P=0)$ for natural neon with
the results calculated by Fugate and Swenson (22) from very precise
direct $C_V$ measurements as a function of volume. The predicted results
agree with the results for $^{20}\text{Ne}$ given by Clusius et al. (24), and they
are consistent with the data of Fenichel and Serin (20) and Fagerstroem
and Hollis-Hallet (21) except for the high temperature tails which
probably are spurious. The analysis of the present data which is given
Figure 1. A comparison of \( C_p \) as calculated from the \( C_V \) results of Fugate and Swenson (22) and as obtained from the smoothed results of Fenichel and Serin (FS, 20), Fagerstroem and Hollis-Hallet (FH, 21), and Clusius et al. (24)
below will be based on the results of Fugate and Swenson (22).

X-ray diffraction data at saturated vapor pressure give accurate lattice parameters (and hence molar volumes) over the entire temperature range for both natural neon (26) and the separated isotopes $^{20}\text{Ne}$ and $^{22}\text{Ne}$ (27), and above 10 K these measurements provide thermal expansion coefficients at saturated vapor pressure which are accurate to 1%. Isothermal bulk modulus measurements have been obtained using X-ray diffraction methods (26) and the extrapolation to $P = 0$ of high pressure equation of state data (28). Information about the elastic constants of natural neon has been provided by two ultrasonic measurements on polycrystalline samples (29,30), two neutron inelastic scattering experiments on single crystals (31,32), and a Brillouin scattering measurement on a single crystal at 24.3 K (33). The ultrasonic measurements are in good agreement with $B_1(T,P=0)$ as determined from X-ray diffraction measurements (26), and the results are summarized by Balzer, Kupperman, and Simmons (30), who give smoothed adiabatic bulk moduli from 0 to 24.5 K. These various values for the adiabatic bulk modulus are compared in Figure 2. The agreement is reasonable at low temperatures, but inconsistencies exist at high temperatures.

There are, however, no previously reported high precision thermal expansion data for temperatures below 10 K. The present experiment gives thermal expansion data for free-standing samples of solid neon for temperatures from 1.5 to 15 K, and the present results are intended to complete (in some sense) our knowledge of the bulk thermodynamic properties of solid neon at low pressures. These data were obtained using an extension
Figure 2. A comparison of $B_s$ values reported by Balzer et al. (30) (+ 0.3 kbar), Skalyo et al. (31), and Gewurtz et al. (33). The $B_T$ values given by Anderson et al. (28) are shown after being corrected to adiabatic conditions. The solid line represents an ad hoc representation for $B_s$ which is explained in the text.
of the capacitance dilatometry technique which was developed for the heavier rare gas solids by Tilford and Swenson (34,35,36). Since relative length changes as small as $3 \times 10^{-10}$ can be resolved for a 3 cm sample with this apparatus, thermal expansion measurements which have a precision of 1% or better can be obtained even close to 1 K for the rare gas solids. Unfortunately, Tilford and Swenson (36) found that capacitance dilatometer data generally are slightly larger (by a constant factor for any given run) than results obtained from X-ray diffraction measurements at temperatures where the two methods have comparable precision. They postulate that bonding between the samples and the copper cell parts introduces elastic strains at the ends of the samples which generate small excess expansions (1 to 5%). Therefore, the capacitance dilatometer results must be calibrated by comparison to other high precision results at high temperatures. This is not a serious problem for solid neon since the X-ray data provide thermal expansion coefficients which are accurate to 1% above 10 K.

The temperature dependence of the thermal expansion coefficient $\beta$ is related directly to the temperature dependence of the heat capacity for a Mie-Grüneisen solid (Equation 1-5), since both the bulk modulus and the molar volume vary slowly with temperature. If accurate measurements of the heat capacity exist, the only new basic information which is obtained from a measurement of $\beta$ is the temperature dependence of the Grüneisen parameter, $\gamma$, through Equation 1-5. The $T = 0$ limit of $\gamma$, $\gamma_0$, gives an average of the third and higher order derivatives of the lattice potential through Equations 1-11 and 1-12. Hence $\gamma_0$ provides a test of
anharmonic portions of the interatomic potentials.

The very precise $C_V(T,V)$ measurements of Fugate and Swenson (22) have been used to formulate a Mie-Grüneisen equation of state for solid neon (28), which includes a slightly temperature-dependent $\gamma$ which corresponds to a molar volume (12.87 cm$^3$/mole) which is smaller than the zero pressure volume (13.39 cm$^3$/mole). The heat capacity equation of state and the high pressure $P(V,T)$ data of Anderson et al. (28), could be made consistent only by postulating a volume dependence for $\gamma(V)$, with $d\gamma/dV > 0$. The latter authors combine these volume and temperature dependences of $\gamma$ with the saturated vapor pressure X-ray thermal expansion results to predict $\gamma(T,P=0)$ for the entire temperature range. A discrepancy was observed between this predicted $\gamma(T)$ for the equation of state and the relation which was obtained from thermodynamic data by Batchelder et al. (26). This discrepancy is due partly to the use of different values of $C_p$ (Figure 1), while the remaining discrepancy could be due to the inconsistencies in the bulk moduli which are illustrated in Figure 2. Their comparison did not extend to $T = 0$ because of the lack of reliable thermal expansion data below 10 K. They did use their postulated volume dependence of $\gamma$ to predict a value of $\gamma_0$ which can be compared directly with the results of the present experiment.

The very rapid variation in $B$ with temperature is a major problem in the display of the data for the entire temperature range. Since reliable $C_V$ data are available, and both $B_S$ and $V$ show only limited temperature dependence, the actual thermal expansion data can be displayed with high sensitivity through a calculation of the Grüneisen
parameter for each data point using smoothed representations of $B_S$, $C_V$, and $V$. For this particular choice of thermodynamic quantities, Equation 1-5c is solved to produce the relation

$$\gamma(V,T) = \frac{1}{2\beta T} \left[ (1 + \frac{4\beta^2 B_S VT}{C_V})^{\frac{3}{2}} \right] - 1, \quad (1-15)$$

which has been used for all Grüneisen parameter calculations in the present work.

In summary, theoretical calculations of the properties of solid neon now appear to be limited in accuracy primarily by inadequate representations of the two-body interatomic potential function. The theoretical results will become more reliable as the potential functions are refined, and experimental work that is both accurate and precise will be required for comparisons of theoretical and experimental results. The Grüneneisen parameter is related closely to the volume dependence of the normal mode frequencies and hence to the anharmonicity of the potential function, so that an accurate experimental knowledge of $\gamma(V,T)$ will provide a test for prospective potential functions. The present work has supplied the low temperature thermal expansion data which did not exist previously, and the experimental Grüneisen parameters at all temperatures now are limited in accuracy only by the inconsistencies in the determination of the adiabatic bulk modulus.
CHAPTER II. APPARATUS AND SAMPLE PREPARATION

The thermal expansion measurements were made using a differential capacitance dilatometer of a type pioneered by White (37,38) and which has been modified for use with the inert gas solids by Tilford and Swenson (34,35,36). In this type of dilatometer, parallel capacitor plates are separated by the samples and the sample length changes are measured by observing changes in the capacitance. The capacitance of two parallel plates is related to the separation \( L_g \) and area \( A \) of the plates by

\[
C = \frac{\varepsilon_0 A}{L_g}.
\]  

(11-1)

The sensitivity to change in separation, which is given by

\[
\frac{dC}{dL_g} = -\frac{\varepsilon_0 A}{2 L_g^2},
\]  

(11-2)

decreases rapidly with increasing separation of the plates. The capacitance dilatometers of White and of Tilford and Swenson are shown schematically in Figure 3; the type used by White is referred to as the "normal" configuration and the modification of Tilford and Swenson is labelled as the "inverted" configuration. The "normal" dilatometer produces a differential measurement, since the separation of the capacitor plates changes only if the sample has a thermal expansion relative to that of the cell; if the thermal expansion of the sample is larger than that of the copper cell, the separation of the plates increases with decreasing temperature. This presents a serious problem in the case of
Figure 3. Normal and inverted capacitance dilatometers
the inert gas solids, because these solids have expansivities which are several orders of magnitude larger than that of copper. For example, since the relative linear expansion of solid neon between 0 K and its triple point (24.6 K) is 1 1/2% as compared to essentially zero for copper, the gap is at its largest value at low temperatures where the highest sensitivity is required. The "inverted" geometry also yields a differential measurement, but in this case the gap is smallest at the lowest temperatures and the highest sensitivity is obtained when it is most necessary. The most stable sample geometry for the "inverted" cell would be a large hollow cylinder, but, following Tilford and Swenson (34,35,36), this choice has been replaced by an equivalent geometry in which three small posts are equally spaced about a 7/8 in. diameter ring. These small posts are used to reduce the strains caused by the bonding of the samples to the copper cell parts and the large differential expansions of the rare gas solids relative to copper.

