1969

Thermal expansion of solid argon from 1 to 25 K

Charles Robert Tilford

Iowa State University

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THERMAL EXPANSION OF SOLID ARGON FROM 1 TO 25 K

by

Charles Robert Tilford

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY Major Subject: Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University Of Science and Technology Ames, Iowa 1969
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INTRODUCTION

The Rare Gas Solids (RGS), solid neon, argon, krypton and xenon, have historically been characterized by an abundance of theoretical work and a relative scarcity of experimental data. The supposedly simple and well-known force law between rare gas atoms made them the most likely candidates for first principle calculations of lattice properties. The simple cubic-close-packed (ccp) crystal structure and the short range nature of the Van der Waals force helps to simplify computational problems. On the other hand the low melting points of the RGS necessitates that all experimental work, including sample preparation, be done at cryogenic temperatures. Several properties unique to the RGS, high vapour pressures, very low strengths and thermal conductivities, and the ability to bond to any known substance, require special experimental techniques. In any case, there has been a continuing interest in the RGS over the last fifty years as is evidenced by the literature cited in several review articles. Dobbs and Jones\(^1\) in 1957 and Pollack\(^2\) in 1964 gave extensive references to both the experimental and theoretical work up to that time. Boato\(^3\) has also written a very readable review article, but with relatively few references.

Within the past five years this situation has definitely changed. Advances in low temperature experimental techniques have led the way to recent experiments on heat capacities, thermal expansions, compressibilities, elastic constants, neutron scattering, etc. These have shown the need for more sophisticated and complicated theories at the same time that large capacity high speed computers became available. The result is
that the RGS are better understood, but no longer regarded as simple as once thought. Anharmonic effects are now known to be quite important, even at 0 K, vacancy effects complicate the picture near the melting points, and the role of many-body forces is not yet understood. In spite of the complexities of the resulting theories the RGS still remain the best place to study fundamental lattice properties, and many of the complications themselves. Some idea of the changes can be had by comparing the theories recently reviewed by Horton with those appearing in Pollack's article.

The rare gas atoms are distinguished by their closed, spherically symmetric electronic shells. Due to their high ionization energies (12-21 eV) they remain in their electronic ground state as solids. The attractive force between two such spherically symmetric neutral atoms is due to induced electric multipoles. Although the time average of these fluctuations is zero, at any moment a charge fluctuation in one atom can induce a corresponding fluctuation in a neighboring atom. London used second order perturbation theory to calculate this attractive force in terms of dipole-dipole, dipole-quadrupole and higher order interactions. These give potential energies varying as $r^{-6}$, $r^{-8}$, $r^{-10}$, etc., $r$ being the interatomic spacing. The leading dipole-dipole term gives the famous Van der Waals potential. When the atoms are so close together that their charge clouds overlap the Pauli exclusion principle requires a repulsive force. The exact form of this repulsion has never been calculated, but it probably leads to an exponential potential, $\exp(-\lambda r)$.

The combination of the Van der Waals attraction and the exponential repulsion is known as the Buckingham potential,
\[ V(r) = \frac{6 \varepsilon n}{n - 6} \left\{ \frac{1}{n} \exp[-n(r/r_0 - 1)] - \frac{1}{6}(r_0/r)^6 \right\}. \]

For computational convenience the exponential term is often replaced by \( r^{-n} \), \( n \) generally being 12 or 13. This is the well-known Mie-Lennard-Jones (MLJ) potential,

\[ V(r) = \frac{n6\varepsilon}{n - 6} \left[ \frac{1}{n}(r_0/r)^n - \frac{1}{6}(r_0/r)^6 \right]. \]

In both cases \( \varepsilon \) is the depth of the potential well, \( r_0 \) is the location of this minimum and \( n \) is a measure of the steepness of the repulsive part of the potential. Both of these potentials have been used in calculating properties of the RGS, but the vast majority of the work has been done with the MLJ potential.

Several criticisms can and have been raised against the use of these potentials in calculating solid state properties. Apart from the fact that their analytical form is only an approximation, it is questionable whether a potential derived for two isolated atoms is suitable for use in a dense solid where many-body, non-additive forces may well be significant. The fact that these potentials have worked quite well, although not uniformly well, in calculating properties of the RGS has assured their continued use, but has not stilled the controversy surrounding them.

Much of this controversy has centered around the evaluation of the parameters \( \varepsilon \), \( r_0 \) and \( n \) in the potentials. As mentioned earlier, theoretical calculations of the repulsive potential are very difficult and it is only recently that a start has been made on doing this.\(^5\) Attempts which have been made to calculate quantitatively the Van der Waals
potential from first principles 6-8 have produced potential coefficients in error by as much as a factor of two.

The most satisfactory calculations of RGS properties have used potential parameters obtained by fitting the potential to experimentally determined 0 K solid state properties, such as the sublimation energy, lattice spacing and compressibility. The parameters thus derived depend very much on the sophistication of the theories used to calculate the fitted properties. A surprising number of otherwise good calculations have been flawed by using outmoded potential parameters derived with older and cruder theories. Currently accepted values of the parameters have been derived by a number of authors, 9-14 and are also given by Horton. 4

A different school of thought insists that since these potentials represent two-body forces the parameters should be derived from two-body effects, i.e., gas phase data. The properties most commonly used to determine potential parameters are the second virial coefficient and gas transport properties, such as viscosity, diffusion and thermal conductivity. 15-19 Unfortunately, it has been shown many times 18,20,21 that the commonly used second virial coefficient does not uniquely determine a potential, even a square well giving good results, and it is a rather general observation that potentials based on gas phase data do not give good results for solid state data. 22,23

Attempts have been made to improve the forms of the simple potentials. The dipole-quadrupole interaction has been added to a MLJ potential, 24 and entirely new potentials have been constructed from gas phase data. 16,25,26 While the addition of the r^-8 term to the MLJ potential does seem to improve agreement with experimental heat capacities, the
composite or polynomial gas phase potentials fail to give good agreement with solid state results. X-ray scattering data and shock compression of liquid argon have indicated deficiencies in the MLJ potential, but the data are not good enough to suggest quantitative improvements, and different sets of data often suggest contradicting "improvements."

In view of their undeniable shortcomings the success of the Morse and MLJ potentials in quantitatively predicting experimentally determined properties appears remarkable. However, this success varies widely depending on the property being calculated and largely depends on the fact that different properties effectively sample different restricted portions of the potential. Gas phase properties are due to collision processes and depend largely on the repulsive portions of the potentials; solid state properties however, depend primarily on the bowl of the potential near the minimum. So, in effect, the analytic form of the potential used is forced to give a best fit of the true potential in a restricted area. This has led to attempts to construct potentials by fitting to different appropriate experimental properties in different regions. Unfortunately this is easier said than done and the resulting potentials are generally too complicated to use. Furthermore, any two-body potential obtained from solid state data is really an effective potential that includes contributions from many-body or non-additive forces.

Attempts have been made to obtain the magnitude of many-body forces by comparing solid state and gas phase potentials. These indicate that many-body energies are 5 to 15% of the total. This however, in view of the previous paragraph, must be regarded as a somewhat circular argument and not much faith can be placed in the results.
If the lattice potential for a class of solids is due solely to two-body central forces, and if that potential can be represented in reduced form for all members of that class, a law of corresponding states should be obeyed. The law of corresponding states says that the equations of state for all solids with this same reduced potential should have the same reduced form and be a function of two parameters, $p^* = f(V^*, T^*)$, where $^*$ denotes variables reduced by some appropriate quantity. The RGS seemed the most likely to obey this classical law of corresponding states until De Boer showed that such is not the case. Rather, because of their large zero point motion, the RGS must be represented by a quantum mechanical reduced equation of state, $P^* = F(V^*, T^*, \Lambda^*)$, where $\Lambda^* = h/r_o (me)^{3/2}$ (this parameter is defined differently by different authors) is the De Boer parameter and is characteristic of the ratio of the zero-point energy to the lattice potential energy. De Boer and several subsequent authors have calculated quantum mechanical reduced equations of state which often compare well with experimental data. Deviations from this equation of state would imply many-body forces since they would violate the basic assumption of two-body central forces. However, the theories used to derive the reduced equation of state are not accurate enough to allow quantitative deductions about many-body forces. The most general use of the law of corresponding states is as a substitute for experimental data when data are available for some but not all of the RGS.

