is the incorrectly located A line since no strong impurity absorption lines have been observed at higher energies than the A line, other than satellites of the A line, during an extensive investigation of the edge absorption spectra of gallium phosphide including doped as well as undoped crystals. The origin of the A absorption line is fully discussed in Ref. (3). Some of the absorption structure attributed by Gorban and Kosarev to intrinsic processes, such as that involving an 8-meV phonon, is not intrinsic but is associated with the presence of the strong A no-phonon line. For these reasons the interpretation of the absorption-edge structure of gallium phosphide proposed by Gorban and Kosarev is incorrect.

ACKNOWLEDGMENTS

The authors are very grateful to R. Loudon for several useful discussions and for working out the selection rules for the indirect transitions in gallium phosphide. We also wish to thank C. J. Frosch for providing exceptionally perfect single crystals of gallium phosphide for these measurements.

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Measurements of X-Ray Lattice Constant, Thermal Expansivity, and Isothermal Compressibility of Argon Crystals*

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Crystals of 99.998% purity argon were prepared by directional solidification of the liquid. The x-ray lattice constant was measured by means of a rotating-camera method, and the volume coefficient of thermal expansion was determined over the range 2.3 to 83.2°K with a precision of about 5 ppm deg^{-1}. The lattice constant extrapolated to 0°K is 5.30017 ± 0.00008 kxu. X-ray diffraction was also used to obtain a value for the isothermal compressibility at 4.25°K of $(3.75\pm0.05)\times10^{-11}$ cm^2 dyn^{-1}. A critical synthesis of existing measurements of elastic-wave velocity and of isothermal compressibility is attempted because comparison of the present results with various theoretical models for crystalline argon is limited by the inaccuracies of elastic data. A set of compressibility values is adopted and new values for several thermodynamic functions of argon are compiled. The observed temperature variations of the Grüneisen parameter and of the Debye temperature are compared with several lattice-dynamical models.

INTRODUCTION

MANY theoretical models for noble gas crystals have been studied. Precise and extensive experimental data on the actual crystals are, of course, also necessary. Existing work, primarily on argon, has been summarized in several review articles.[1-4] According to these, much of the experimental information presently available is qualitative and practically none has been obtained from single-crystal specimens. The present paper reports a study, by means of x-ray diffraction, of several properties of pure massive crystals of argon: lattice constant, thermal expansivity, and isothermal compressibility.

X-ray measurements of the lattice structure and lattice constant of solid argon at a single temperature were reported as early as 1924 by Simon and von Simson[5] and in 1925 by De Smedt and Keesom.[6] More extensive determinations of lattice constants of microcrystalline specimens in a range above 20°K were made by Dobbs and co-workers[7] in 1956 by means of a powder camera. They achieved an accuracy of 0.06%, but were forced to stop taking measurements at 60°K because of grain growth. Powder diffractometers have been used more recently over a wider temperature range by Bolz and Mauer[8] and by Barrett and Meyer.[9] Barrett and Meyer were able to extend their measurements to 64°K by cold working their specimens and then annealing them to produce suitable polycrystalline x-ray samples. They also obtained one single-crystal measurement at 81°K with the same diffractometer

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but with reduced accuracy. Their estimated error at low temperatures was not greater than 0.014%.

We have used a single-crystal back-reflection camera with an accuracy of 15 ppm for lattice constant and 6 ppm for expansion. The volume coefficient of thermal expansion of argon has thereby been determined with an accuracy, at temperatures above 10°K, comparable to that of the heat capacity measurements of Flubacher, Leadbetter, and Morrison.[10] Unfortunately, elastic measurements of comparable accuracy are not yet available. To extend the available temperature range, we have measured the isothermal compressibility at 4.25°K. A critical synthesis of the existing elastic data, mostly at intermediate temperatures, then permits tabulation of several thermodynamic functions of solid argon to be made. The present results are then compared with some calculations in the literature for Born–von Kármán lattices. Some reasonable agreements are achieved within the uncertainties of existing elastic data and some discrepancies are noted. It is evident that anharmonic effects must be taken into account in any precise analysis of the thermodynamic functions of argon crystals.