Because of the very low triple point temperature of solid neon, all sample preparation and manipulations must be done by remote handling to avoid vaporizing the samples. The samples are grown in a mold which is attached to the capacitance cell and are dropped from the mold by a method similar to that described by Tilford and Swenson (34,35,36). The capacitance cell then is assembled at 4.2 K using remote tools which consist of Allen wrenches soldered onto the ends of stainless steel rods which are more than four feet long. A heated shield surrounds the cell during the sample manipulations and cell assembly to prevent frost deposits which interfere with visual observations of the cell.
Cryostat

The basic cryostat design has been changed only slightly since the previous work \((34,39)\), although the entire system has been rebuilt. The sample growth and manipulation and the capacitance cell assembly must be observed visually so the main vacuum jacket and the liquid nitrogen and liquid helium containers are constructed of glass. The glass vacuum jacket which contains the capacitance cell near its lower end, is about 54 in. long, has a 4 in. diameter for most of its length and a 6 in. diameter bulge near the upper end. This bulge provides storage space for cell parts during the early stages of the experiment. Glass-to-metal graded seals (4 in. diameter) are used to attach the vacuum jacket to the rest of the system at both ends; the upper seal is soldered into a brass flange which bolts to the Dewar head, while the lower seal is indium-soldered into a stainless steel flange. A ridge on the lower flange mates with a groove on the stainless steel base plate, so that a reliable vacuum seal is made when the two pieces are bolted together with an indium gasket (0.01 in. thick). This seal has remained vacuum tight even when subjected to repeated thermal cyclings to liquid helium temperatures.

The room temperature flange of the glass vacuum jacket is sealed at various times during the experiment by three different plates, each of which can be clamped down on an O-ring to produce a vacuum seal, and two of which are transparent. The plates used during the early portion of the experiment when visual observation is important are made of plexiglass. One plexiglass plate has feedthroughs for the mold fill tube,
the masher plate assembly (see below) support, the frost shield support, and various manipulating tools. A second plexiglass plate has feedthroughs for the sample chamber can support and the Allen wrench which is used to tighten the screws at the base of the can. The feedthroughs in these plates are either conventional glass-to-metal O-ring vacuum connectors or packing gland seals. During the data-gathering portion of the experiment, a metal top plate is used, from which radiation shields are suspended into the vacuum space. This top is designed for high vacuum operation and contains a large pumping line and an ion gauge tube and thermocouple gauge for monitoring the pressure in the vacuum space.

Details of the capacitance cell and the lower end of the glass jacket are shown in Figure 4. All pumping lines and electrical leads to the cell pass through the lower flange and are brought to the Dewar head along the outside of the vacuum jacket so that access to the top of the cell is unrestricted. The sample chamber line is vacuum-jacketed all the way to the Dewar head and is attached to a separate temperature controller block so that it can be isolated from the liquid helium bath and maintained at a temperature well above 4 K to reduce cryopumping of the neon samples to cold spots in the line. For the lowest temperature work, the cryopumping is not an important effect, and the sample chamber line can be thermally anchored to the bath by filling its vacuum jacket with helium exchange gas.

A gold-plated copper can surrounds the capacitance cell to provide an isothermal environment and a vacuum tight enclosure. The can contains
Figure 4. Details of capacitance cell and sample chamber
helium exchange gas during an experiment to aid in the establishment of thermal equilibrium and to inhibit the sublimation of the neon samples when measurements are made at temperatures above 10 K. An indium seal is used to make the can vacuum tight, and it has proved possible to obtain a leak-tight seal when the joint is assembled at 4.2 K.

The guard ring for the lower capacitor plate also serves as the base for the sample mold, so it contains an indium-filled groove and three small copper posts that are not shown on the diagram. The lower capacitor plate has been cast into the guard ring using an insulating epoxy resin (Stycast 2850GT/11, Emerson & Cuming) to provide an insulating joint which defines the capacitor area. Both the plate and the guard ring have been ground flat and smooth and are gold-plated. The diameter of the capacitor plate (including one half the insulating ring) was measured using a traveling microscope, and the room temperature value for the plate area was calculated to be 0.8509 cm$^2$. The reference capacitor is included in the cell to measure dielectric effects of the exchange gas and generally is used to test the system. The thermometry block contains both a germanium resistance thermometer and a platinum resistance thermometer for temperature measurements from 1 to 350 K.

The masher plate and spacer ring are used to obtain samples of equal length. The samples are grown slightly longer than needed so that when the cell is assembled the masher rests on top of the capacitor plate which in turn is in contact with the samples. The masher then is drawn down using stainless steel screws until it rests snugly on the spacer ring. In this process, it forces the top capacitor plate to "mash" the
the samples to the point where they have equal lengths to about 0.05 mm. This insures that the capacitor plates will be sufficiently parallel for reliable measurements. A complete discussion of the effects of a tipped capacitor plate and the requirements for a reliable measurement are given in Reference 34 and will not be repeated here.

The temperature controller block contains two 120 ohm wire-wound heaters as well as carbon and platinum resistance temperature sensors. Experience has shown that a more suitable location for the sensors would be on or near the thermometry block inside the can since temperature gradients apparently exist between the temperature control block and the sample chamber can. These allow sizeable variations in the cell temperature to occur even though the control block is maintained at a constant temperature. The resistances of the sensors are monitored with a 400 Hz ac Wheatstone bridge. The off-balance signal from a phase-sensitive detector is fed into a current-adjusting type controller (L & N M-Line Series 71, Model CI) which in turn controls the current supplied to one of the heaters. The other block heater is attached to a manually-controlled constant voltage supply (Harrison 6206A) and provides an auxiliary heat input if required. The temperature controller for the sample chamber line has a wire-wound 100 ohm heater and a carbon resistance sensor. A gold-iron differential thermocouple measures the temperature difference between the two temperature controller blocks for calibration of the carbon sensor, and a simple battery-powered dc bridge circuit measures the resistance of the carbon sensor. The temperature
is monitored on a chart recorder and the power input to the heater is adjusted manually to obtain the desired temperature.

Several types of ultraminiature coaxial cable have been used in the cryostat. Tilford (34) used cables with a 0.02 in. O.D. stainless steel outer conductor and a #38 copper center conductor (UT-20SS, Uniform Tube). These were replaced by Rehak (39) with cables which had a #42 stainless steel center conductor. Constant drifts in the resistive component of the bridge balance which were observed when using this cable were attributed to a change in resistance of the lead as the liquid nitrogen or liquid helium level in the bath varied. This effect was eliminated by replacing the stainless steel lead to the low side with a copper coaxial cable which has an O.D. of 0.008 in. and a 0.0025 in. center conductor (UT-8, Uniform Tube).

Capacitance Measurement

A schematic diagram of a simple ratio transformer three-terminal capacitance bridge is shown in Figure 5. This type of capacitance measurement, which was developed by Thompson (40), allows the precise measurement of small capacitances (approximately 1 pF) in spite of several thousand pF in cable capacitance. The ratio transformer is used to adjust the voltage input to the standard capacitor until the currents in the two arms of the bridge are equal. The balance condition is given in Figure 5, and if $C_s$ is chosen correctly the capacitance can be read directly from the ratio transformer setting.
AT BALANCE \( V_x j\omega C_x = V_S j\omega C_S \Rightarrow C_x = C_S \frac{V_S}{V_x} \)

--- SHIELD

Figure 5. A schematic diagram of a three-terminal capacitance bridge
The detailed bridge circuit which was used for the present measurements is shown in Figure 6. The major additions to Figure 5 include the use of two ratio transformers and standard capacitors in a parallel arrangement to obtain higher resolution, and the use of a small circuit to balance the resistive component of the off-balance signal. The null detector is a narrow-band lock-in amplifier and dual phase-sensitive detector from which the capacitive and resistive off-balance signals are displayed simultaneously on a two-pen chart recorder. Descriptions of the dividing transformer, the ratio transformers, and the standard capacitors are available in Reference 34. The standard capacitors are located in a temperature-controlled box and their effective total capacitance is stable at the $10^{-8}$ pF level. The 1068 Hz oscillator provides a maximum of 300 volts peak-to-peak to the transformer, and a maximum input to the cell of 140 volts peak-to-peak. The oscillator is removed physically from the rest of the bridge components since broadcasting from the output transformers of the oscillator is picked up by leads on the capacitance side of the main transformer. With the oscillator some 15 feet away from the rest of the system, the residual voltage measured in the circuit with the input to the transformer shorted is about 30 nV. This pick-up is assumed to remain constant at the nV level during the period of the measurements.

