

THERMAL EXPANSION COEFFICIENTS FOR SOLID ARGON FROM 1 TO 25 K*

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Measurements of the coefficient of linear thermal expansion accurate to 1% are reported for free-standing samples of solid argon for temperatures from 1 to 25 K. These data were obtained using a differential parallel-plate-capacitor technique and at low temperatures can be represented by $\alpha = (3.34T^3 + 0.030T^5) \times 10^{-8} \text{ K}^{-1}$ ($1 < T < 6 \text{ K}$). When combined with other data, these results can be used to obtain Grüneisen parameters which are systematically 10% lower than those reported for anharmonic theories. Preliminary data also showed a low-temperature thermal expansion anomaly which is believed due to the spin-split ground state of O_2 impurities.

The rare-gas solids historically have been a favorite subject for lattice dynamical calculations, largely because of the relative simplicity of their interatomic potentials. The availability in the last few years of reliable experimental data has spurred the theoretical interest in these solids. Most of this theoretical work, reviewed by Pollack¹ and more recently by Horton,² has used a quasi-harmonic or a conventional anharmonic perturbation approach. Discrepancies between theory and experiment at high temperatures have led recently to the application to the heavier rare-gas solids of the self-consistent phonon approach which was developed originally to deal with extremely anharmonic solid helium.³ This approach has been extended in an improved self-consistent approximation (ISC) to include odd derivatives of the potential and has been applied to solid neon and argon.⁴⁻⁶ While the ISC gives significantly better agreement with experimental high-temperature thermodynamic properties, the classical perturbation and self-consistent theories blend together at low temperatures.⁴ Hence, low-temperature results are probably more sensitive to the potential used than the type of theoretical approximation.

Measurements of the volume thermal expansion coefficient [$\beta = (\partial \ln V / \partial T)_p$] provide a fairly severe test for a theory since this quantity involves both a pressure and a temperature derivative of the free energy. Indeed, one of the primary problems of recent theoretical work on the rare-gas solids has been to understand the x-ray lattice-parameter measurements (and derived thermal expansions) of Simmons and co-workers.⁷⁻⁹ These x-ray data, however, lack the precision necessary for accurate thermal-expansion determinations much below 20 K. In the case of argon the accuracy in β decreases from $\pm 0.5\%$ at 30 K to $\pm 4\%$ at 10 K and continues to decrease roughly as the cube of the temperature.

We have used a parallel-plate-capacitance technique to make linear-thermal-expansion measurements on free standing samples of solid argon. These measurements, which extend from 35 to 1 K, are accurate to $\pm 0.75\%$ over almost the entire temperature range. We believe that these are the first high-sensitivity thermal-expansion measurements in the liquid-helium range on a solidified "permanent" gas.

The samples consist of three posts 1 cm diam and 3 cm long which were grown from the melt in Mylar tubes. Since argon has a fcc structure and hence an isotropic thermal expansion, no attempt was made to obtain single crystals. The samples were transferred to the capacitance cell and dropped from the mold onto a copper base plate. A 1-cm-diam lower capacitor plate is imbedded in the center of this plate. The upper capacitor plate is suspended from a plate resting on top of the samples. This inverted arrangement has the advantage that the gap between the capacitor plates decreases with the temperature to give maximum sensitivity to gap change at low temperatures. The capacitor plates must be parallel, and hence the sample lengths must be identical. This is accomplished during the assembly of the cell at 65 K by a built-in jig which deforms the samples so that they have the same length. This arrangement also allows the gap separation to be changed during the experiment by raising the cell temperature above the assembly temperature. Thus, the data can be checked for systematic errors by taking data for a given sample for different capacitor gaps. Typical low-temperature gaps were 0.2 to 0.3 mm.

During manipulation of the samples and assembly of the cell at 65 K the samples were surrounded by an atmosphere of helium gas to prevent sublimation. The gas pressure was reduced to 0.1 Torr or less for the low-temperature measurements.