Extensive calculations have been made of the effect of three-body forces on the stability of different crystal structures. The commonly used two-body potentials predict a hexagonal-close-packed crystal structure for the RGS while all experimental evidence, with but one
nondefinitive exception, have shown the crystal structure to be pure cubic-close-packed. Barron and Domb37 some time ago suggested that this discrepancy might be due to the failure to take account of many-body or non-central forces. Jansen and Zimering38-40 have explicitly calculated three-body repulsive energies which will stabilize the ccp structure and Rossi and Danon41 also claim the same result if the three-body energies amount to 15 to 20% of the total. These results, however, are of questionable reliability and importance. The calculated energy difference between the two phases is only 0.01%, much less than the accuracy of the calculations, and can be reversed by rather small changes in the two-body potential.42 In addition, the three-body calculations entail severe approximations; Jansen's calculations, for instance, depend on the difference between first and second order perturbation contributions, and employ charge distributions more appropriate for a metallic or covalently bonded substance.43

There are many possible experiments that would shed light on the magnitude of many-body forces, but it is only recently that one has been performed with sufficient accuracy to provide even a useful estimate. Losee and Simmons44,45 measured both the x-ray lattice parameter and bulk thermal expansion of krypton near its melting point and obtained the concentration of thermally generated vacancies. Numerous calculations have been made of the contributions of many-body forces to lattice defects due to both charge overlap and third order perturbation corrections to the Van der Waals force46-49 (see Ref. 45 for more extensive references). Losee and Simmons, using an estimate of the lattice and electronic relaxation around the vacancy sites, concluded that many-body forces contribute
25% of the ground state energy. They later decided that this is not as reliable a value as first thought, but have not yet published a new value.

Using potential parameters calculated by Zucker including the triple-dipole interaction Brown has calculated values of \( \Theta_0^C \), the calorimetric Debye temperature at 0 K. These agree better with experimental values than ones calculated from potential parameters calculated using an anharmonic two-body calculation. However, this does not give any quantitative information about three-body forces. Zucker and Chell maintain that quantitative information can be obtained from the Cauchy ratio

\[ B = \left( C_{44} - C_{12} \right)/C_{12}. \]

Two-body calculations have always indicated that \( B > 0 \), but by adding the triple-dipole interaction to the two-body calculation Zucker and Chell have found \( B < 0 \) for argon, krypton and xenon. Unfortunately the elastic constants are not available experimentally.

The present situation is that most workers recognize the deficiencies of the MLJ and Morse potentials and agree that many-body forces probably are significant, although very few agree on how significant. Until more reliable experimental and theoretical evidence is available this question will remain unsettled and the simple two-body potentials will have to be regarded as effective potentials covering a multitude of sins.

Given an acceptable or usable potential the problem remains of calculating measurable thermodynamical properties. This means calculating the Helmholtz free energy, \( F(V,T) = U - TS \), where \( U \) is the internal energy and \( S \) is the entropy. \( F \) can be used to derive:

- the pressure, \( P = -\left( \frac{\partial F}{\partial V} \right)_T \),
- the entropy, \( S = -\left( \frac{\partial F}{\partial T} \right)_V \).
the specific heat at constant volume, 
\[ C_V = -T \frac{\partial^2 F}{\partial T^2} V \]

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

and the volume thermal expansion coefficient, 
\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{B_T} \left( \frac{\partial^2 F}{\partial T \partial V} \right). \]

From these quantities the dimensionless Grüneisen parameter,
\[ \gamma = \frac{V \beta B_T}{C_V} \quad (1) \]
can be defined. If \( F \) can be written as \( F(T,V) = T \Phi \left( \frac{\partial(V)}{T} \right) \), then 
\[ \gamma = -\frac{\partial \ln \theta}{\partial \ln V} \]
and is a constant at all temperatures. Experimentally, 
\( \gamma \) is nearly constant for most substances. The elastic constants are obtained similarly from the appropriate strain derivatives of the free energy.

The free energy will have two parts, a temperature-independent static lattice energy \( U_0 \), obtained by summing the given potential over all interacting atoms, and a kinetic energy due to atomic motion. For simple potentials such as the Morse or MLJ the summation over interacting atoms has been tabulated so that \( U_0 \) is readily obtained. The kinetic energy in an insulating crystal such as the RGS is due to vibrations which can be treated as a set of coupled harmonic oscillators. These contribute not only a thermal energy but also a zero point energy, which is relatively important in the weakly bound RGS (see Table 1). The free energy, 
\[ F = -kT \ln Z, \]
where \( Z \) is the partition function, 
\[ Z = \sum \exp(-\varepsilon_n/kT) \]
and \( \varepsilon_n \) are the allowed energy states. The free energy then becomes
Table 1. Static lattice and zero point energies of the RGS in units of $10^{-16}$ ergs/atom taken from Ref. 4

<table>
<thead>
<tr>
<th>Element</th>
<th>$U_0$</th>
<th>$E_{zp}$ (q.h.)</th>
<th>$E_{zp}$ (anh.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>-413.0</td>
<td>84.0</td>
<td>-2.88</td>
</tr>
<tr>
<td>Ar</td>
<td>-1409</td>
<td>116.7</td>
<td>-0.88</td>
</tr>
<tr>
<td>Kr</td>
<td>-1950</td>
<td>93.4</td>
<td>-0.358</td>
</tr>
<tr>
<td>Xe</td>
<td>-2745</td>
<td>83.6</td>
<td>-0.192</td>
</tr>
</tbody>
</table>

$$F(V,T) = U_0(V) + \sum_{\omega} \left[ \frac{1}{2} \hbar \omega + kT \ln[1 - \exp(-\hbar \omega/kT)] \right]$$

where the sum is over all allowed frequencies. The calculation of thermodynamic properties thus becomes the lattice dynamical problem of calculating the allowed frequencies of vibration of the solid, or equivalently, the frequency distribution $g(\omega)$. Since the thermal expansion involves both a temperature and a volume derivative of the free energy it depends on the volume derivatives of the allowed frequencies.

The first successful attempt at explaining the non-classical behaviour of solids at low temperatures was Einstein's treatment of a solid as a collection of independent quantum oscillators with a single characteristic frequency. In 1912 Debye attempted to take the non-independent nature of the $N$ particles in a solid into account by allowing a spectrum of $3N$ frequencies, the density of the allowed frequencies varying quadratically.
with the frequency up to a maximum frequency related to the velocity of sound and the lattice spacing of the solid. These frequencies are associated with traveling waves having a uniform distribution of momentum and a constant velocity for a given mode of propagation. This assumption of a constant velocity can be even partially justified only for the long wavelength low energy modes dominating at very low temperatures. The velocity of short wavelength higher frequency modes will surely depend on the direction of propagation in a discrete solid as well as the frequency, which typically goes up to $10^{13}$ Hz. In spite of these unrealistic assumptions the Debye theory is amazingly successful at all temperatures so that many thermodynamic quantities are expressed in terms of their deviation from the Debye theory.

Again in 1912, Born and von Karman established the basis for most modern lattice dynamics. Like Debye they treated the solid as a set of $N$ coupled harmonic oscillators with $3N$ normal modes having a uniform distribution of allowed momenta. The allowed frequencies, however, are the roots of the eigenvalue equation resulting from the equations of motion for the oscillating particles, with the interatomic potential approximated by a parabola. The latter is the well known harmonic approximation.

The task of solving the eigenvalue equation for $10^{24}$ coupled harmonic oscillators for all directions in the crystal is formidable and essentially impossible without large capacity computers. Blackman$^{52,53}$ made the first efforts in this direction, but was restricted by the computational problems. Because of this, several approximate methods of obtaining the frequency distribution were developed. Montroll$^{54-56}$ developed an expansion
of the frequency spectrum in terms of Legendre polynomials and the moments of the frequency distribution $\mu_n = \sum \omega^n$. The even moments $\mu_{2n}$ are obtained from the trace of the $n$th power of the dynamical matrix, which depends only on force constants obtainable from the interatomic potential. The odd moments are identically zero. In practice it is possible to obtain as many as thirty or forty moments, and different thermodynamic properties have been calculated in this way. Several authors have shown how thermodynamic information can be obtained from just a few moments. Salter derived an often used approximation for the zero point energy, $E_z = 9/8Nk\Theta_\infty = (h/k)\left[(5/3)\mu_z\right]^{1/3}$, and Barron and Klein expressed the elastic constants in terms of the first few moments. Another approximation to the frequency spectrum involves solving the equations of motion in symmetry directions and interpolating between. Leighton and Houston both developed methods for doing this, Houston making an expansion in terms of Kubic polynomials. Presently numerical techniques and large computers are used to directly solve the equations of motion for the allowed frequencies for thousands of different momentum values.

The harmonic approximation, on which much of the early lattice dynamics was based, assumes that the atomic oscillations are so small that the potential can be expanded in a Taylor series about its minimum and only the second order term kept, the first order term being identically zero. In the RGS the large zero point motion invalidates the assumption of small oscillations even at 0 K and effectively "blows up" the lattice so that the equilibrium position is displaced well away from the potential minimum. In addition, the total potential energy for a given atom has its minimum shifted away from that of the two-body potential because of the
contributions of distant neighbors. The so-called quasiharmonic approximation takes both of these effects into account by expanding the potential about the true equilibrium position. Although only the second derivative is retained, the volume dependence of the allowed frequencies is taken into account by allowing the equilibrium position to change. Quasiharmonic calculations have been made for many of the properties of the RGS.²⁷,²⁸,⁵⁸ Perhaps the most notable example of quasiharmonic calculations is Horton and Leech's sixty¹ exhaustive survey of the thermodynamic properties of the different MLJ potentials. Presently quasiharmonic calculations are done primarily as a starting point for true anharmonic calculations.