I. EXPERIMENTAL METHOD

Cylindrical single crystals were prepared by solidification of a seed crystal, annealing of this seed in contact with the melt, and finally directional solidification of the liquid argon at $\sim 1\ \mathrm{mm\,h^{-1}}$ with the solid-liquid interface being nearly plane. Details of the procedure and of the structural characteristics of the crystals obtained are described elsewhere.[11] Starting material was Matheson Company research grade argon, of nominal 99.998% purity, which has a stated impurity content (in ppm) of $CH_4<1$, $CO_2<1$, $H_2<5$, $N_2<5$, and $O_2<5$. Throughout growth, annealing, and the subsequent measurements the specimens were contained within a 3-mm-diam, 24-mm-long tube of 0.012-mm Mylar sheet. After growth, a few tenths mm of crystal surface was evaporated to allow the crystals to sit without external constraint during measurements.

In the absence of direct temperature measurements within the fragile argon crystal specimens, we have assumed thermal contact between the x-rayed surface of the specimens and the working thermometers via a copper post in the metal cryostat.[12] Temperatures above 20°K were referred to a platinum resistance thermometer calibrated on the NBS 1955 scale; temperatures between 2.3 and 20°K were referred to a doped encapsulated germanium resistance thermometer calibrated on the NBS Provisional Scale 2–20 (1965). A second germanium thermometer was used as the working thermometer in the range 2.3 to 30°K. It was calibrated, in the cryostat, from the primary thermometers at different times under normal working conditions.

Incident x rays may heat the crystal slightly, but measurements at widely different x-ray intensities at 4.2°K did not show any systematic difference in the lattice constant.

Taking into account all of these factors and possible temperature gradients in the cryostat, we estimate that the reported temperatures are accurate to ±0.03°K.

Temperature differences over a narrow range are of course known more precisely. During measurements the temperature was continuously controlled to about ±0.01°K and recorded to ±0.001°K so that time averages of the temperature could be obtained by graphical integration.

During compressibility measurements the specimen was immersed in purified liquid helium. The helium gas was supplied from a cylinder by means of a high pressure dome regulator, an adsorption purifier, and a manifold which also led to a test gauge and to a deadweight tester. Reported pressures are believed accurate to 0.05 atm.

A large oscillating back-reflection camera was used for the x-ray measurements.[13] Cobalt $K\alpha_1$ radiation ($\lambda=1.78531$ kxu) diffracted from (531) planes of the argon crystal was recorded on film for Bragg angles in the range 75.5° to 85.1°. To obtain the lattice constant, the diffraction peak was recorded by suitable rotation of the camera on both sides of the normal to the diffracting planes. For expansivity measurements the peak was recorded on only one side. During such work, lattice constant determinations were taken at regular intervals to check the alignment of the x-ray camera and to determine accurately the location corresponding to 90° Bragg angle on the camera back. The method permits the use of massive single crystals which, unlike polycrystalline samples, may be examined at temperatures near their melting point. This x-ray method represents an increase in accuracy over previous work[9] by a factor of about 20.

II. RESULTS

A. Lattice Constant

Five separate measurements were made on one argon crystal to determine the lattice constant at 4.25°K. A mean value of 5.30017±0.00008 kxu (possible error) was obtained, as corrected for refraction. The possible error was calculated from the camera geometry,[13] but the average absolute deviation of the five points from the mean was only 0.00003 kxu.

These five measurements were taken over a period of nine days, during which the crystal was cycled twice

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TABLE I. Smoothed values of some thermodynamic functions of crystalline argon versus temperature T. All values apply to solid at the saturated vapor pressure. Linear expansion $\Delta a = a(T) - a_0$, where a_0 is the lattice constant extrapolated to 0°K; x-ray density ρ; x-ray coefficient of volume thermal expansion β; isothermal compressibility χ; isobaric heat capacity C_p; entropy corrected to volume at 0°K, S_0.