The resolution of the capacitance measurement is limited in practice by the sensitivity of the null detector and the magnitude of the cable capacitance. All shields are grounded, so the cable capacitance introduces a finite impedance to ground for all points in the circuit. In
Figure 6. The detailed capacitance bridge circuit which was used for the present measurement.
the following discussion, the cables connecting the capacitors to the transformers will be referred to as the "high" side and the cables connecting the detector to the capacitors will be designated the "low" side of the circuit. The cable capacitances on the high side shunt the transformer outputs, but, since the transformers have very low output impedances, this is a negligible effect. On the low side, the shunting of the detector by the cable capacitance lowers the effective input impedance of the detector from 50 Megohms to typically 100 kΩ. The detector voltage sensitivity which is required to detect a departure from bridge balance of magnitude \( \delta C \) is given by

\[
\delta V = \frac{V \delta C}{C_C}
\]

(11-3)

where \( V \) is the input voltage to the capacitance cell and \( C_C \) is the cable capacitance on the low side of the system. For the present apparatus, the low side cable capacitance is approximately 1400 pF and the input voltage to the cell is about 50 volts rms, so a voltage sensitivity of 3.5 nV rms is required to obtain a resolution of \( 10^{-7} \) pF. Voltage sensitivities of this magnitude were not available previously, so a large inductor (10 to 15 henrys) and a small variable capacitor (0-200 pF) were used to parallel-tune the detector input so that the shunt impedance due to \( C_C \) was greatly increased. This method was effective, but troublesome, since the phase angle of the signal changes rapidly with small changes in tuning and constant realignment of the phase sensitive detector was required. Changes in the liquid helium level in the Dewar and changes of the cell temperature also produced small changes in cable capacitance,
and frequent adjustments of the variable capacitor were required to maintain maximum sensitivity. This complication no longer is necessary since the amplifier sensitivity has been increased by the use of a low noise FET input stage and the addition of an active noise filter to the phase sensitive detector outputs. For example, the shorted input noise level of the detector used in the present system is less than 3nV peak-to-peak with a 10 second time constant, so bridge resolutions of $10^{-7}$ pF are obtained using the modified detector without encountering the difficulties of operating a highly tuned circuit. The phase angle of the signal is now quite stable, and only infrequent minor phasing adjustments are required.

**Thermometry**

Temperatures are measured by comparing the resistance of the thermometer to the resistance of Leeds and Northrup (L & N) wire wound NBS-type standard resistors using a standard four-terminal dc potentiometric technique with current reversal to minimize the effects of thermal emf's. The potentiometer (L & N, Type K-5) current is supplied by a Dynage Batt-Sub constant voltage supply and the thermometer current is obtained from a locally-built constant current supply of the type described by Kroeger and Rhinehart (41). A Keithley model 150AR microvolt-ammeter is used as a null detector, with the off-balance signal displayed on a chart recorder to monitor temperature drifts.

The germanium resistance thermometer (Cryocal, Serial No. 748) was calibrated locally in terms of $T_X$, a temperature scale based on paramagnetic salt thermometry (42), and the calibration for this thermometer
is given in Appendix A. The platinum resistance thermometer (L & N, Model 8164, Serial No. 1654277) was calibrated by the National Bureau of Standards on the NBS 1955 scale. The calibrations of the two thermometers were compared at five points between 20 K and 36 K. While the platinum temperatures were 2 mK higher than the germanium temperatures, this difference is quite consistent with the accuracies of the calibrations. The platinum thermometer was not used for any of the thermal expansion measurements, but it occasionally was used to monitor temperatures during the sample condensation and solidification procedures.

Frost Shield and Sample Mold

The walls of the glass vacuum jacket are kept free of neon frost deposits in the immediate vicinity of the capacitance cell by a heated frost shield. A sheet of 0.005 in. Mylar is attached to two brass rings using C-7/W epoxy (Armstrong Products) to form a transparent cylindrical shield about one foot long which just fits inside the vacuum jacket walls. Approximately 200 ohms of #36 manganin heater wire is wound helically on the shield (~1 cm pitch) and is epoxied to the Mylar using Armstrong C-7/H-20 epoxy. The brass rings are attached to a stainless steel tube which supports the shield and allows it to be manipulated from the Dewar head, and the heater leads are brought to the Dewar head through this support tube. A piece of pipe cleaner is inserted into the lower end of the tube to eliminate the vapor oscillations which initially occurred in the tube.

The mold which is used to grow the solid neon samples is similar to that used by Tilford and Swenson (34,35,36) and it is shown schematically
in Figure 7. The samples, which are 3 cm long, are grown in Mylar tubes which are epoxied into the top and bottom pieces. A 3/16 in. stainless steel tube contains the heater leads and connects the mold to an external glass vacuum system (not shown) which contains a mercury diffusion pump. Twelve 2-56 stainless steel screws are used to hold the mold in position on the lower capacitor plate and guard ring and to compress the indium gasket sufficiently to provide a leak-tight seal for the base of the molds. The three copper posts on the guard ring pass through the base plate of the mold so that the solid samples are located in the tubes entirely above the base plate. The base plate of the mold has been machined so that the three tubes are connected at the base so that liquid heights in the three tubes are equalized by hydrostatic pressure.

The mold tubes are fabricated by wrapping two turns of 0.0015 in. Mylar onto a Teflon mandrel and cementing them together with the C-1/E epoxy resin (Armstrong Products). The heater wires (0.002 in. manganin, 75 ohms/foot) are wrapped with a density of ten turns per inch and are epoxied to the tubes with Armstrong C-7/H20 epoxy resin. Both of these epoxies are transparent when cured and with care it is possible to produce tubes which are rather clear. The tubes are cut to the appropriate length (6.3 cm) and are epoxied into the brass top piece and copper base with Stycast 2850GT/9 epoxy (Emerson & Cuming). This is a somewhat touchy operation since the coarse consistency of the 2850GT/9 adhesive may cause the tubes to collapse as they are inserted into the end pieces. The top and base heaters then are epoxied into place, and all lead connections are made on a terminal board (not shown) just above the top piece.
Figure 7. Schematic diagram of sample mold. The top portion of the spacer ring is not shown.
The completed mold is leak-tested at 77 K by attaching a spare base plate and submerging the mold in liquid nitrogen while the mold is pressurized with helium gas. Any leak which is large enough to cause serious difficulties will produce a stream of bubbles in the liquid nitrogen. Leaks in the mold were patched with considerable success by painting the leak with an acetone-diluted hobbyist's adhesive (Goo, Walther Specialties). The mold was leak-tested routinely in this fashion before every run and was patched until no bubbles appeared.

Sample Solidification and Manipulation

The mold is evacuated at room temperature and is flushed several times with high purity neon or helium gas to minimize the possibility of obtaining thermal expansion anomalies due to oxygen (34,35,36) or hydrogen (22,23) impurities. The capacitance cell and mold are cooled to 77 K, the mold is flushed again, and the cell is cooled to 25 K. An appropriate amount of neon is condensed into the mold, the base plate temperature is allowed to drop below the triple point temperature of neon while the top of the sample is held above the triple point, and solidification of the samples begins at the lower end. As the solid-liquid interface moves through the sample at 1 to 2 cm/hr, the top heater is used to keep the vapor pressure over the liquid (as measured with a mercury manometer) 100 to 200 torr above the neon triple point pressure. If the liquid cools below the triple point, it solidifies very rapidly from the top down and the resulting solid is permeated with voids. The samples then must be remelted and the growing process repeated. The
solidification can be accomplished in 2 to 4 hours if about 20 millitorr of helium exchange gas is admitted to the vacuum jacket. If the exchange gas is not used, sufficient heat is conducted down the stainless steel fill tube and the heater leads to slow the solidification process nearly to a halt. As the samples solidify, the base plate temperature generally is allowed to fall slowly to 18 to 20 K. After the solidification is completed, the top heater power is very slowly reduced so that the top of the sample is allowed to cool slowly toward the base plate temperature, with a crude temperature measurement provided by the vapor pressure of the solid. The samples are cooled to 4.2 K in about one hour, an atmosphere of helium gas is admitted to the mold over the samples, and the vacuum jacket is filled with an atmosphere of helium exchange gas. The entire sequence from the initial liquid helium transfer to solid samples at 4.2 K can be accomplished in 6 to 8 hours, but on occasion it has required considerably more time when difficulties with voids have been encountered.