The higher order or anharmonic contributions to the energy are treated as perturbations which modify the quasiharmonic frequencies and the partition function from which the free energy is derived. The frequencies are now allowed to be a function of both volume and temperature and the free energy is \( F = F_{\text{qh}} + F_3 + F_4 \), where \( F_3 \) and \( F_4 \) represent the perturbation contributions of the third and fourth order terms in the potential. Approximations have been derived for the so-called anharmonic frequency shifts sixty² but a thorough calculation must extend out to second-order perturbation terms. The third-order contribution, being odd, does not appear in the first-order perturbation calculation, but as can be seen from Table 1 the third-order contribution is a significant fraction of the fourth-order contribution. This basic perturbation calculation is complex, particularly in its temperature dependence, and various approaches and approximations have been developed to expedite it. sixty³-six⁹ Perturbation calculations have been done for the RGS with varying degrees of success.⁹,⁷⁰-⁷⁶ While giving better results than quasiharmonic calculations, particularly
at higher temperatures, it appears that for the RGS higher order anharmonic corrections beyond $F_3$ and $F_4$ are significant. $^{69,72,76}$

The lattice dynamical methods discussed thus far all have proved useful to some extent in dealing with the RGS. However, they all fail when applied to solid helium where the assumptions of small oscillations or the applicability of perturbation theory are not at all justified due to the very large zero point motion. At the equilibrium position in low pressure solid helium the second derivative of the MLJ potential is negative, leading to imaginary frequencies. In response to this problem a new approach, though suggested many years ago, has just been rediscovered and developed in recent years. This so-called self-consistent approach uses a trial or variational wave function to average the force constant or second derivative of the potential over the region traversed by an atom. Very recently this has been applied to solid argon and neon, $^{77}$ but with results that are not obviously better than those obtained with standard perturbation theory. One drawback of the self-consistent theory is that it uses a Gaussian wave function, which, being even, does not average in the odd derivatives of the potential. This has been remedied in the improved self-consistent theory so that all derivatives of the potential are included. This improved theory has been applied to solid argon $^{78}$ and neon $^{79,80}$ and does appear to be an improvement over both the standard perturbation calculations and the original self-consistent theory at higher temperatures. Figure 1, taken from Ref. 78, shows the relative success of these three approaches in calculating the thermal expansion of solid argon and the way in which they come together at lower temperatures.
Figure 1. Different theoretical calculations of the thermal expansion coefficient of solid argon.
ZERO-PRESSURE VOLUME EXPANSIVITY IN $10^{-4}$ DEG.$^{-1}$

![Graph showing zero-pressure volume expansivity vs. temperature in $10^{-4}$ deg.$^{-1}$]

- TEMPERATURE (°K)
- PT
- ISC
- SC
- EXPT
In solid helium the large zero point motion requires wave functions with significant probability densities well away from the lattice site. In order to prevent charge overlap and satisfy the Pauli exclusion principle it is necessary to multiply the product wave function by a short range correlation function which goes to zero as two atoms approach one another. This additional refinement has been applied to solid neon by Mullin and Hansen. Mullin claims that short range correlation effects are negligible for neon; Hansen claims they are significant. In any case, it is undoubtedly true that they are negligible for the heavier RGS and are not the main theoretical problem at the present, even for neon.

Much of the theoretical development of lattice dynamical theories and the thermodynamic derivatives has focused on specific heats. Once the frequency distribution is known the specific heat follows in a very straightforward manner. But perhaps more important is that specific heat measurements are relatively easy to make and experimental data always have been available for the theorist to explain. Einstein's first theory of the quantized oscillator was proposed in response to experimental evidence showing deviations in specific heats from the classical law of Dulong and Petit at low temperatures.

It only recently has become technically possible to make low temperature thermal expansion measurements and theoretical interest has correspondingly lagged. The standard optical interferometer method of measuring length changes is simply not sensitive enough to make meaningful measurements in the low temperature or quantum mechanical region. It was not until the early 1950's that Bijl and Pullan used a variable capacitor
in a tuned tank circuit to make measurements on simple metals showing
temperature variations in the classically constant Grüneisen parameter \( \gamma \) (Eq. 1). This prompted Barron's pioneering work\(^{85,86}\) based on an analysis of the volume derivatives of the moments of the frequency spectrum, showing theoretically that the \( \gamma \) should vary with temperature. This was followed by Blackman's\(^{87,88}\) calculation of \( \gamma \) in terms of elastic constants and their volume derivatives. The development of the three terminal parallel plate capacitor technique by White\(^{89}\) and the differential transformer technique by Swenson and co-workers\(^{90}\) have permitted accurate measurements on many substances down to 1 K.

Attempts have been made for some time to obtain thermal expansion measurements on the RGS. The special problems associated with these solids have prevented until recently anything but rather crude bulk density or polycrystalline x-ray measurements.\(^{2,91}\) Simmons and co-workers' success in growing large single crystals of the RGS and their development of a high resolution x-ray camera has resulted in accurate thermal expansion measurements down to moderately low temperatures (10 to 25 K) for neon, argon and krypton.\(^{92-96}\) These papers have summarized earlier bulk expansion measurements and polycrystalline x-ray results. The single crystal x-ray measurements have prompted several theoretical calculations of the thermal expansions and Grüneisen parameters in the moderate and high temperature regions where these measurements are most accurate. It appears that perturbation and self-consistent calculations meet with some success at moderate temperatures\(^{76,78,79}\) but at higher temperatures the extreme anharmonicity and unknown effect of vacancies still cause trouble.
While the RGS are anharmonic at all temperatures, the anharmonic effects are much smaller at low temperatures and vacancy effects are completely absent. Furthermore, at sufficiently low temperatures the long wavelength, low energy normal modes dominate and the specific heat and thermal expansion can be expanded in odd powers of the temperature, starting with $T^3$. Thus in this limit the solid becomes Debye-like, and the Grüneisen parameter is the logarithmic volume derivative of the characteristic temperature or energy of the solid. The theory is generally more tractable at low temperatures and the results are less model dependent. Since both the specific heat and the thermal expansion go to zero as $T^3$ the difficulty of measuring them goes as $T^{-4}$. The x-ray technique has a length change sensitivity of about 6 parts in $10^6$, which is inadequate to measure the low temperature thermal expansion coefficients which may be of the order of $10^{-7}$ to $10^{-8}$ K$^{-1}$. The present work is the first high resolution thermal expansion measurement on an unconstrained "solid gas." A preliminary report has been made of the present work. Accurate measurements can be made down to 1 K using the length change sensitivity of 3 parts in $10^{10}$.

A number of other experimental measurements have been made in recent years. Compression measurements have been made at high pressures and different temperatures for xenon and neon, argon, and krypton, using a piston displacement technique. Low pressure measurements have been made by measuring the x-ray lattice parameter as a function of pressure for neon, argon, and krypton. Heat capacity measurements have been made on neon, argon, krypton, and xenon. In
the case of argon and krypton these measurements extend down to 0.3 K. There is some disagreement outside of reported experimental error between different overlapping measurements, particularly for xenon, but in general these measurements are accurate to 1%.

Accurate measurements of the elastic constants of the RGS would be of considerable importance, but are very difficult to perform and existing measurements reflect this. The velocity of transverse waves as a function of temperature has been obtained from the resonant torsional frequency of a suspended argon rod. The longitudinal velocity has been obtained from optical diffraction patterns due to density fluctuations set up by ultrasonic waves in solid argon. Conventional ultrasonic measurements of the longitudinal sound velocity have been made in solid argon, but the results are uncertain because of an uncertainty in the crystal orientation.

Attempts have been made to obtain the frequency distribution by measuring the absorption of light in argon with a xenon impurity. The difficulties in preparing oriented single crystals of the RGS and cooling them down to 4.2 K have been a severe hindrance in making inelastic neutron diffraction measurements. A preliminary report has been made on measurements at 4.2 K on a large single crystal of argon. Measurements have also been made on krypton at 79 K and on neon at two different densities and temperatures.