Sample length changes as small as 0.1 \AA at a gap of 0.2 mm were detected using a capacitance bridge with thermostatted standards and a resolution of 10^{-7} pF , patterned after that used by White.¹⁰ Calibrated platinum and germanium resistance thermometers were used for temperature measurement.

Data were taken on three different sets of samples, using several different gaps and initial or annealing temperatures. A slight hysteresis in the length as a function of temperature was observed if the temperature was not changed monotonically. However, when the temperature was changed systematically in one direction only (up or down) the data were smooth and reproducible to within limits determined by temperature control and length sensitivity. This reproducibility varied from about 1% at the lowest temperature to 0.1% at higher temperatures. Unfortunately the accuracy of the data is not as good. An apparent constant systematic error of several percent is found when the data above 20 K are compared with the more accurate x-ray data.⁷ We believe that this effect is caused by bonding of the samples to the copper cell parts, causing the areas of the sample ends to be constrained, thereby effectively contributing a volume expansion rather than a length expansion for a short portion of the sample near the ends. An attempt was made to minimize the effects of bonding by the use of three posts rather than a hollow cylinder for the sample geometry.

Data obtained from the third sample are shown in Fig. 1. Length changes calculated from these data were compared with the relative x-ray lat-

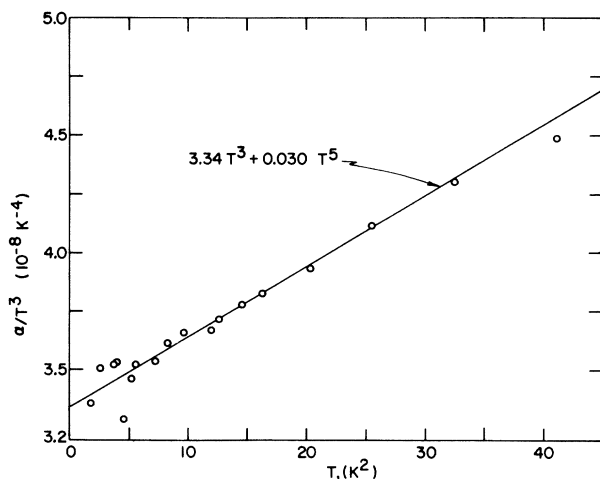


FIG. 1. A plot of the low-temperature thermal expansion data for solid argon (open circles). The solid line represents a best fit.

tice-parameter changes⁷ between 25 and 35 K and found to be $(3.4 \pm 0.2) \%$ high throughout this temperature interval, presumably due to sample bonding. The measured expansions were scaled down by 3.4% and corrected for the expansion of the copper upper capacitor plate (0.5% maximum). The results plotted in Fig. 1 show the expected T^3 behavior.

Our smoothed linear-thermal-expansion values (α) were used to calculate the Grüneisen parameters [$\gamma = 3\alpha(\rho\chi_S C_p)^{-1}$] shown in Fig. 2. The adiabatic compressibilities (χ_S) and density (ρ) values used are those given by Peterson, Batchelder, and Simmons.⁷ Specific-heat data (C_p) below 11 K were taken from Finegold and Phillips,¹¹ while those for above 11 K are as given by Flubacher, Leadbetter, and Morrison.¹² The theoretical curve results from a classical anharmonic perturbation calculation using a Lennard-Jones (12, 6) nearest-neighbor model¹³ and an estimate by Klein¹⁴ of the volume dependence of Θ_0 . The uncertainty in the experimental curve is perhaps 3%, and is obtained by combining the estimated errors in the thermal expansion (1%), the specific heat (1-2%), and the compressibility (1-2%). The disagreement between the experimental and the theoretical curves (10%) is real, and possibly reflects deficiencies in the Lennard-Jones potential used in the theoretical calculations rather than the theory. Similar disagreement between theory and experiment is seen at higher temperatures for the other rare-gas solids, and experimental data for the low-tempera-