The screws at the base of the mold are loosened using the special Allen wrench, the frost shield is lowered into place around the cell, and the vacuum jacket is evacuated again. After the vacuum jacket pressure falls below 1 torr, power is supplied to the frost shield heater, the cell temperature is raised to about 14 K and the base heater is turned on. The solid neon which bonds the base of the mold to the lower capacitor plate and guard ring sublimes away and the mold and samples pull away with the samples still bonded to the Mylar tubes. The cell temperature is raised to 18 K and the mold is raised to permit inspection
of the bottom plate for pieces of solid air or other debris which might hold the capacitor plates apart. If the plate is clean, the mold is rotated by 60° and lowered until its base plate rests on the copper posts in the guard ring. The tube and base heaters are turned on and the samples soon slide from the tubes. The samples usually stand upright on the guard ring and the mold can be raised gently without incident. As soon as the mold is above the samples the frost shield heater is turned off.

After the samples are standing safely, the mold is raised to the top of the vacuum jacket and the masher plate assembly (which has been stored and precooled in the vacuum jacket bulge) is lowered slowly toward the samples and allowed to cool to 4.2 K. It then is lowered gently onto the samples. The masher plate is screwed down tightly on the spacer ring, constraining the top plate so that the samples are adjusted to the same length by plastic deformation. When the masher plate is securely in place, the mold, frost shield and plexiglass top are removed from the vacuum jacket and replaced with the plexiglass top piece that supports the sample chamber can. Some solid air is introduced into the vacuum space as snow during this procedure, but the amount can be kept at a reasonable level if the exchange is made rapidly. This snow, however, must be removed from the indium gasket before the can is lowered into place. The can is lowered toward the cell very slowly so that it has time to cool from 300 to 4 K without transferring appreciable heat to the samples. After the can has cooled and has been lowered into place, twenty-four 4-40 stainless steel screws are used to tighten the
the can down on the indium gasket to provide a leak-tight enclosure for the cell. Usually, the screws are tightened several times over a period of 2 to 4 hours to compensate for creeping of the indium and then the plexiglass top piece is replaced with the metal vacuum jacket head that is designed for high vacuum operation and the vacuum jacket is evacuated.

The samples are compressed thermally by raising the cell to a temperature between 12 and 20 K. The thermal expansion of copper is negligible below 20 K, so the vertical distance from the guard ring to the masher plate remains essentially unchanged. The samples therefore are not allowed to expand as they warm and plastic deformation occurs. The cell is held at the maximum temperature for at least five minutes to establish thermal equilibrium and then is cooled to 4 K. The samples contract as the cell cools, and the top plate is pulled away from the masher plate and becomes electrically isolated. During all thermal compressions, the sample chamber is filled with 0.5 to 1.5 atmospheres of helium exchange gas to reduce sublimation of the neon samples which occurs for temperatures above 12 K. The 4.2 K length of the samples can be reduced at any later time by raising the cell temperature above the previous maximum to produce a further thermal compression. Measurements therefore can be made on a single set of samples using significantly different capacitor gaps.

Physical Properties of Solid Neon Samples

The heavier rare gas solids were found by Tilford (34,35,36) to bond tenaciously to other materials, e.g. the copper guard ring and top plate, but somewhat contradictory observations were made for neon during
this experiment. The thermal expansion results indicate that bonding does occur (this will be discussed in a later chapter), but a set of samples which was dropped from the mold when the cell was at 15 K fell over easily when they were bumped accidently. Samples dropped with the cell at 18 K generally were observed to stand quietly and are thought to have bonded to the guard ring, although the final set of samples exhibited very strange behavior as they were standing free. All three samples wobbled with frightenly large amplitudes for several minutes and they stabilized only after the cell temperature was lowered by several Kelvin. The cell temperature had risen as high as 19.5 K during this sample drop, apparently causing uneven sublimation from the bases of the samples.

The solid neon samples are quite clear when they are dropped from the mold tubes, but their surfaces become somewhat frosty in appearance as they stand on the guard ring, probably because of thermal etching. The samples almost certainly are polycrystalline, but the grain size of the crystallites was not investigated.

The resistance of solid neon to plastic deformation is sufficiently small that the "mashing" of the samples can be accomplished at 4.2 K by finger-tightening the screws which draw the masher plate tightly down onto the spacer ring. This was true even for the case where a set of samples was compressed by more than 1/8 in. In one occasion, a set of samples was not suitable for measurements, so an Allen wrench was used to test the mechanical properties of the samples. The surfaces of the samples could not be damaged noticeably with the tool, in marked contrast
to the result of similar experiments conducted on parahydrogen samples (see Appendix E). Only one sample was observed to sag noticeably under its own weight, and that sample is thought to have been weakened by voids which were observed near the base of the sample and probably were caused by sublimation through a leak in the base of the mold. Voids were not observed in any other samples.

Technical Difficulties

Seven sets of solid neon samples actually were grown, but measurements were obtained for only two sets. One of the sets of samples was lost because of the sagging sample mentioned in the previous section, four sets of samples were lost either directly or indirectly because of the presence of excessive amounts of solid air, and one of the measurements was brought to a premature end by an accident involving solid air.

The vacuum space is surrounded by liquid helium during the entire operation, so any air that enters the vacuum space immediately is condensed as a solid which flutters down upon the capacitance cell as snow or clings to the glass walls of the vacuum jacket. In the latter case, it often is dislodged during subsequent manipulations and almost all of the air originally entering the cell ends up at the capacitance cell sooner or later. Small amounts of solid air can be tolerated on certain portions of the capacitance cell, but if pieces which are larger than the intended minimum gap width (0.2 mm) land on the lower capacitor plate, the two capacitor plates will be constrained, and the thermal expansion measurement fails. Smaller pieces lying on the capacitor plate
can produce local dielectric anomalies, so it is desirable to keep the plate as clean as possible as the cell is assembled.

The general problems with the solid air made it necessary to proceed cautiously and deliberately throughout the entire manipulation and cell assembly operation, and to maintain a constant check for loose vacuum connections on the top plate. The plexiglass top plate and its feedthroughs were checked before every run with a leak detector to be sure that no leaks existed at that time. Whenever wrenches were to be inserted or removed through the seals on the top plate, the exchange gas pressure in the vacuum jacket was raised to 1 to 2 psi over atmospheric pressure, so that gas would be blown outward through any opening, and the vacuum jacket was held slightly above atmospheric pressure when the wrenches were rotated in the seals or a supporting tube was raised or lowered.

Some solid air always is introduced into the system during the exchange of top flange covers but if the snow can be avoided until that time, the chances of success are improved greatly. Some manipulation of the loose air particles is possible, since the vapor oscillations which develop in a tube with a closed upper end and open lower end can be used as an effective blow-gun. Considerable turbulence is generated in the very dense exchange gas at the cell, and the air particles can be blown about almost at will, although it is not possible to control where they land. This proved to be an effective way of cleaning the indium gasket before the can was lowered, and it could be used to clean the lower capacitor plate if necessary. The "blow-gun" method also proved far more
convenient and reliable than the previous method of using a vacuum pump and a tube to make a crude vacuum cleaner.

The helium exchange gas in the vacuum jacket also added a number of difficulties to the experiment. Since much of the gas in the jacket is at 4 K, an enormous mass of helium [equivalent to 2 or 3 liquid liters] is required to bleed the system to atmospheric pressure. The pumping lines at the Dewar head therefore were modified so that the flash gas from the helium Dewar could be bled into the vacuum jacket. Approximately one half hour is required to bleed the vacuum jacket to atmospheric pressure, and a similar length of time is required to evacuate the system to 1 torr when starting from atmospheric pressure. Therefore, much of the time spent on the manipulation and cell assembly procedure is consumed by the manipulations which involve large changes in the exchange gas pressure.

Much of the solid neon which sublimes away during the lifting of the mold and the dropping of the samples condenses as a solid frost on the walls of the glass vacuum jacket. It thus becomes impossible to see into the vacuum space, and, since it is necessary to monitor visually the dropping of the samples and the subsequent assembly of the cell, such neon deposits cannot be tolerated. Attempts at scraping the frost off the walls with a stainless steel tube were partially successful but not reliable, and they generally introduced substantial amounts of solid air into the vacuum jacket. The transparent heated frost shield was used to eliminate this problem. The extreme optical clarity of the neon samples, and the fact that the shield never was completely free of frost, made the sample dropping and cell assembly operations very difficult to carry out.
CHAPTER III. RESULTS

Thermal expansion data are obtained by making simultaneous temperature and capacitance measurements at a series of fixed temperatures. The temperature is changed by 10 to 20% of the mean temperature $T$ for data points at temperatures below 10 K and by 1 K for data points taken at higher temperatures. The use of temperature intervals larger than 0.1 $T$ introduces a small error into the results, but the magnitude of the error can be calculated and the increased precision resulting from larger changes in temperature and capacitance more than compensates for the uncertainty introduced by the correction. Because of sample bonding effects, the present results must be normalized by comparison with results obtained above 10 K by X-ray diffraction methods (26).