The references cited in this chapter are not an exhaustive list of the work on the RGS. A deliberate attempt has been made to focus on "first principle" calculations, insofar as such a thing exists, and the
experimental work which they have tried to explain, primarily measurements of thermodynamic quantities, i.e., derivatives of the free energy. In any case, it does appear that progress has been made in understanding some of the fundamental properties of the RGS. The recent self-consistent results[77-79] appear particularly encouraging at high temperatures.
APPARATUS

In the Introduction several experimental problems unique to the RGS were mentioned. Chief amongst these are their low triple point temperatures and high vapour pressures (see Table 2). Not only must all sample preparation and handling be done at low temperatures, but it must be done quickly and in as nearly an isothermal environment as possible to avoid excessive sublimation of the solid. Solidification of the samples must proceed from the liquid in order to eliminate voids in the solid, but must proceed slowly due to the low thermal conductivity of the solid which is generally less than that of glass. If the surface of the liquid cools below the triple point, hollow vapour-filled tubes of solid about 0.1 mm in diameter, known as vapour snakes, will propagate through the liquid with a speed of up to several cm/sec ruining the sample. Thermal expansions for the RGS are abnormally high, argon having a 3% change in length

Table 2. Triple points of the rare gases from Ref. 2

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature (K)</th>
<th>Pressure (Torr)</th>
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<tr>
<td>Ne</td>
<td>24.56</td>
<td>323.5</td>
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<td>Ar</td>
<td>83.810</td>
<td>516.86</td>
</tr>
<tr>
<td>Kr</td>
<td>115.78</td>
<td>548.7</td>
</tr>
<tr>
<td>Xe</td>
<td>161.37</td>
<td>612.2</td>
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</tbody>
</table>
between the triple point and 0 K, so that once solidified the solid must be cooled slowly or the combination of low thermal conductivity, high thermal expansion, and low strength will cause damaging strains in the solid. Strains on cooling also are caused by the unique ability of the RGS to bond firmly to all known substances, including Teflon. The thermal expansions of most substances are two or more orders of magnitude smaller than those of the RGS and the differential contraction at the interface can cause large strains. At higher temperatures the RGS are very soft, argon having a yield strength of about 3 bars at the triple point.\textsuperscript{114} As the temperature decreases the yield strength rises exponentially and the RGS eventually become brittle at low temperatures. Fortunately, the high rate of annealing in the RGS helps to relieve many of the strains and imperfections in the solid. Single crystals are not required since the thermal expansion is isotropic for a cubic structure.

The parallel plate capacitor technique of measuring length changes measures the capacitance of two parallel plates, one fixed and the other movable. The length of the gap between the plates then is computed from $L = \varepsilon_0 A/C$, or more importantly, the sensitivity from $\Delta L/L = -\Delta C/C$. The capacitors are of the three terminal type where the third terminal is a grounded shield or guard surrounding at least one of the leads. The capacitance is defined only by the area of the plates facing each other and is independent of the leads.

As pioneered and used by White\textsuperscript{89} the sample, generally metallic, is mounted in, but insulated from, the capacitance cell. The top of the sample forms one capacitor plate and a fixed plate is mounted in the cell directly above the sample. This is the "Normal" configuration shown in
Figure 2. The change in \(L_g\) with temperature is obtained from the change in capacitance. The change in length of the sample is the sum of the change in \(L_g\) and the change in length of the cell. The cell is constructed of a material with a known thermal expansion much smaller than that of the sample so that the correction for the thermal expansion of the cell is small.

Unfortunately, as the sample cools and contracts the gap \(L_g\) increases. Since the sensitivity \(\Delta C = -\Delta L_g (\epsilon_0 A/L_g^2)\) varies inversely as the square of the gap, minimum sensitivity is available at low temperatures where the thermal expansion is rapidly approaching zero. For a material like copper the change in \(L_g\) is small enough that the change in sensitivity is not critical. However, for argon the sensitivity would be reduced by as much as a factor of 100. For this reason the "Inverted" arrangement shown in Figure 2 must be used for a substance like argon. The fixed plate is now at the bottom of the sample and the movable plate is suspended from the top of the sample. The gap now closes up as the sample contracts and maximum sensitivity is available when it is needed. The change in length of the sample is given by the change of \(L_g\) and a correction for the thermal expansion of the portion of the movable plate extending down below the top of the sample.

The above discussion then suggests a hollow cylinder sample geometry with the capacitor plate hanging in the center. However, the bonding and thermal contraction problem makes three small posts preferable to the cylinder, if the posts will remain standing during the assembly of the capacitance cell under less than ideal conditions.
Figure 2. Normal and inverted capacitance cells
Because of the problems to be solved in growing and handling the samples, the uncertainty as to which sample geometry would work best, the problems in designing a capacitance cell for this measurement, and the large size of the apparatus, it was decided to grow the samples in one dewar and measure them in another. While adding the additional problem of transferring the samples from one dewar to the other, it added the flexibility of having the experiment broken into two parts.

Sample Growth

Figure 3 is a sketch of the apparatus used to grow and transfer three 3/8 in. diameter 3 cm long samples which are equally spaced on a 7/8 in. circle. This is the geometry actually used in the thermal expansion measurements. The samples have to be grown in a transparent mold with very little thermal conduction. Glass was tried but proved to be too thick. The 2 in. long molds were made of two thicknesses of 1.5 mil Mylar epoxied together with Armstrong C-1 epoxy on a Teflon mandrel. They were wound with a 2 mil Manganin heater, ten turns to the inch, and epoxied into two brass end pieces with Armstrong A-12 epoxy. The top end piece has a 3/16 in. stainless steel (SS) tube soldered into the top to carry the gaseous argon and heater wires down from the dewar head. The argon is distributed to the three tubes through channels in the brass and the wires exit through a nylon and epoxy seal soldered into the bottom of the end piece. A heater is wound on the top end piece to help control the rate of solidification. A heater and thermocouple are attached to the bottom end piece so that its temperature can be controlled when the
Figure 3. Sketch of the crystal growth and transfer apparatus
6" DIA. BULGE IN VACUUM JACKET

GLASS TRANSFER DEWAR

BASE WITH INDIUM SEAL

3/16" S.S. TUBE

3/8" MYLAR TUBES

2" DIA. GLASS VACUUM JACKET

HEATER

2" KOVAR SEAL

NYLON AND EPOXY SEAL

BASE WITH INDIUM SEAL

1/2" S.S. TUBE
samples are dropped from the tubes, preventing them from freezing to the end piece. Around the outside of the bottom end piece are sockets for 12 2-56 socket head screws used to screw the mold down to the base. A raised ridge on the bottom of the end piece fits into a groove in the base filled with indium, forming a vacuum seal. The base has three posts which fit up into the Mylar tubes slightly past the bottom end piece so that the samples grow entirely in the tubes. The base is mounted on a 6 in. long 3/8 in. diameter SS tube that is connected to the dewar head with a 3/16 in. SS tube running through the bath so that it can be evacuated or filled with exchange gas to vary the heat leak into the bath.

The base and mold are contained within a 4.5 ft long glass vacuum jacket. The vacuum jacket is 2 in. in diameter at the bottom and 3 in. in diameter at the top where it is fastened to a brass dewar head. About halfway up there is an 11 in. long 6 in. diameter bulge. A 3/16 in. diameter SS tube passes through the bath from the dewar head to the bottom of the vacuum jacket so that pre-cooled helium can be blown through the vacuum jacket. A compact glass transfer dewar suspended from the dewar head by a 3/4 in. SS tube is stored in the bulge. A brass block with an indium seal identical to that in the mold base is secured to the bottom of the transfer dewar. The entire apparatus is contained within a glass liquid nitrogen dewar having a 6.5 in. inside diameter and 1 in. viewing slits on the side. The dewar is sealed to the dewar head so that it can be evacuated to reduce the temperature of the liquid nitrogen to as low as 65 K.

The mold is screwed down to the indium seals using a 4 ft long 1/8 in. SS rod with the appropriate size Allen wrench soldered into the end. This
wrench, the tube supporting the transfer dewar and the tube carrying argon to the mold all pass through an assortment of rotating vacuum seals which form part of the dewar head and which allow the various components to be moved about as necessary. The tube carrying argon to the mold is connected to a glass vacuum system mounted near the dewar. It is equipped with a mercury diffusion pump and cold trap so that the mold may be pumped clean, and assorted valves for regulating the flow of the gas. The gas pressure is monitored on a mercury manometer.

The procedure for growing a set of samples is as follows. The indium seals are first sprayed with Fluorglide, a Teflon dispersion, to prevent cold-soldering of the indium to the brass. The mold then is screwed to the base and tested for leaks. If none are found the vacuum chamber is pumped out and the mold is pumped and flushed and finally filled with pure argon gas. The dewar is filled with liquid nitrogen which has a normal boiling point of 77 K. This works quite well for solidifying argon at 84 K. After three or four hours the base of the mold reaches the temperature where liquefaction, then solidification, of the argon starts. The argon pressure is maintained just above the triple point and the required 3 cm length of sample will grow in four or five hours. Unfortunately, the three samples do not grow at the same rate and a considerable amount of time, up to three or four days, and an inordinate amount of luck are required to adjust the three samples to within ±0.05 in. of the required length using the heaters on the tubes and the top end piece. Once finished the samples are first cooled to 77 K and then to 65 K by pumping on the liquid nitrogen over about a 24 hour period. The mold then is unscrewed
from the base, but remains attached to it since the solid argon has bonded the two pieces together. A 100 ohm heater in the bottom of the base is used to heat it up rapidly to the triple point of argon at which point the mold, with the samples securely bonded to the Mylar tubes, is pulled away. Helium exchange gas is added to the vacuum jacket to slow down sublimation from the exposed base of the samples. The low thermal conductivity of the solid argon prevents damage to the samples during this heating process.