T (deg)	$10^4\Delta a/a_0$[a]	ρ[a] (g cm^{-3})	$10^4\beta$[a] (deg^{-1})	$10^{11}\chi$ (cm^2 dyn^{-1})	C_p[b] (J mol^{-1} deg^{-1})	S_0[c] (J mol^{-1} deg^{-1})	C_v[d] (J mol^{-1} deg^{-1})
4	0.00±0.06	1.7710±0.0001	0.03±0.05	3.75±0.05[a]	0.175	0.057	0.175
6	0.05	1.7710	0.24	3.7_5[e]	0.691	0.209	0.691
8	0.37	1.7708	0.72	3.7_6	1.773	0.542	1.770
10	1.06	1.7705	1.38	3.7_7	3.305	1.093	3.294
12	2.24	1.7698	2.16	3.7_9	5.134	1.848	5.100
15	5.00	1.7684	3.48	3.8_3	8.12	3.289	8.01
20	12.79	1.7641	5.55	3.9_3	12.51	6.155	12.16
25	23.31	1.7587	7.14	4.0_5	16.02	9.182	15.30
30	36.45	1.7518	8.54	4.2_1	18.67	12.12	17.49
35	51.73	1.7437	9.69	4.3_8	20.85	14.90	19.13
40	68.84	1.7349	10.68	4.5_9	22.54	17.48	20.25
45	87.52	1.7252	11.64	4.8_3	23.87	19.87	20.95
50	107.91	1.7148	12.54	5.1_0	25.13	22.07	21.54
55	129.89	1.7037	13.49	5.4_2	26.27	24.12	21.94
60	153.52	1.6919	14.50	5.8_1	27.31	26.04	22.19
65	179.04	1.6793	15.63	6.2_7	28.36	27.82	22.34
70	206.72	1.6657	16.99	6.8_2	29.71	29.49	22.60
75	236.94	1.6509	18.55	7.4_6	31.33	31.06	22.94
80	270.10	1.6349	20.31	8.2_4	33.17	32.58	23.34
83	291.55	1.6247	21.47	8.7_6	34.84	33.47	24.02

[a] Present x-ray diffraction work. Error in the density is estimated possible error including uncertainties in the x-ray wavelength and in x-ray camera geometry. Error in other quantities is estimated from the scatter of data points.

[b] Data from Ref. 10. Error is estimated by those authors at ±2% at the lowest temperatures, decreasing to ±0.2% for $T > 20$°K but increasing to ±0.5% at the highest temperatures.

[c] Calculated from C_p values, with a further correction to the volume at 0°K, V_0, by the term $3V_0\beta\Delta a\, a^{-1}\chi^{-1}$. Errors including uncertainty in χ rise to ±0.33 J mol^{-1} deg^{-1} at 83°K.

[d] The error in these values due only to the uncertainty in χ, arising from use of the expression $C_v = C_p - \beta^2 TM\rho^{-1}\chi^{-1}$, rises to ±1.3 J mol^{-1} deg^{-1} at 83°K.

[e] Calculated for this and higher temperatures from adiabatic values in Table II. At the higher temperatures, the values may be uncertain by ±10%, but the temperature dependence over a narrow range is probably more precisely determined.

to low temperature (2.7 and 2.3°K) and twice to high temperature (64 and 83.2°K). The camera center was moved to a different part of the crystal for two of the determinations. No systematic variations were observed for any of these changes. The value of the lattice constant was confirmed by a single measurement on the crystal that was subsequently used for the compressibility determination. Its value differed from the above mean value by 0.00004 kxu.

Densities, shown in Table I, were obtained from the present lattice-constant and expansion measurements, using values of 39.948 g mole^{-1} for the molecular weight M and 1.002059 for the kxu-to-angstrom conversion factor.[14]

B. Thermal Expansion

Table I shows smoothed values for the total relative expansion referred to a value extrapolated to 0°K. The actual data collected for one crystal during extensive thermal cycling within the temperature range are collected in the Appendix. No irreversibility was apparent so the points taken after heating are not distinguished from those taken after cooling. The values given apply to argon in equilibrium with saturated vapor.

The smoothed values were obtained from least-squares machine fits of the lattice-expansion data points to various low-order polynomials in overlapping temperature ranges. The mean absolute deviation of the individual data points from the final smoothed function was less than 6 ppm. The coefficient of volume thermal expansion β is also given in smoothed form in Table I.