Data Acquisition and Analysis

The temperature of the cell as measured by the germanium thermometer is controlled to 0.1 mK until the samples reach thermal equilibrium (as defined by a constant capacitance reading). The thermometer current, the potential drop across the thermometer, and the capacitance value are recorded. The cell temperature then is raised to the next data point temperature and the above procedure is repeated. The off-balance signals from the germanium thermometry potentiometer and from both phases of the capacitance bridge are displayed continuously on chart recorders and are monitored for thermal and electronic stability. Thermometer resistances then are calculated, and the data point temperatures are obtained using the thermometer calibration given in Appendix A.
For the cell geometry used in this experiment, the length of the neon sample $L_s$ is the sum of the length of the copper centerpost $L_c$ and the distance between the capacitor plates $L_g$. The linear thermal expansion coefficient for the sample then is given by

$$\alpha_s = \frac{1}{L_s} \left( \frac{\partial L_s}{\partial T} \right)_p$$

(III-1)

$$= \left( \frac{L_c + L_g}{L_c + L_g} \right) \{ \left( \frac{\partial L_c}{\partial T} \right)_p + \frac{\varepsilon \varepsilon_0}{C} \left( \frac{\partial A}{\partial T} \right)_p - \frac{\varepsilon \varepsilon_0}{C^2} \left( \frac{\partial C}{\partial T} \right)_p \} \right. \left. + \frac{\varepsilon \varepsilon_0}{C} \left( \frac{\partial \varepsilon}{\partial T} \right)_p \right\} \}$$

(III-2)

$$= \left[ \frac{L_c + 2L_g}{L_c + L_g} \right] \alpha_{Cu} - \frac{L_g}{L_c + L_g} \left\{ \frac{1}{C} \frac{\partial C}{\partial T}_p - \frac{1}{\varepsilon} \frac{\partial \varepsilon}{\partial T}_p \right\}.$$

(III-3)

Here, $\alpha_{Cu}$ is the linear thermal expansion coefficient for copper and $\varepsilon$ is the dielectric constant for the helium exchange gas between the capacitor plates. A copper cylinder was used in place of the neon samples for a calibration run to verify that spurious contributions due to the cell geometry and misalignment of cell parts are negligible for this experiment. Since $\alpha_{Cu} < 10^{-3} \alpha_s$ for the entire temperature range of the measurement, and to a good approximation dielectric constant changes are negligible, the data may be analyzed using
$$\overline{a(T)} = -\frac{\varepsilon_o A}{\varepsilon_o A + C L_C} \frac{1}{C} \frac{\Delta C}{\Delta T}. \quad (111-4)$$

Here $\Delta C < 0$ is the change in capacitance, $\Delta T > 0$ is the change in temperature, and $\varepsilon_o$ is the permittivity of free space. The correction for the use of finite temperature intervals is given by

$$\overline{a} - a_s = \left(\frac{1}{24}\right) a_s''(T) (\Delta T)^2, \quad (111-5)$$

where $a_s''(T)$ is the second derivative with respect to temperature of $a_s(T)$ evaluated at $\overline{T}$. This correction requires a knowledge of $a_s(T)$, so an iterative procedure is used to calculate this difference. A more complete discussion of Equation 111-5 is given by Case (43) and will not be repeated here.

**Results for Two Sets of Samples**

Measurements actually were obtained for only two sets of neon samples, although seven sets were grown. The two sets of samples will be designated as "Neon-1" and "Neon-2" in the following discussions. Measurements were made for Neon-2 using two different capacitor gaps, and the data for the smaller gap will be referred to as "Neon-2'." The Neon-1 samples were vaporized accidentally during a liquid helium transfer, so these data are incomplete. Pertinent information concerning the Neon-1, Neon-2 and Neon-2' samples is given in Table 1. There are considerable differences in sample history and capacitor plate separation, so that systematic errors which could be introduced by sample history or
Table 1. Neon sample characteristics

<table>
<thead>
<tr>
<th></th>
<th>$L_c^a$</th>
<th>$L_g^b$</th>
<th>$T_{\text{max}}^c$</th>
<th>Length Adj.$^d$</th>
<th>Gas Grade$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon-1</td>
<td>2.9299</td>
<td>0.53</td>
<td>18</td>
<td>&lt; 1</td>
<td>Research</td>
</tr>
<tr>
<td>Neon-2</td>
<td>2.9543</td>
<td>0.40</td>
<td>12</td>
<td>~ 3</td>
<td>High Purity</td>
</tr>
<tr>
<td>Neon-2'</td>
<td>2.9543</td>
<td>0.24</td>
<td>19</td>
<td>&gt; 3</td>
<td>High Purity</td>
</tr>
</tbody>
</table>

$^a$Length of the copper centerpost at room temperature.

$^b$Capacitor plate separation at 4.2 K.

$^c$Maximum temperature for thermal compression procedure.

$^d$Estimated total plastic deformation during "mashing" and thermal compression.

$^e$All neon gas was obtained from Air Products and Chemicals, Inc. The purity of the research grade is guaranteed to exceed 99.998%, while the high purity grade is prepared using the identical procedure, but the purity is not guaranteed and a separate analysis is not furnished for each container.
by tipped capacitor plates should be observable in a comparison of the various data sets.

The actual raw data for each of the samples are given in Appendix B. The present results are systematically larger than the X-ray results of Batchelder et al. (26) for temperatures between 10 and 15 K. Similar deviations have been observed for the heavier rare gas solids by Tilford and Swenson (34,35,36) who attribute the excess expansion to sample bonding effects, and their procedure of scaling the capacitance dilatometer results to match the X-ray results is followed here.

In order to display the data with high sensitivity for the entire temperature range, the strong temperature dependence of the thermal expansion coefficient is normalized by using smoothed representations for $C_V$, $B_g$, and $V$ in Equation 1-15 to calculate a Gr"uneisen parameter for each data point. The actual choices of $C_V$, $B_g$, and $V$ are discussed in the following chapter since they are not important here. Figure 8 shows a comparison of the three data sets after the Neon-1 and Neon-2 data for $\alpha(T)$ have been reduced by 3.6% and the Neon-2' data have been reduced by 1.0%. The agreement is better than 1% at all temperatures even though the capacitor gaps for the Neon-1 and Neon-2' samples (Table 1) differed by more than a factor of two. A polynomial function then was fitted to the scaled values of $\alpha$ using least squares fitting techniques to obtain a smooth representation for $\alpha(T)$. Smoothed values of the volume coefficient of expansion $B$ and the relative lengths $((L(T) - L_0)/L_0)$ are given for various temperatures in Table 2. The $\alpha$ values correspond to the solid line in Figure 8. The details of the calculations and the smoothed
Figure 8. A comparison of the Neon-1, Neon-2 and Neon-2' results after the data have been reduced by 3.6, 3.6 and 1.0% respectively for the three samples. The smooth lines are discussed in Chapter IV of the text.
Table 2. Smoothed values for volume expansion coefficient and relative length change for solid neon

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\beta \times 10^6$ (K$^{-1}$)</th>
<th>$\frac{\Delta L}{L_0} \times 10^6^a$</th>
</tr>
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<tbody>
<tr>
<td>0.5</td>
<td>0.1005</td>
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<tr>
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<td>2305</td>
</tr>
<tr>
<td>14.0</td>
<td>2108</td>
<td>2956</td>
</tr>
</tbody>
</table>

$^a\frac{\Delta L}{L_0} = \frac{L(T) - L_0}{L_0}$  (See Appendix C for details of calculation).
representation for \( \alpha \) are given in Appendix C. The smoothed values of \( \beta = 3\alpha \) as given by the capacitance and X-ray experiments are compared in Figure 9. The deviation corresponding to 0.5% \( \beta \) also is shown to emphasize the excellent (if somewhat forced) agreement of the two methods between 10 and 14 K. The deviations below 8 K are larger than the estimated X-ray error estimate, but the X-ray results for natural neon (26) and the separated isotopes (27) are not consistent within these estimates for some temperatures below 10 K, so it is reasonable to assume that the X-ray errors in \( \beta \) have been underestimated. Since the primary X-ray data are the relative changes in the lattice parameter \( ([a(T) - a_0] / a_0) \), more reasonable test of consistency is a comparison of relative length changes obtained by integrating the present expansion results and the changes measured by X-ray diffraction. Figure 10 shows such a comparison, and the agreement is completely consistent within the X-ray error estimate. The results of the present experiment are consistent with the X-ray results, and they are of significantly greater precision and accuracy at temperatures below 10 K. The scaling adjustment is very small for the Neon-2' sample and between 10 and 15 K the unscaled Neon-2' data differ by no more than 1% from the smoothed X-ray results.