The mold and samples then are raised up into the bulge and are manipulated into place inside the transfer dewar. The mold is screwed down to the base and sealed inside the transfer dewar to protect the samples from contamination when they are transferred through the air. The transfer dewar and samples now are ready to be pulled out of the vacuum jacket and to be moved to the experimental dewar. This is done as quickly as possible and no detectable damage ever was done to the samples.

Although they were never used for a thermal expansion measurement, samples also were grown in the form of a hollow cylinder. A mold and base much as used for the three posts were used, but the mold was a 1.25 in. diameter Mylar tube. The base had an inflatable \( \frac{3}{4} \) in. diameter tube made of \( \frac{3}{4} \) mil Mylar in the center around which the sample grew. Inflated with helium during solidification it could be deflated and collapsed when the sample was solid so that the sample could be pulled free. The rest of the process was identical to that used for the three posts.
Capacitance Cell

Figure 4 is a sketch of the all copper capacitance cell. The 1 cm diameter lower capacitor plate was wrapped with two turns of 1.5 mil Mylar and forced into the guard ring, which also serves as the base on which the samples rest. The guard ring and capacitor plate then were lapped flat and smooth. The thermometer block has wells for calibrated platinum and germanium thermometers. The base plate has an indium gasket which forms a seal between the base plate and the can. The helium pot is used to cool the apparatus down to 1 K. The temperature control block contains carbon and platinum sensors and a heater which are used with an electronic temperature controller to control the temperature above 2 K. All parts are securely screwed together. They are supported by three \( \frac{3}{4} \) in. SS tubes soldered into the base of the vacuum jacket and the helium pot; one of these tubes also acts as a pumping line for the helium pot. Three 1/8 in. SS tubes pass from the base plate through the helium pot out into the bath. Two of these carry and shield the capacitor leads; the third carries thermometer leads. The two shielding the capacitor leads continue on through the bath up to the dewar head and are used to control the exchange gas in the can during operation. The capacitance cell is contained within a 4 in. diameter glass vacuum jacket, 4.5 ft long with a 5.5 in. diameter 11 in. long bulge near the top. The capacitance cell is fastened to the bottom of the vacuum jacket which in turn is fastened to the dewar head. A 3/16 in. SS tube running through the bath from the dewar head to the bottom of the vacuum jacket allows pre-cooled helium to be flushed through the vacuum jacket. The entire apparatus is suspended in a double set of
Figure 4. Sketch of the capacitance cell
MASHER
SPACER RING
LOWER CAPACITOR PLATE AND GUARD RING
BASE WITH INDIUM GASKET
1/8" S.S. TUBE
4" KOVAR SEAL

CAN
TOP CAPACITOR PLATE
ARGON SAMPLES
THERMOMETER BLOCK
He⁴ POT
TEMPERATURE CONTROL BLOCK
4" GLASS VACUUM JACKET
glass dewars with 1 in. viewing slits on the side. The inner or helium dewar has an inside diameter of 6.5 in. and an outside diameter of 8 in.; the outer dewar has corresponding dimensions of 9.75 in. and 12.5 in. Both dewars are sealed at the top so that their contents can be pumped down below their normal boiling points. The entire apparatus is suspended from three inflated inner tubes for vibration isolation.

When a set of samples is grown and ready to be transferred, both dewars are filled with liquid nitrogen and the inner dewar is pumped down to 65 K. The sample mold in the transfer dewar then is moved quickly from the sample-growing dewar into the capacitance cell dewar. While the top of the vacuum jacket is open during the transfer a stream of helium is flushed up through the vacuum jacket to keep air out. Once the top of the vacuum jacket is sealed up again the sample mold is unscrewed from the bottom of the transfer dewar, the mold is lifted out and manipulated past the transfer dewar using the bulge in the vacuum jacket, and lowered down to the capacitance cell. The bottom end piece of the mold fits down inside the spacer ring until it almost touches the guard ring. The vacuum chamber is evacuated and the heaters wound on the Mylar tubes turned on. The warm surface of the crystal sublimes away and after about ten minutes the samples slip out of the Mylar tubes to rest on the guard ring. Helium exchange gas is immediately added to reduce the sublimation of the now fully exposed samples and the mold is carefully pulled away.

The mold is placed back in the transfer dewar and the two are "stored" in the neck of the vacuum chamber. The top capacitor plate and masher have been "stored" in the bulge of the vacuum jacket, the capacitor plate is hung from the masher, and the masher is suspended by a
$\frac{3}{4}$ in. SS tube from the dewar head. These two now are lowered down until the top capacitor plate rests on top of the samples. The masher then is screwed down onto the spacer ring forcing the capacitor plate down and mashing the samples to a predetermined uniform length.

The transfer dewar, mold and long Allen wrenches used to assemble the capacitance cell now are removed from the vacuum jacket and the can is inserted, with a flow of helium gas again keeping air out. When the can has cooled to 65 K it is lowered down onto the base and screwed down onto the indium gasket with 24 4-40 screws, sealing the capacitance cell from the vacuum jacket. The rotating seals used to manipulate and assemble the parts of the cell are removed from the dewar head and replaced with a high vacuum valve. The vacuum jacket is flushed with nitrogen and pumped out, the liquid nitrogen is blown out of the inner dewar, liquid helium is transferred in and the apparatus is started cooling. An atmosphere of helium is maintained in the capacitance cell until it has cooled down to about 25 K to inhibit sublimation. This is particularly important since the 1/8 in. lines passing out through the 4.2 K helium bath act as a pump, freezing out argon vapour. At all times a pressure of at least 10 microns of helium exchange gas is left in the sample chamber to help assure temperature equilibrium. As soon as the samples start cooling below the assembly temperature they contract and the upper capacitor plate pulls away from the masher and is supported only by the insulating argon samples. If it is later desired to shorten the low temperature gap, the samples can be heated up beyond the initial assembly temperature, say to 70 K, and then cooled back down. The gap will be shortened by the thermal
contraction between 70 K and 65 K. This not only allows the sensitivity to be increased, but various systematic errors that would be a function of the gap can be checked.

Instrumentation

The capacitance bridge shown schematically in Figure 5 is an a.c. current balance bridge developed by Thompson. The center-tapped secondary of the transformer puts out voltages equal in magnitude and 180° out of phase. The entire voltage is applied to the unknown capacitor if it is smaller than the standard, and a fraction of the voltage determined by the ratio transformer is applied to the standard. When the currents from the unknown and standard sides of the bridge are equal and opposite a null is achieved and the ratio of the unknown to the standard is equal to the ratio of the voltage applied to the standard to that applied to the unknown. This can be read directly from the setting of the ratio transformer. These bridges are capable of high resolution and accuracy, the accuracy being limited in practice primarily by the standard capacitor. The transformer and ratio dividers are wound using very high permeability Supermalloy toroids. For practical purposes these are almost perfect devices.

The actual bridge which we built and used is shown in Figure 6, the cable shields having been left off. The transformer for this bridge is wound on a Supermalloy toroid (Arnold Engineering #6T6100-S2-AA) with a 213 turn primary and a 200 turn main secondary. The main secondary was checked and the two taps were found to be equal and opposite to within a
Figure 5. Three terminal capacitance bridge
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

--- NULL DETECTOR

--- RATIO TRANSFORMER
Figure 6. Capacitance bridge used in this experiment
SHIELDS ARE NOT SHOWN

![Circuit Diagram]

- 5 Dial Ratio Trans.
- 38.5 kΩ
- 20.100 pf
- 100 pf STANDARD
- 0.200 µf
- 0.1 pf STANDARD
- 7 Dial Ratio Trans.
- 1078 Hz
few parts in $10^7$. Additional taps are available one-tenth of the full voltage for use in the quadrature and to effectively reduce the 100 pf standard to 10 pf. The quadrature circuit is used to compensate for a difference in the slight phase shift of the two capacitors. The ratio transformers are commercial Gertsch Ratiotrans. The seven dial Ratiotran (model 1011R) is accurate to 1 part in $10^6$ and the five dial Ratiotran (model RT-60) is accurate to 1 part in $10^5$. The five dial Ratiotran connected to the 100 pf standard normally is not changed during a measurement so its accuracy is not critical. More importantly, these Ratiotrans have input impedances of about 200,000 ohms and output impedances of a few ohms so that circuit loading is not a problem. Three decades of the seven dial and five dial Ratiotrans overlap allowing comparative checks between the Ratiotrans and the two standards. The standards are commercial General Radio three terminal standards. The 100 pf standard (type 1404 B) is accurate to better than 0.01% with a temperature coefficient of less than $4 \times 10^{-6}/K$, while the 0.1 pf standard (type 1403 N) is accurate to 0.1% with a temperature coefficient of less than $40 \times 10^{-6}/K$. These standards are kept in a temperature-controlled box with a temperature drift of less than $10^{-3}$ K/12 hours. The oscillator, which is of local design and construction, is stable to ±0.1 Hz at 1078 Hz with a variable output of up to 200 volts peak to peak. Thus a maximum of 100 volts is available at the secondary of the transformer. The lock-in detector has a shorted input noise of 50 nanovolts and an input impedance of 25 to 50 megohms on the direct input. This detector displays both capacitive and quadrature off-balance simultaneously on separate meters.
The capacitances between conductors and cable shields do not affect the measured capacitance. The cable capacitance on the high side merely shunts the transformer and ratio dividers and that on the low side shunts the detector. The shunting of the transformers is unimportant because of the low output impedances of these devices. However, the shunting of the detector seriously reduces its sensitivity and the resolution of the bridge. This shunting can be reduced greatly by "tuning out" the cable capacitance with a parallel high Q inductor to form a tuned parallel tank circuit. A 9 Henry inductor wound on a ferrite core was used for this. Fine tuning is achieved with an additional variable capacitor, and a bridge impedance of 15 megohms can be obtained. This high impedance does raise the noise level in the detector, but with the bridge tuned in this manner a change of $10^{-7}$ pf can be detected. The total capacitance measured in the experiment varied from 1 to 8 pf.