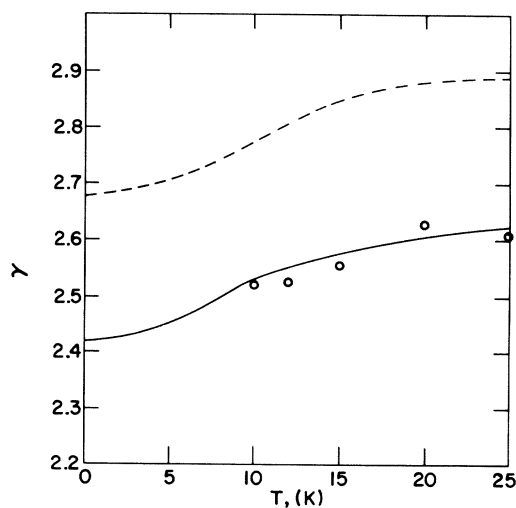


FIG. 2. A comparison of smoothed experimental (solid line) and theoretical (dashed line) Grüneisen parameters γ for solid argon. The open circles are from Ref. 7 which reports x-ray expansion measurements.

ture thermal expansion coefficient would be useful for these substances.

The first two samples measured showed a large anomaly at low temperatures. This at first was thought to be an instrumental effect and no attempt was made to take accurate data or obtain a reliable analysis of these samples. However, an analysis of the second sample showed an O_2 impurity of $1 \pm 0.5\%$. This is believed due to an air leak into the vacuum system used to handle the argon during sample growth and implies an N_2 concentration of from 2 to 6%. Although it is difficult to determine the exact form of the anomaly due to the poor data and the unknown effect of the rather large O_2 and N_2 impurities on the lattice properties, it is now felt that the anomaly is due to transitions in the spin-split ground state of the molecular O_2 .¹⁵ Figure 3 shows the "anomaly" contribution found in the second sample compared with the lattice contri-

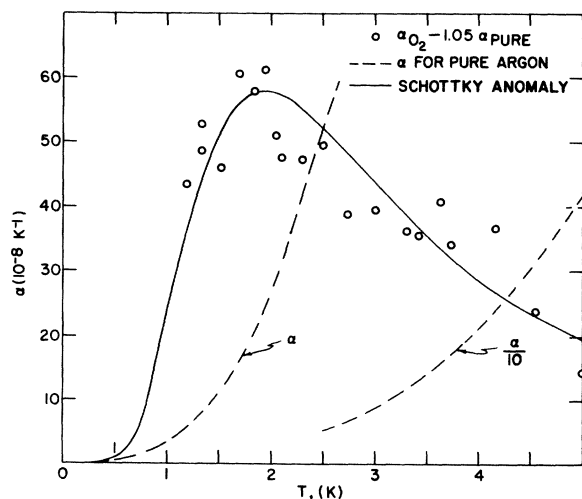


FIG. 3. Contribution of the coefficient of anomalous thermal expansion which was observed for argon samples with approximately 1% O_2 impurity. The Schottky curve was calculated as described in the text from the analysis of specific-heat anomalies due to O_2 impurities in solidified gases given by Burford and Graham (Ref. 15). The thermal expansion coefficient α for pure argon is given for comparison.

bution of pure argon and a normalized two-level Schottky curve. The Schottky curve has a characteristic temperature of 5.14 K, a peak temperature of 1.98 K, and a doubly degenerate upper level. These same parameters were used by Burford and Graham to fit a specific-heat anomaly in solid CO and N_2 caused by O_2 impurities.¹⁵ A comparison of the calculated molar specific-heat anomaly with the thermal-expansion anomaly gives the product of the O_2 concentration and the Grüneisen parameter for the anomaly as 0.017, indicating a Grüneisen parameter of from 1 to 3. The third set of samples, which showed no anomaly (Fig. 1), was grown from argon with only 2 to 3 ppm O_2 impurity using a clean, leak-free, glass gas-handling system. It is clear that further experiments are needed to evaluate quantitatively the effect of O_2 impurities on both the thermal expansion and specific heat of the rare-gas solids.

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