Error Sources

There are several significant sources of experimental uncertainty which must be considered. The most serious of these is the sample bonding effect, since the size of this correction cannot be evaluated unless other high precision data are available. Hence, the capacitance dilatometer results do not provide an independent check of the other data.
Figure 9. Absolute deviation of the present results for the volume expansion coefficient for solid neon from the X-ray diffraction results of Batchelder et al. (26)
Figure 10. Absolute deviations of the relative length changes obtained by integrating the present expansion results from the relative lattice parameter changes measured directly for solid neon by Batchelder et al. (26)
A second problem occurs because the high heat capacities and very low thermal conductivities of the solid neon samples make it difficult to establish thermal equilibrium in the capacitance cell. The thermal equilibrium can be improved by adding exchange gas to the sample chamber, but the exchange gas introduces uncertainties in the capacitance through its dielectric constant and it affects the observed length changes through the very large compressibility of solid neon. Care has been taken to minimize the errors from these sources which will be discussed in more detail.

The sample bonding effect refers to an anomalous contribution to the thermal expansion which causes the capacitance dilatometer results to be consistently higher than other high precision measurements by a proportionality factor (1 to 5%) which is an apparent constant for any single run. The extra thermal expansion is thought to be due to elastic strains which result when the solid sample bonds to the copper plate at the upper end and the guard ring at the lower end. Because of the strength of the bond, the samples are not allowed to expand laterally, and a small part of the sample near the ends undergoes a length change which is closer to the volume expansivity than to the linear expansivity. Very little plastic deformation occurs because the data are reproducible upon thermal cycling below a given maximum temperature. In particular, Tilford and Swenson (34,35,36) found the scaling factor to depend on the maximum temperature at which the samples were mashed. They attributed this effect to a rounding of the sample ends by sublimation at the higher temperatures, and hence to smaller sample constraints. The same effect
is observed in the present experiment when the data for the Neon-2 and Neon-2' are compared. The excellent agreement between the scaled capacitance data and the X-ray data (Figures 9 and 10) suggests that the errors introduced by the scaling are small.

Significant systematic error could be introduced by the existence of thermal gradients inside the capacitance cell. Because the solid neon samples have very large heat capacities and very small thermal conductivities, they may not be at the same temperature as the germanium thermometer unless a substantial amount of helium exchange gas is used in the sample chamber. One set of measurements which was taken with a very small helium exchange gas pressure in the sample chamber gave expansion results which were 10% too small at low temperatures, but approximately correct at temperatures above 10 K when the vapor pressure of the neon became sufficiently large to provide some thermal exchange. Helium exchange gas levels on later runs were kept above 100 millitorr at low temperatures and at 1 torr or more for temperatures above 5 K.

An estimate of the error which is introduced by thermal gradients (and inelastic deformation) was obtained in the following manner. The sample temperature was increased to $T_1$ and was stabilized at that temperature as a capacitance value $C(T_1)$ was measured. The sample temperature then was increased to $T_2$ while making sure that it never exceeded $T_2$ and a corresponding capacitance $C(T_2)$ was read. Finally, the cell temperature was decreased back to $T_1$, and a new reading $C'(T_1)$ was obtained. If the temperature then was cycled between $T_1$ and $T_2$, the values of $C'(T_1)$ and $C(T_2)$ were reproduced as long as the sample temperature did
not exceed $T_2$ or fall below $T_1$. The difference $(C(T_1)-C'(T_1))$ could be due to temperatures gradients (which could be different in the two cases) or due to sample deformation. Similar checks, with monotonic cooling and with varying exchange gas pressures, suggested that the primary problem can be ascribed to the thermal properties of the samples, not inelastic deformation. The differences $(C(T_1)-C'(T_1))$ which were observed in these experiments for the customary exchange gas pressures correspond to differences in the thermal expansion coefficients which varied from roughly 1% at 8 K, to 0.5% at 14 K, and only 0.3% at 4 K. These effects should be unimportant in practice since data always were taken with monotonic changes in sample temperature. The thermal gradient problem was especially troublesome in the case of the Neon-2 and Neon-2' data, since a small leak in the vacuum jacket resulted in poor thermal isolation of the dilatometer from the bath. Valid data were obtained for the Neon-2 samples only after an ad hoc operating procedure was established which maintained a reasonable pressure ($10^{-5}$ torr or less) in the vacuum space, and many of the earlier Neon-2 data points were discarded.

The helium exchange gas in the sample chamber can is quite dense so dielectric effects are important. If $\varepsilon \neq 1$, a systematic error of relative magnitude $(\varepsilon - 1)$ is introduced into the expansion measurement. Tests performed using the reference capacitor indicate that $(\varepsilon - 1) = 10^{-3}$ for a helium exchange gas pressure of about 10 torr at 6 K, so that an ideal gas law estimate of the maximum allowable exchange gas pressure (in torr) can be given by $P = 5T/3$. A second dielectric effect is encountered if the density of the exchange gas does not remain constant.
during a data point, since the last term in Equation 11-3 then may become important. The density of the gas must change to some extent since the exchange gas pressure in the sample chamber triples as the cell goes from 2 to 6 K and gas moves out of the sample chamber into the vacuum line. A measurement performed with the reference capacitor indicated that, beginning with an exchange gas pressure of about 150 millitorr at 1.5 K, the contribution of the last term is about 10^{-7}/K between 2 and 6 K and is about three times larger below 2 K. This effect then is important only when \((\Delta C/C) \lesssim 10^{-4}\). Both dielectric error contributions tend to make the measured thermal expansion coefficients too large.

Another adverse effect of the exchange gas occurs because of the very large compressibility of the solid neon samples. As the temperature of the cell increases, the pressure in the cell increases rapidly, especially at the lowest temperature. This pressure increase results in a compression of the samples which causes the measured expansions to be too small. The magnitude of the compressibility effect can be estimated by considering the length as a function of temperature and pressure \(L_s(P,T)\), from which

\[
\frac{1}{L_s} \frac{dL_s}{dT} = \frac{1}{L_s} \left( \frac{\partial L_s}{\partial T} \right)_P + \frac{1}{L_s} \left( \frac{\partial L_s}{\partial P} \right)_T \frac{dP}{dT}.
\]

The definitions of the thermal expansion and the bulk modulus can be used to produce

\[
\alpha = \frac{1}{L_s} \frac{dL_s}{dt} + \frac{1}{3B_T} \frac{dP}{dT}.
\]
Since
\[
\frac{1}{L_s} \frac{dL_s}{dt}
\]
is measured in the experiment, the relative error in \( \alpha \) is given by
\[
\frac{\delta \alpha}{\alpha} = \frac{1}{3\alpha B_T} \frac{dP}{dT} = \frac{1}{\beta B_T} \frac{dP}{dT}
\]
For an ideal gas, \( \frac{dP}{dT} = \frac{P\Delta T}{T} \) so the exchange gas effect is given by
\[
\frac{\delta \alpha}{\alpha} = \frac{P\Delta T}{\beta B_T T}
\]
At 2 K, an exchange gas pressure of 2000 millitorr could introduce an error of as much as 0.5% in the thermal expansion measurement. The magnitude of this effect drops rapidly as the temperature increases since the thermal expansion coefficient in the denominator increases as \( T^3 \). The large vapor pressure of the neon samples also can contribute a compressibility effect at high temperatures. The thermal expansion of neon at saturated vapor pressure differs from the zero pressure thermal expansion by less than 0.1% below 16 K, but the difference rises to 1% at 20 K and about 3% at the triple point.

The exchange gas errors cannot be eliminated completely, since, if the pressure is held constant to reduce the compressibility effect, the dielectric effect is enhanced, while if the density is kept constant, the compressibility contribution is a maximum. Fortunately, the two effects alter the expansion measurement in opposite directions and hence tend to
cancel, so the net errors are somewhat smaller than estimated above.