The resistance thermometry is rather standard. A Leeds and Northrup (model #8164, serial #1676930) NBS-type platinum thermometer calibrated by the National Bureau of Standards down to 11 K was used at the higher temperatures. A Cryo Cal germanium thermometer (serial #748) with a 4.2 K resistance of 335 ohms was used up to 28 K. The germanium thermometer was calibrated on the high end against the platinum scale, below 4.2 K against the helium vapour pressure scale, T58, and in between against T618, a constant volume gas bulb scale. The two thermometers could be cross-checked in situ.

The resistances were measured using a Leeds and Northrup type K5 potentiometer, Leeds and Northrup NBS-type standard resistors and a Keithley 150A null detector. A 10 ohm standard (serial #1730192) and a
current supply delivering 2 or 10 milliamps are used with the platinum thermometer. A 100 (serial #1715239) or 1000 ohm (serial #1725407) standard, depending on the temperature, and a current supply delivering 1, 2, 5, 10, 20, 50, or 100 microamps are used with the germanium thermometer. Both thermometers could be read easily to a millidegree.
RESULTS

Six sets of samples were grown and transferred using the apparatus and techniques described in the previous chapter. Successful measurements were made on three of these sets, the first two of which showed a low temperature anomaly while the last behaved as expected for pure argon. During the course of all of the measurements several different checks were made for consistency and accuracy.

The platinum (♯1676930) and germanium (♯484) thermometers were cross-checked between 11 and 30 K and found to differ by as much as 100 millidegrees at the higher temperatures. When improved thermal anchoring for the thermometer leads failed to help, the germanium thermometer was replaced with ♯748. This thermometer agreed at all points checked with the platinum thermometer to within ±2 millidegrees, which is consistent with the original calibration.

Thermal expansion data were taken both with the sample heating and cooling. While a small hysteresis was observed if the temperature was cycled, the data were reproducible and independent of the direction of temperature change when the temperature was consistently changed in one direction. At higher temperatures data taken in different directions agree to within 0.3%. Temperature control was easier to achieve with the apparatus warming, so most of the data were taken in that direction.

The area of the lower capacitor plate (A) was measured using a traveling microscope and included half of the area of the gap between the capacitor plate and the guard ring. This measurement was checked by measuring the capacitance between the lower capacitor plate and a flat
copper block resting on sapphire spacers above the capacitor plate. The measured height of the spacers then was used to obtain an effective area for the capacitor plate. The two most reliable measurements using the sapphire spacers agreed with the traveling microscope value, 0.800 cm$^2$, to within ±0.2%. A third less reliable value differed by 0.6% (see Appendix 1). The length of the upper capacitor plate ($L_c$) suspended below the top of the samples was found to be 1.146 in. = 2.911 cm using a micrometer accurate to ±0.0001 in. This length and the area of the capacitor plate are both corrected for thermal expansion down to 60 K, where they are 2.902 cm and 0.7952 cm$^2$ respectively. The thermal expansion of copper is such that these quantities change only by ±0.01% and ±0.02% over the temperature range from 75 to 0 K.

The measurement of the length change of the samples is a differential measurement relative to copper. The measured changes must be corrected for the thermal expansion of the upper capacitor plate; that is, the length of copper suspended from the top of the samples. If the length of the upper capacitor plate is $L_c$ and the length of the gap between the capacitor plates is $L_g = \epsilon_o A/C$, where $A$ is the effective plate area at 60 K, the thermal expansion of the sample is

$$\alpha_{\text{argon}} = \left[ \frac{L_c}{L_c + L_g} \right] \alpha_{\text{copper}} - \left[ \frac{L_g}{L_g + L_c} \right] \frac{dc}{dT}. \quad (2a)$$

Note that $\frac{dc}{dT} < 0$. The thermal expansion coefficient for copper ($\alpha_{\text{copper}}$) is generally 0.1 to 0.2% of that measured for argon and is never more than 0.5%. Hence, since $L_c/(L_c + L_g) \approx 0.99$, Eq. (2a) can be simplified to
\[ \alpha_{\text{argon}} = \alpha_{\text{copper}} - \left[ \frac{L_g}{(L_c + L_g)} \right] \frac{1}{C} \frac{dC}{dT}. \]

This relationship was used together with published values of \( \alpha_{\text{copper}} \) to analyze the data.

Two likely sources of systematic error are tipped or non-parallel capacitor plates, and a layer of argon (dielectric constant = 1.55) on the capacitor plates. If the plates are tipped, the measured capacitance will be multiplied by a factor \( 1 + \frac{1}{2} X + \frac{1}{8} X^2 + \cdots \) and the sensitivity by \( 1 + \frac{1}{2} X + \frac{1}{8} X^2 + \cdots \), where \( X = \frac{B^2 \sin^2 \theta}{L_g} \) (see Appendix 2). \( B \) is the diameter of the capacitor plate, \( L_g \) the gap in the center, and \( \theta \) the angle of tilt. A layer of argon of thickness \( Y \) will multiply both the capacitance and sensitivity by a factor \( 1/(1 - 0.355Y/L_g) \) (see Appendix 2). Both of these sources of error depend on the gap between the capacitor plates, \( L_g \). As will be shown below, measurements of both the thermal expansion and relative length change agree with accurate x-ray measurements at higher temperatures to within a constant factor independent of the gap, indicating that these sources of error are negligible.

The most significant test of the present data is made by comparison with x-ray lattice parameter measurements of Peterson, Batchelder, and Simmons. Reliable data cannot be taken with the present method much above 35 K because the 1/8 in. lines going from the capacitance cell to the 4.2 K helium bath act as a pump when the samples are warmed and start to sublime. At elevated temperatures a steady decrease in sample length could be observed at constant temperature presumably due to this effect. On the other hand, the x-ray technique lacks sufficient sensitivity to provide reliable thermal expansion data at low temperatures. However, the
two sets of data can be compared in the 25 to 35 K region where the x-ray technique achieves considerable accuracy. The x-ray measurements have a stated accuracy of \( \pm 6 \times 10^{-6} \) for the relative length change \( \Delta a/a_0 \), and an accuracy of \( \pm 5 \times 10^{-6} \) K\(^{-1} \) for the volume thermal expansion coefficient, \( \frac{3}{a} \frac{da}{dT} \). At 25 K the percentage accuracies given for the x-ray data are \( \pm 0.25\% \) in the relative length change from 0 K, and \( \pm 0.7\% \) for the thermal expansion coefficient. At 35 K these accuracies become \( \pm 0.12\% \) and \( \pm 0.5\% \) respectively.

All of the higher temperature capacitance cell data were compared with the x-ray data and found to lie systematically several percent higher than the x-ray data. The amount of this deviation depended on the sample and its history. If after an initial set of measurements were made the sample were raised back up to the 70 K temperature region and another set of measurements made, the results of the second set of measurements deviated less from the x-ray measurements than before. The deviation for a given set of data is very constant, the variation generally being less than the uncertainty of the x-ray data. Figures 7 and 8 show such a comparison for the data from the "pure" sample. The thermal expansion coefficient \( \alpha \) has been divided by \( T \) and the relative length change by \( T^2 \) to facilitate the display of the data. The dashed line is drawn through smoothed points obtained from a computer fit of the actual x-ray data. The circles (o) are the present data. The values of the capacitor plate gap \( L_g \) are given at the temperature extremes to indicate the variation of this parameter. The deviation determined from the relative length change capacitance data is \( 3.6 \pm 0.2\% \) except at 26 K where it is \( 3.2\% \). Similarly, the thermal expansion values differ by \( 4.0 \pm 0.2\% \). Data points at
Figure 7. Comparison of the present relative length change data with the x-ray measurements
Figure 8. Comparison of the present thermal expansion measurements with the x-ray measurements
O PRESENT DATA

- SMOOTHED X-RAY VALUES

\[ \frac{\alpha}{T} \times 10^{-6} \text{ K}^{-2} \]

\[ T \text{ (K)} \]

\[ Lg = 0.306 \text{ MM} \]

\[ Lg = 0.377 \text{ MM} \]
lower temperatures are consistent with these values if the larger limits of error of the x-ray measurements are taken into account. The data shown are part of a set taken after the apparatus was assembled and had been warmed no higher than 68 K. Later the apparatus was warmed to 74 K to shorten the gap and another set of data taken. Unfortunately no low temperature data were obtained in this later run since the upper capacitor plate came to rest on a small particle of "dirt" 1/8 mm thick at 10 K. However, data were taken between 25 and 40 K where the gap changed from 0.320 to 0.185 mm, roughly a factor of 2. The discontinuity in the data at 10 K prevents a comparison of the relative length change, but the thermal expansion measurements deviated from the x-ray measurements over this temperature range, 25 to 40 K, by 2.2 ± 0.2%. For both sets of data the variation in the deviation is completely random.