Measurements made on two additional crystals gave substantial agreement with the above expansion (within 30 ppm in over-all relative lattice expansion for the better of the two crystals). The experimental conditions for these other series of measurements, however, were found to contain possible sources of systematic error so were not used in the final compilation. The data for one crystal were taken with camera oscillation ranges that were possibly too small. The 90° Bragg angle for the camera was not determined with sufficient accuracy for the other set of measurements.

C. Compressibility

A determination of the compressibility of a different argon crystal was made at 4.25°K. Lattice-constant measurements on the specimen were made at seven successively higher pressures up to 20 atm. The procedure was repeated as the pressure was decreased, with measurements taken at ten pressure intervals. The data are shown in Fig. 1. A straight line was fitted to the last 27 of the data points by a least-squares method, and the slope was used to calculate the compressibility.

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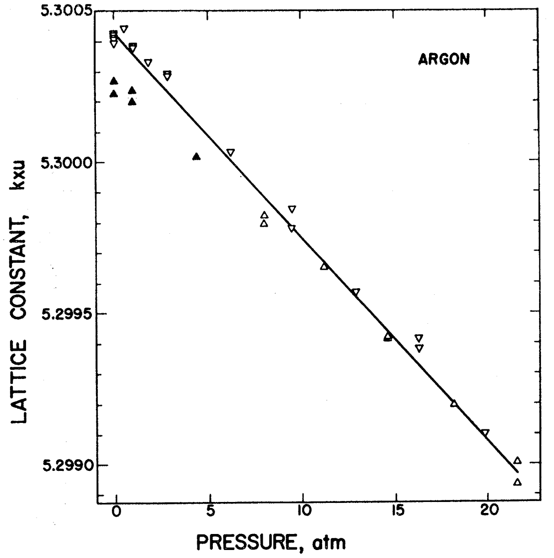

FIG. 1. Lattice constant of argon at 4.25°K immersed in liquid helium at various pressures. The line corresponds to a volume compressibility of 3.75×10^{-11} cm^2 dyn^{-1}. The initial anomalous lattice constant changes are discussed in the text, Secs. II C and III B.1. △—increasing pressure; ▽—decreasing pressure; ▲—first data points.

The final result is subject to some interpretation, as the cycle showed evidence of hysteresis at low pressures. The observed lattice constant increased slightly when the helium pressurizing fluid was brought into contact with the argon crystal. This observed lattice expansion appeared to saturate after the lattice constant had increased about 0.00018 kxu. The compressibility of the crystal as measured by x-ray diffraction after the saturation was $(3.75\pm0.05)\times10^{-11}$ cm^2 dyn^{-1}, where the stated error is the standard deviation of the slope of the fitted straight line.

The original lattice constant was obtained after the crystal was held at 30°K for 2 h under vacuum. Further pressurization again produced the same hysteresis. After the second pressurization, even 60 h of annealing above 78°K would not return the lattice parameter to its original value. Following this last high-temperature annealing, a mass spectrographic analysis, of sensitivity 0.005% for bulk helium content, of a sample taken from this crystal did not reveal any helium.

A series of measurements was performed on a new crystal to see if a threshold pressure for the helium existed, below which the lattice-constant change would be insignificant. If such a threshold exists, it is well below 1 atm.

III. DISCUSSION

A. Lattice Constant and Thermal Expansion Coefficient

The present determination of the lattice constant as a function of temperature agrees, in general, with previous values within their rather large possible errors.[3,9] A few significant variations outside previous stated error occur at isolated temperatures, as shown in Fig. 2. Previous volumetric density determinations,[15] also shown in Fig. 2, appear generally rather inaccurate. This inaccuracy in volumetric measurements is probably associated with voids incorporated into the solid specimens during their preparation.[16]

The present evaluation of the expansion coefficients also agrees with previous estimates within their rather large stated errors, except at the highest temperatures. Figure 3 shows the comparison. The expected error in the present work is too small to be shown in the figure.