The total systematic error in the present experiment cannot be estimated reliably, but the precision and reproducibility of the data and the agreement with the X-ray results (Figures 9 and 10) suggest that the results are accurate to ± 0.5% near 10 K. A comparison of the thermal expansion results with the accurate volume-dependent heat capacity results using the Grüneisen parameter suggests that the measured expansions probably are 1% too low at low temperatures. This difference is reflected as the difference between the solid and dashed lines in Figure 9. The smoothed results (Table 2; Table D1 in Appendix D) reflect this adjustment. The smoothed results for β given here have an uncertainty of less than ± 0.5% at 10 K, and of ± 1% at temperatures below 4 K where systematic errors may be important.
CHAPTER IV. DISCUSSION

The present results can be discussed best in terms of the Grüneisen parameter at zero pressure $\gamma(T)$ since high quality heat capacity data exist for solid neon. The low temperature limiting value of $\gamma(T)$, $\gamma_0$, in general provides basic information about the anharmonicity of the interatomic potential function, and in this case it also can be used to test the volume dependence postulated for $\gamma_0(V)$ by Anderson et al. (28) from experimental heat capacity and high pressure equation of state results. Reliable theoretical calculations of the properties of solid neon below 10 K are not available for comparison with the present results, since an accurate description of the two-body interatomic potential does not exist as yet.

Smoothed representations of $C_V(T, V_0(T))$, $B_S(T)$, and $V_0(T)$, where $V_0(T) = V(T, P=0)$, are required to calculate Grüneisen parameters for each of the thermal expansion data points. The X-ray diffraction measurements of Batchelder et al. (26) provide molar volumes which are quite accurate, so that $V_0(T)$ is known to better than 0.1%. The differences in the values for the adiabatic bulk modulus in Figure 2 suggest systematic experimental problems, so two different representations of $B_S(T)$ (Table D1, Appendix D) will be used to demonstrate explicitly the effect of these inconsistencies on $\gamma(T)$. One of these representations is that of Balzer et al. (30), which is based primarily on ultrasonic data. The other representation which is shown as the ("average") solid line in Figure 2, is an \textit{ad hoc} interpolation of the existing data which is chosen to agree with the Brillouin scattering result of Gewurtz et al. (33) at 24.3 K and an
"average" of all data (Figure 2) at 0 K. The "average" representation for $B_S(T)$ was used in the individual data point calculations (Figure 8). Fugate and Swenson (22) have measured directly the heat capacity at constant volume $C_V(V,T)$ for solid neon close to $V_o$ (13.39 cm$^3$/mole) and at four smaller molar volumes, and these results have been extrapolated to $V_o(T)$ to produce $C_V(T,P=0)$ and $C_p(T,P=0)$ (Figure 1). These $C_V$ values have not been published previously for solid neon, and they are given also in Appendix D.

The Grüneisen parameters calculated for each of the individual data points are shown in Figure 8. The dashed line at low temperatures indicates the choice of smoothed values which best represent the data from the present experiment. The $C_V(V,T)$ results (22) can be represented in a reduced form as $C_V(V,T) = C_V(T/\Theta_o(V))$ to better than 0.1% for $T/\Theta_o \leq 0.08$, so solid neon can be described to this precision by a Mie-Grüneisen equation of state below 5 or 6 K. Hence, the Grüneisen parameter must be temperature-independent and equal to $\gamma_o$ up to at least 5 K. The solid line in Figure 8 results from this criterion, with $\gamma_o = 2.58$. Anderson et al. (28) postulated $\gamma_o(V) = 0.194 \pm 0.002V$, which gives $\gamma_o(V_o) = 2.60 \pm 0.03$. The two values differ by less than 1%, but the large uncertainty (± 2%) in $B_S(T=0)$ introduces a similar uncertainty into $\gamma$, as calculated from the thermodynamic data, so the agreement may be fortuitous. The present results neither confirm nor contradict the postulated volume dependence for $\gamma_o$.

Thermal expansion coefficients which are accurate to 1% are provided for the entire temperature range by a combination of the present results...
and the X-ray results of Batchelder et al. (26), and smoothed values of \( \beta \) are given in Appendix D. The smoothed thermodynamic properties given in Appendix D then may be used to calculate two different sets of \( \gamma(T) \) from Equation 1-15 which will differ through the bulk moduli which are involved. The dashed line in Figure 11 was calculated using the bulk moduli which are based on the Brillouin scattering data (33) while the dot-dashed values are calculated using bulk moduli from the summary of Balzer et al. (30). The decrease in the latter \( \gamma(T) \) relation above 10 K is not as large as that obtained by Batchelder et al. (26) primarily because they used an average of the FH and FS results in Figure 1, while the smoothed \( C_V \) results of Fugate and Swenson have been used here. The actual smoothed values of \( \gamma \) are given in Appendix D as \( \gamma_{AV} \) and \( \gamma_{BKS} \), respectively.

Anderson et al. (28) have used their postulated volume dependence for \( \gamma(V) \), the intrinsic temperature dependence for \( \gamma \) given by Fugate and Swenson (22), and \( V_0(T) \) as given by Batchelder et al. (26) to calculate the "equation of state" values for the zero pressure Grüneisen parameter which are given by the solid line in Figure 11. Their relation has an accuracy of one or two percent at best. The \( \gamma \)'s which are calculated from the equation of state are consistent with those calculated from the "average" bulk moduli to within the experimental uncertainties, although the intrinsic temperature dependence of \( \gamma(T) \) between 5 and 10 K may be slightly larger than that suggested by Fugate and Swenson (22). The uncertainties in the "average" bulk moduli (and the corresponding \( \gamma \)) are 2\% or so at both low and high temperatures, but may be greater at intermediate
Figure 11. Comparison of Gr"uneisen parameters for solid neon as estimated from equation of state data (22,28), and as calculated from thermodynamic properties for two different choices of $B_s$ (Figure 2)
temperatures (Figure 2). The results based on the ultrasonic measurements (30) do not display even qualitatively the same temperature dependence as do the other two curves, with differences of more than 10% in absolute magnitude at the highest temperatures. These differences reflect directly the differences between the Brillouin scattering and ultrasonic $B_S$ measurements near the triple point, and suggest that undetected systematic errors exist in the ultrasonic measurements.
CHAPTER V. SUMMARY

The present data (after scaling to match the X-ray values above 10 K) provide the accurate low temperatures thermal expansion data which did not exist previously for solid neon. Heat capacity, molar volume, and bulk modulus data are available, so the most convenient way of comparing the experimental data with theory is through the use of the Grüneisen parameter. The $T=0$ value, $\gamma_0 = 2.58 \pm 0.05$, is limited in accuracy primarily by the bulk modulus determination. Unfortunately, reliable theoretical calculations do not exist for solid neon, primarily because an accurate two-body interatomic potential is not available. As better potentials are developed, the present results will provide an excellent test for the theory.

The present results can be combined with the X-ray thermal expansion coefficients (26) to calculate $\gamma$ for the entire temperature range. These $\gamma$'s also are limited in accuracy by the uncertainties in the bulk modulus (Figure 2), and in particular by the large (10%) differences at high temperatures between bulk moduli which are obtained from ultrasonic measurements (30) and Brillouin scattering (33) results. A comparison of the present results with $\gamma$'s deduced from heat capacity and high pressure equation of state data suggests that the ultrasonic data may be in error. As more accurate determinations of the temperature dependence of the bulk moduli become available, the accuracy of $\gamma(T)$ will increase accordingly, especially at the intermediate temperatures. A complete description of the bulk thermodynamic properties of solid neon for temperatures between 0 K and the triple point now lacks only an accurate determination of the bulk modulus.
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Marvin Anderson for his assistance during the sample manipulations;

The author's daughter, Rachel, for her contribution as a source of cheer during even the most trying times;

The author's wife, Cathleen, for her patience, understanding, and encouragement during the completion of the present work.
Germanium Resistance Thermometer Calibration

The temperature $T_X$ corresponding to a given resistance $R$ for the germanium resistance thermometer (Cryocal Serial No. 748) is given by:

$$\ln T_X = \sum_{n=0}^{8} A_n (\ln R)^n.$$

Here $R$ is the resistance of the thermometer and the coefficients are given for three temperature ranges by:

**0.9 < T < 5.0 K**:

- $A_0 = -0.5194884196779D03$
- $A_1 = 0.7238326620569D03$
- $A_2 = -0.4279656167371D03$
- $A_3 = 0.1415752671206D03$
- $A_4 = -0.287430946296D02$
- $A_5 = 0.3674081125161D01$
- $A_6 = -0.289249302985D00$
- $A_7 = 0.1284283743274D-01$
- $A_8 = -0.2465874745667D-03$