Since the deviation of the capacitance cell measurements from the x-ray measurements is independent of the gap, it is safe to assume that the deviation is caused neither by plate tippage nor a dielectric layer. The most probable explanation of this systematic error is that the samples have bonded to the copper cell parts. This constrains the areas of the ends of the samples so that a short length of the sample near the ends contributes a volume expansion to the length change. When heated to sufficiently high temperatures the samples readily sublime. When observed visually, this sublimation is most effective in rounding off the ends of the samples, which would reduce the area of the end. Since the effect of the area of the end being constrained will depend on the ratio of the diameter of the end to the length of the sample the effect is reduced each time some of the end sublimes away.
The comparison between the present data and the x-ray data leads to
the following conclusions. A systematic error, possibly due to sample
bonding, exists in the present data. This error is constant to ±0.2%
over a significant range of temperature and gap. Since the change in gap
going from 25 to 1 K, 0.300 to 0.220 mm, is less than the change in the
region of comparison, 0.386 to 0.300 mm, it is reasonable to scale the
data over the entire temperature region so that it agrees with x-ray data
between 25 and 35 K. This conclusion is further supported by the second
set of data where the error was constant from 40 to 25 K with a gap chang­
ing from 0.323 to 0.167 mm, which "spans" the gaps in the low temperature
region of the first set of data. The 0.4% difference in the deviations
of the relative length change and thermal expansion measurements falls
within the error of the x-ray thermal expansion measurements, ±0.5%. For
this reason the 3.6% scale factor obtained from the relative length change
comparison should be used.

The capacitance cell data are shown in Tables 3 and 4 and Figures 9
and 10. The actual "raw" data are given in Table 3, corrected only for
the thermal expansion of copper. Table 4 gives "smoothed" values of the
thermal expansion and Grüneisen parameter γ [Eq. (1)] along with the other
quantities used to calculate γ up to 25 K. The smoothed thermal expansion
values have been divided by 1.036 to make them agree with the x-ray meas­
urements between 25 and 35 K. Figure 9 shows the normalized low tempera­
ture data in the form of an \( \alpha/T^3 \) vs \( T^2 \) plot. This indicates that the
thermal expansion can be represented by

\[
\alpha = (3.34 T^3 + 0.030 T^5) \times 10^{-8} K^{-1}
\]

up to about 5.5 K. Figure 10 is a plot of the Grüneisen parameters in
Table 3. Raw capacitance cell data. Capacitance values are given as read from the two ratio transformers. Total capacitance is obtained by adding the two numbers. Thermal expansion values have been corrected for the thermal expansion of copper.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Capacitance (pf)</th>
<th>Mean Temperature (K)</th>
<th>Thermal Expansion (K^-1)</th>
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</thead>
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<td>3.1000 963286</td>
<td>1.323</td>
<td>8.04 x 10^-8</td>
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Table 4. The circles (o) are calculated from x-ray thermal expansion measurements as given by Peterson et al., which have a stated accuracy of ±0.9% at 20 K and ±3.5% at 10 K. The theoretical curve is due to Klein, Horton, and Feldman. The resolution of the present thermal expansion data is determined by the length sensitivity (0.1 Å) at low temperatures and temperature control at higher temperatures. The resolution and accuracy of the thermometers are not limiting factors. As can be seen in Figures 7 and 8 the
Table 4. Normalized and smoothed thermal expansions and Grüneisen parameters. Specific heat values up to 12.5 K are from Ref. 104; those given from 10.0 K on up are from Ref. 103. Bulk moduli and molar volume values are from Ref. 93 as are the thermal expansion values above 25 K.

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resolution at higher temperatures is about $\pm 0.1\%$. From Figure 9 the scatter in the low temperature data is about $\pm 2\%$ at the lowest temperatures. The use of an $\alpha/T^3$ vs $T^2$ plot however allows a much better definition of the low temperature thermal expansion. The 'extreme' curves that can be drawn through the data vary from the curve shown at 0 K by $\pm 0.5\%$. Taking
Figure 9. Normalized low temperature thermal expansion data
$a/T^3 = 3.34 T^3 + 0.030 T^5$
Figure 10. Smoothed Grüneisen parameters
account of the resolution of the data, the probable accuracy of the com-
parison with the x-ray data and accuracy of the x-ray data itself, the
accuracy of the present data is probably ±0.75% below 4 K and ±0.5% above
4 K. All systematic errors, including those associated with determining
the effective plate area are compensated for in the normalization of these
data to the x-ray values.

The accuracy of the experimental Grüneisen parameters given in Figure
10 is harder to assess. Finegold and Phillips make no mention of the
probable errors of their specific heat data which disagree by 1 to 2% with
those of Flubacher, Leadbetter, and Morrison in the region where the two
sets of data overlap. The bulk moduli have a stated accuracy of ±1.3% at
0 K, but become essentially estimates above 10 K. In view of this, the
values of the Grüneisen parameter are probably no more accurate than ±3%
over our whole temperature range (1 to 25 K).

The first two samples measured showed very anomalous behaviour at low
temperatures. This at first was thought to be a problem with the apparatus.
It was not until measurements were completed on the second sample that it
was discovered that a similar anomaly had been seen by Burford and Graham
in the heat capacities of solid CO and N₂. They attributed this anomaly
to O₂ impurities in the gas. Molecular oxygen has two unpaired electronic
spins which give rise to a "spin-split" triplet ground state with a doubly
degenerate upper level and a splitting of 5.14 K. A Schottky curve with
these parameters fits the specific heat anomaly rather well independent of
the host and concentration, implying that the anomaly is indeed a molecular
effect.
The second set of thermal expansion samples was analyzed and found to contain $1 \pm 0.5\% \text{O}_2$. This apparently came from an undetected air leak into the vacuum system used to handle the argon gas. Unfortunately no attempt was made to take high precision data on this sample, and it is rather hard to determine what the anomalous contribution is since the large $\text{N}_2$ impurity will affect the lattice contribution. Figure 11 is an attempt to show the anomalous thermal expansion, the lattice contribution having been taken as 1.05 times that for pure argon. The shape of the Schottky curve shown is the same as that which fits the specific heat anomaly. The lattice contribution is shown as a dotted line for comparison. Using the concentration of $\text{O}_2$ in the thermal expansion sample and the molar $\text{O}_2$ specific heat found by Burford and Graham$^{120}$ a Grüneisen parameter of from 1 to 3 is obtained for the $\text{O}_2$ contribution.

The third or "pure" sample was grown from 99.999% pure argon with 2 or 3 ppm $\text{O}_2$ using a thoroughly leak-tested glass high vacuum system. As can be seen in Figure 9, there is no evidence of an anomaly in this sample.
Figure 11. Thermal expansion anomaly due to $O_2$ impurities in argon
$a_{o2} = 1.05 a_{pure}$

$\alpha$ for pure argon

Schottky anomaly
DISCUSSION

The comparison between theory and experimentally determined thermodynamic quantities is not as straightforward as it might appear. In principle, experimental heat capacity or thermal expansion data could be inverted to obtain the lattice frequencies and their volume derivatives. This is impossible in practice since the thermodynamic quantities are an average of the contributions of the $10^{24}$ or so lattice frequencies. The only possible comparison then is between the calculated and experimentally determined thermodynamic properties. The success of the theory, and the potential used, is determined by the closeness with which the theory can predict the measured quantity.

Unfortunately, good theoretical calculations with which to compare thermal expansion results are at the present rather rare, particularly when compared with the wealth of calculations of quantities such as the specific heat and bulk modulus. Specific heats and bulk moduli have been known experimentally for a number of years. Furthermore, these quantities are relatively easy to calculate, the specific heat being obtained directly from the frequency distribution and the bulk modulus depending mainly on the temperature independent static lattice energy. Thermal expansions, on the other hand, involve both a volume and temperature derivative of the free energy and are more difficult to calculate. Until the x-ray measurement of Simmons and co-workers very little had been done in the way of calculating thermal expansions for the RGS. These measurements have prompted a good deal of theoretical work which has concentrated on medium and higher temperatures, since this is the region in which the data exist.
Figure 1, which does not permit a meaningful comparison between theory and experiment below 20 K, is typical of the published theoretical calculations of the thermal expansion.