B. Compressibility, χ

As stated in Sec. II C, the present x-ray determination of compressibility must be regarded with some caution until a fuller investigation of the apparent hysteresis effect is carried out. More complete evidence is required before a unique atomic mechanism, if present, can be identified and quantitative estimates made of the expected influence of such atomic conditions on x-ray diffraction studies which are necessarily carried out near the specimen surface.[17] Nevertheless, the present work is the first isothermal measurement reported for argon at low temperature and low pressures. This is important because of the large pressure and temperature dependence of the compressibility. We shall assume that the present value is characteristic of bulk crystalline argon in the following discussion.

1. Present Value at 4.25°K

Some comparison of the present χ with previous work is then possible. The previous work is of various types. An extrapolation by Dobbs and Jones[1] from high-temperature sound-velocity data gave an estimate of 4.0×10^{-11} cm^2 dyn^{-1}. A variational calculation by Bernardes[18] using a simple Heitler-London wave function and a 6–12 Lennard-Jones potential gave an estimate of 4.3×10^{-11} cm^2 dyn^{-1}. Study by Beaumont,

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[15] The various references are given in Ref. 3.

[16] V. G. Manzhelii and A. M. Tolkachev, Fiz. Tverd. Tela. **5**, 3413 (1963) [English transl.: Soviet Phys.—Solid State **5**, 2506 (1964)].

[17] We have examined various possible explanations of the effects observed during our compressibility studies. One possible interpretation of the lattice constant increase is that the helium pressurizing agent diffused interstitially into the surface layers of the argon lattice. A crude estimate of this possible diffusivity of helium in solid argon at 4.2°K was calculated by analysis of the deviation of the first five data points from the straight-line fit to the other points. From the time dependence of this deviation the diffusion was calculated, using the relation

$$C(x,t)=C_\infty[1-\operatorname{erf}(x/2D^{1/2}t^{1/2})]$$

for a saturable diffusion. As noted in Sec. II C the deviation was apparently pressure-independent at pressures >1 atm. The deviation was assumed to be proportional to this concentration $C(x,t)$, and the distance x was taken as half of the effective penetration, 16 μm, of the x rays. The estimate of the diffusivity made in this manner yielded a value of about 10^{-11} cm^2 sec^{-1}.

[18] N. Bernardes, Phys. Rev. **120**, 807 (1960).

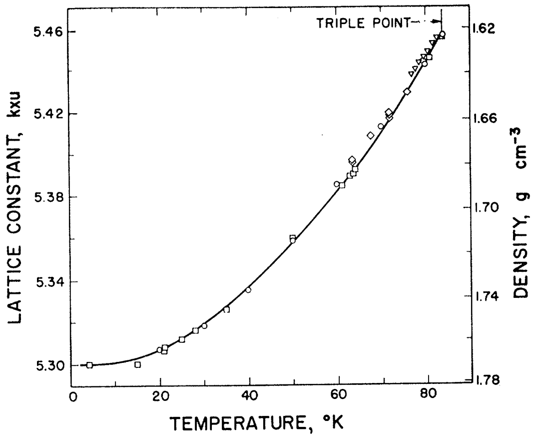

FIG. 2. Comparison of the present x-ray measurements of thermal expansion and of density of solid argon with previous work (see references of Ref. 3). Estimated possible error in the present work is ±0.00008kxu units. □—Barrett and Meyer; ○—Dobbs *et al.*; △—Clusius and Weigand; ◇—Piercey; ▽—Smith; solid line—present work.

Chihara, and Morrison[19] of heat capacity data together with a series of quasiharmonic 6-m potential calculations by Horton and Leech[20] yielded a value 3.9×10^{-11} cm^2 dyn^{-1}. More recently, Barron and Klein[21] obtained a value 3.83×10^{-11} cm^2 dyn^{-1} by considering the strain dependence of the first few even moments of the lattice frequency distribution for a 6–12 potential model. The present x-ray value $(3.75\pm0.05)\times10^{-11}$ cm^2 dyn^{-1} is very close to the latter prediction.