**5.0 < T < 18.0 K**:

- $A_0 = -0.3815612050146D03$
- $A_1 = 0.6278623346040D03$
- $A_2 = -0.4410623079505D03$
- $A_3 = 0.1750387451978D03$
- $A_4 = -0.4304360356050D02$
- $A_5 = 0.6722427918039D01$
- $A_6 = -0.6512742179429D00$
- $A_7 = 0.3577028909213D-01$
- $A_8 = -0.8520114043803D-03$

**18.0 < T < 77.0 K**:

- $A_0 = 0.9350631481001D01$
- $A_1 = 0.1539595292040D02$
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- $A_3 = 0.5626686244357D02$
- $A_4 = -0.3380278110109D02$
- $A_5 = 0.1202741814300D02$
- $A_6 = -0.2546015721159D01$
- $A_7 = 0.2970316312295D00$
- $A_8 = -0.1472371491677D-01$. 
Unscaled Thermal Expansion Data for Solid Neon

The following pages give the actual linear thermal expansion data for the solid neon samples. The point number designates where each data point record is located in the experimental record books. The first digit refers to the book number, the second, third, and fourth digits give the specific page, and the last digit locates the specific point on the page. The temperatures have been calculated from the thermometer resistances as is described in Appendix A, and the capacitance values have been recorded directly from the ratio transformer settings. The mean temperature is the arithmetic average of the initial and final temperatures, and the $\alpha$'s have been calculated from Equation 111-4 and corrected by iteration using Equation 111-5. The magnitude of this finite temperature interval correction also is given for each point; these corrections have been calculated for temperatures below 10 K using the expression for $\alpha$ given in Appendix C, and have been defined as zero above 10 K. The data are displayed in Figure 8, after the Neon-1, Neon-2 and Neon-2' data have been divided by 1.036, 1.036 and 1.010, respectively, to compensate for sample bonding effects.
Table B1. Unscaled Thermal Expansion Data for Neon-1

<table>
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<th>Point No</th>
<th>Temp (K)</th>
<th>Capacitance (pF)</th>
<th>Mean Temp (K)</th>
<th>( \alpha \times 10^5 ) (K(^{-1}))</th>
<th>Finite ( \Delta T ) Correction (%)</th>
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Table B2. Unscaled Thermal Expansion Data for Neon-2

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<th>Finite $\Delta T$ Correction (%)</th>
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Smooth Representation for $\alpha(T)$ and Relative Length Change Calculation

A smoothed representation for $\alpha(T)$ was obtained by fitting a polynomial of the form

$$\alpha(T) = \sum_{n=1}^{5} a_{2n+1} T^{2n+1}$$  \hspace{1cm} (C-1)

to the scaled linear thermal expansion coefficient data. The fit coefficients are given by:

\begin{align*}
a_3 & = 2.64936361881191 \times 10^{-7} \text{ K}^{-4} \\
a_5 & = -3.61717129128174 \times 10^{-10} \text{ K}^{-8} \\
a_7 & = 4.03694530218155 \times 10^{-10} \text{ K}^{-10} \\
a_9 & = -1.71378717854584 \times 10^{-11} \text{ K}^{-12} \\
a_{11} & = 3.45340426293902 \times 10^{-13} \text{ K}^{-14} \\
a_{13} & = -4.04747418927561 \times 10^{-15} \text{ K}^{-16} \\
a_{15} & = 2.8884389686663 \times 10^{-17} \text{ K}^{-18} \\
a_{17} & = -1.23431721780422 \times 10^{-19} \text{ K}^{-20} \\
a_{19} & = 2.89895017852397 \times 10^{-22} \text{ K}^{-22} \\
a_{21} & = -2.87382980178041 \times 10^{-25} \text{ K}^{-24}
\end{align*}

where the root-mean-square deviation of the fit is 0.35%. The values for $\alpha$ given by Equation C-1 and these coefficients are somewhat lower than the values chosen to represent the data below 4 K. This difference corresponds to the deviation between the dashed and solid lines in Figure 8, and all tabulated values for $\beta$ ($\beta = 3\alpha$) have been adjusted to correspond to the solid line. The coefficients given for Equation C-1 are valid for temperatures less than 14 K, and the smoothed values of $\beta$ are given in Table 2 and Table D1 in Appendix D.

The thermal expansion coefficients obtained in the present work can be integrated to obtain the relative length changes $((L(T) - L_o)/L_o)$. The
definition of the thermal expansion coefficient can be integrated to obtain

\[ \int_{L_0}^{L_T} \frac{dT}{T} = \int_{0}^{T} \alpha \, dT, \]

which leads to

\[ \frac{L(T) - L_0}{L_0} = \exp\{ \int_{0}^{T} \alpha \, dT \} - 1. \]

Equation C-1 then can be used to write

\[ \frac{L(T) - L_0}{L_0} = \exp\{ \sum_{n=1}^{2n+2} a_{2n+1} T^{2n+2} \} - 1. \]

The relative length changes given in Table 2 for temperatures above 4 K have been calculated from this relation. Those for lower temperatures correspond to the solid line in Figure 8.
### Table D1. Smoothed Thermodynamic Functions for Solid Neon

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<th>T (K)</th>
<th>$C_V(T, P = 0)$ (mJ/mole-K)</th>
<th>$\beta \times 10^6$ (K$^{-1}$)</th>
<th>$V_0(T)$ (cm$^3$/mole)</th>
<th>$B_S$ (kbar)</th>
<th>$\gamma_{AV}$</th>
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*Extrapolated from results of Fugate and Swenson (22).*

*Values obtained from the present work for T < 14 K, and from Batchelder et al. (26) for T ≥ 15 K.*

*Calculated from densities given by Batchelder et al. (26).*

*'Average' $B_S$ (Figure 2).*

*Calculated using 'average' $B_S$.*

*Obtained from Balzer et al. (30).*

*Calculated using $B_S$ from Balzer et al. (30).*
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APPENDIX E

Comments on Attempted Solid Hydrogen Expansion Measurement

Thermal expansion measurements on samples of solid hydrogen and deuterium originally were planned to be a part of this experiment. The hydrogen measurements were abandoned, however, when it became apparent that the physical properties of solid hydrogen are such that the present apparatus is not of the optimal design for such measurements. The observations made during one attempted hydrogen measurement will be described here.

A set of parahydrogen samples was grown using the same mold and the same solidification technique which was used in the solid neon experiment. The sample solidification takes place much more rapidly for the hydrogen samples than for the rare gas solids, and this set of samples was grown in 45 minutes. During the attempt to free the mold and samples from the lower capacitor plate and guard ring (starting at 4.2 K), one of the samples remained bonded both to its mold tube and to the copper post on which it was grown so that it was plastically deformed as the mold was raised. This sample stretched to a length approximately three times its original length, and its behavior was very similar to that of hot plastic.

The two samples which remained standing were knocked over quite easily (with the cell at 4.2 K) with the remote tool. The temperature of the cell then was raised to the triple point of hydrogen (14 K), and at no point were the crystals observed to stick to the cell parts. A
similar observation was made for a set of neon samples, and a complementary observation is that no attempt to knock over a neon sample was unsuccessful. The extreme deformation of the one hydrogen sample that is described above indicates that the sample most certainly was bonded to the copper post, and one sample which fell out of the cell onto the indium gasket at the base of the can was bonded to the glass vacuum jacket after some time. In general, the sample bonding properties for hydrogen appear to be quite similar to those for solid neon.

The resistance to plastic deformation of these samples is extremely small, as is emphasized by the fate of the ruined sample. The samples which had been knocked over were probed with a remote tool to test their physical hardness. The tool could be pushed entirely through the sample quite easily (solid neon could not be noticeably marked) and at one point a sample was impaled on the end of the tool for several minutes.

The observations outlined above suggest that the solid hydrogen samples probably are not sufficiently strong to support the rather massive top plate assembly which is used in the inverted capacitance cell (Figure 3). The temperature range for the solid hydrogens is sufficiently small so that the normal cell geometry (Figure 3) could provide adequate sensitivity for precise thermal expansion measurements even at low temperatures. This suggests that the low side capacitor plate could be located in the center of the masher plate, and that a very light copper top plate could be supported by a solid cylindrical sample 3 cm or more in diameter. The capacitance then would measure the distance between the top plate and the masher plate. The capacitor plates could be
clamped together during the sample manipulations and cell assembly, thereby greatly reducing the probability that particles of solid air could get between them and ruin the measurement. Sample bonding effects could be a problem across the face of such a large sample, and further investigations of the plastic flow stresses and the sample bonding effects in the solid hydrogens would be a necessary prelude to attempted thermal expansion measurements.