Theoretical values for the Grüneisen parameter are more common. The most recent calculation for argon\textsuperscript{76} is displayed in Figure 10. The value at 0 K is an estimate by Klein of the volume derivative of $\Theta_0$. The higher temperature values are obtained from a conventional perturbation calculation, including the third and fourth order terms in the free energy, using a MLJ 6-12 potential and nearest neighbor interactions. Unfortunately, the error in the experimental Grüneisen parameters is much larger than that in the thermal expansion since the Grüneisen parameter is a combination of several experimental values. However, it is apparent that a systematic discrepancy of about 10\% exists between the theory and experiment. This discrepancy continues at much higher temperatures even when the anharmonic calculation is replaced with the more successful Improved Self-Consistent calculation. The apparent equivalence of the different theoretical models at low temperatures tempts one to blame the discrepancy in the theoretical value on the potential used.

It is expected that the present results will spur additional theoretical interest in the thermal expansion of the RGS, particularly at low temperatures. While the calculations are difficult, comparison with experiment will provide a significant test of the theory. This comparison will be more meaningful if the present results can be extended to the other RGS. The large range of atomic masses in the RGS causes a correspondingly large variation in the relative importance of the zero point motion and anharmonic effects as can be seen in Table 1. While neon is very "quantum
mechanical" and anharmonic, xenon is almost "classical." At the same time, present theoretical results predict that many-body effects become increasingly important as the mass increases. No reliable thermal expansion measurements exist for xenon at any temperature so that it is not even possible to make accurate conversions between constant pressure and constant volume specific heats. X-ray measurements have been made on krypton, but "die" around 20 K. The situation is better for neon, where the x-ray results are reliable down almost to 4 K.

Although it is quite plausible to ascribe the anomaly in the first two samples to an O\textsubscript{2} impurity, the present data obviously do not definitely prove that such is the case. This could be settled by measuring samples purposely doped with O\textsubscript{2}, preferably with two different concentrations, such as 0.2 and 1%. This would demonstrate whether the anomaly is due to O\textsubscript{2}, and if it is, show whether it is a cooperative or molecular effect, i.e., what is the concentration dependence? It would also provide a quantitative measure of the volume dependence of the effect responsible for the anomaly if the specific heat anomaly found in CO and N\textsubscript{2} is assumed to be truly host independent.

The present technique also could be modified to obtain low pressure bulk modulus values by pressurizing the sample chamber with helium. This has been done using the x-ray technique but suffers from the lower sensitivity of this method and the half hour required to expose the x-ray film, which leads to severe temperature control problems. Although high pressure piston displacement measurements have been made,\textsuperscript{98,99} the bulk modulus remains the weakest link in calculating the high temperature Grüneisen
parameters. The present technique hopefully could improve on these measurements at low pressures by a factor of four or five.

Experience gained from the present work indicates that it should be possible to modify the present apparatus so that the samples can be grown in the capacitance cell. This would simplify matters, particularly if measurements are made on the other RGS.
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To Bob Fugate and Marvin Anderson for their help, particularly in transferring samples and assembling the capacitance cell.
To Mel Colter, Roger Junck, Harris King, and Bob Knight for constructing different parts of the apparatus, particularly those they did correctly.
And to those of his friends and relatives who never believed he did this to avoid honest employment.
APPENDIX 1

The insulating gap between the capacitor plate and guard ring must be taken into account when determining the area of the plate. In practice this is generally done by including one-half of the gap width in the radius of the plate. This was done for the present apparatus using a traveling microscope to make measurements across several different diameters of the plate. The average area found was $0.800 \text{ cm}^2$ with a root mean square deviation of 0.2%. Although the area of this plate is not critical since the data are normalized to the x-ray measurements, it was checked by measuring the capacitance between the plate and a flat copper block supported by three sapphire spacers. The plate area is then determined by the measured height of the spacers and the measured capacitance.

The spacers were measured with a micrometer known to be accurate to ±0.0001 in. This is a limiting factor only with the 21 mil spacers. Another source of error is due to dents and nicks in the copper guard ring on which the spacers rest. These will cause high spots which will result in measured areas less than the true area. In an attempt to minimize this error several measurements were made with each set of spacers with the spacers in different configurations. Table 5 gives the results of these measurements. The high and low capacitance values are given for each set of spacers along with the average value of all of the readings.

All of these values agree to within the combined errors with the traveling microscope values. The first two most reliable values indicate that the approximation of including half of the gap in the area of the plate is probably good to ±0.2%.
Table 5. Plate areas determined by capacitance measurement

<table>
<thead>
<tr>
<th>Spacer heights (in.)</th>
<th>Extreme capacitances (pf)</th>
<th>Average capacitance (pf)</th>
<th>Plate area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1884</td>
<td>0.14805</td>
<td>0.1481</td>
<td>0.8007</td>
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<td>1.305</td>
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</tr>
<tr>
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<td></td>
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</tr>
</tbody>
</table>
APPENDIX 2

Two possible sources of error in the present measurement are tipped or non-parallel capacitor plates and a coating of dielectric, e.g., solid argon, on the capacitor plate.

If the tip of two "parallel" capacitor plates is such that the difference between the greatest and smallest separation is small compared to the mean separation, one can calculate the capacitance of the tipped plates by averaging the separation over the plate area. For circular plates of radius $B$, mean separation $L_g$, and tip angle $\theta$ (angle between the plates), this means averaging $L_g + r \sin \theta \cos \phi$ over the area of the plate. So,

$$C = \varepsilon_0 \int_0^\varphi \int_0^{2\pi} \frac{r \, dr \, d\varphi}{L_g + r \sin \theta \cos \phi}$$

$$= \frac{2\pi \varepsilon_0}{\sin^2 \theta} L_g \left\{ 1 - \left[ 1 - \left( \frac{B^2 \sin^2 \theta}{L_g^2} \right)^{\frac{1}{2}} \right] \right\}.$$

Rearranging the algebra, letting $X = \left( \frac{B^2 \sin^2 \theta}{L_g^2} \right)$ and expanding the square root one has

$$C = \frac{\varepsilon_0 \pi B^2}{L_g} \left[ 1 + \frac{1}{4} X + \frac{1}{8} X^2 + \frac{5}{256} X^3 + \cdots \right].$$

Note that $\left( \frac{\varepsilon_0 \pi B^2}{L_g} \right)$ is the value for parallel plates, so the term in brackets is a correction factor.
The sensitivity is given by

\[ \frac{dC}{dL_g} = - \frac{\varepsilon_0 \pi B^2}{L_g^2} \left[ 1 + \frac{1}{4} x + \frac{1}{8} x^2 + \frac{5}{256} x^3 + \cdots \right] \]

\[ + \frac{\varepsilon_0 \pi B^2}{L_g} \left[ -\frac{1}{2} \frac{x}{L_g} - \frac{1}{2} \frac{x^2}{L_g} - \frac{15}{128} \frac{x^3}{L_g} + \cdots \right] \]

\[ = - \frac{C}{L_g} - \frac{\varepsilon_0 \pi B^2}{L_g^2} \left[ \frac{1}{2} x + \frac{1}{2} x^2 + \frac{15}{128} x^3 + \cdots \right]. \]

Neglecting the difference between \( C/L_g \) and \( \varepsilon_0 \pi B^2/L_g^2 \) this becomes

\[ \frac{dC}{dL_g} = - \frac{C}{L_g} \left[ 1 + \frac{1}{2} x + \frac{1}{2} x^2 + \frac{15}{128} x^3 + \cdots \right]. \]

The correction factor for the sensitivity is the term in brackets.

Two parallel plates of area \( A \) with separation \( L_g \) and a layer of dielectric of thickness \( Y \) with dielectric constant \( K \) have a capacitance of

\[ C = \frac{K \varepsilon_0 A}{(L_g - Y)K + Y} \]

\[ = \frac{\varepsilon_0 A}{L_g \left[ 1 - \frac{Y}{L_g} (1 - Y/K) \right]} \]

So \( 1/(1 - (Y/L_g)(1 - Y/K)) \) is a correction factor.

The sensitivity is given by

\[ \frac{dC}{dL_g} = - \frac{\varepsilon_0 A}{L_g^2 \left[ 1 - \frac{Y}{L_g} (1 - \frac{1}{K}) \right]^2} = - \frac{C}{L_g \left[ 1 - \frac{Y}{L_g} (1 - \frac{1}{K}) \right]} \]
Hence, the same correction factor is applied to the sensitivity as to the capacitance. The dielectric constant for solid argon is 1.55 so \(1 - 1/K = 0.355\).