2. *Temperature Dependence of* χ

Before detailed comparisons of the present thermal expansivity measurements can be made with theory, the compressibility must be evaluated over the entire temperature range below 83.8°K. Several measurements at high temperature are available for this purpose, including measurements of the longitudinal and transverse sound-wave velocities. Barker and Dobbs[22] measured both wave velocities on polycrystalline samples at temperatures between 65 and 80°K. Jones and Sparkes[23] measured the resonant frequency of torsional vibration of a suspended polycrystalline rod between 18 and 65°K. They then deduced the transverse-wave velocity over this temperature range by normalizing their data by means of a few of the earlier measurements of Barker and Dobbs. From the scattering of light, Lawrence and Neale[24] obtained values for the longitudinal-wave velocities at temperatures between 54 and 83°K, also on polycrystalline samples.

We have constructed a plausible temperature variation of the adiabatic compressibility χ_s from smooth curves of both elastic wave velocities, consistent with all of the previously mentioned data. Values for the velocities at 0°K were first calculated from the present measured value of χ_s and the experimental Debye temperature Θ_0^c deduced by Beaumont and coworkers.[19] The relations

$$\chi_s=[\rho(v_l^2-4v_t^2/3)]^{-1}, \tag{1a}$$

$$\Theta_0(0)=\frac{h}{k}\left[\frac{4\pi V}{9N}\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)\right]^{-1/3} \tag{1b}$$

yield values, $v_t=944$ m/sec and $v_l=1640$ m/sec.

The data of Jones and Sparkes were then renormalized to the calculated 0°K value and used to determine the temperature dependence of v_t up to 65°K. The longitudinal velocity in the temperature range from 54 to 83°K was obtained from the average of the data of Barker and Dobbs and the data of Lawrence and Neale. To determine the shapes of the curves in the regions where data were lacking, we required that the temperature dependence of the ratio v_t/v_l be monotonic and smooth. The resulting smooth velocity curves were used to calculate the adiabatic compressibility over the entire temperature range. The corresponding isothermal value at 65°K is consistent with that measured by Stewart.[25]

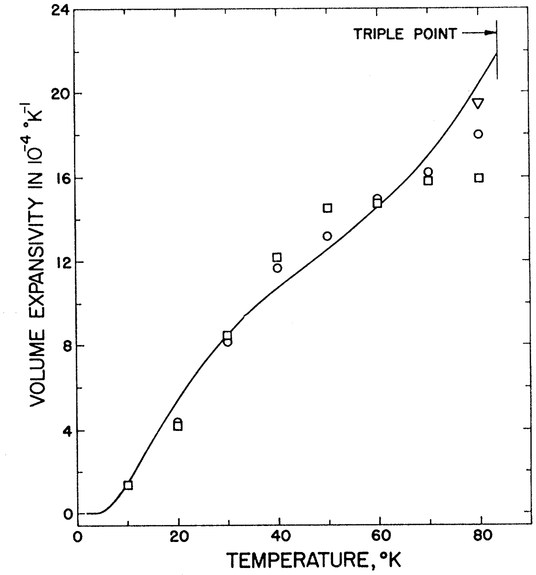

FIG. 3. Comparison of the present values of volume coefficient of thermal expansion of argon with previous work (see references of Ref. 3). Error estimated in the present work is $\pm5\times10^{-6}$ deg^{-1}. □—Bolz and Mauer; ○—Dobbs *et al.*; ▽—Smith; solid line—present work.

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[19] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) **A78**, 1462 (1961).

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[24] D. J. Lawrence and F. E. Neale, Proc. Phys. Soc. (London) **A85**, 1251 (1965).

[25] J. W. Stewart, J. Phys. Chem. Solids **1**, 146 (1956).

TABLE II. Summary of some elastic properties of solid argon as a function of temperature, as obtained from the discussion in Sec. III B.2 of the text. v_l and v_t are longitudinal and transverse elastic wave velocities, respectively. χ_s is the adiabatic compressibility. σ_s is the adiabatic Poisson ratio. Estimated possible errors in the various elastic quantities are relatively large (see text); detailed values given here represent the possible dependence upon temperature. The last two columns show derived values of the relative lattice expansion and of the coefficient of thermal expansion, respectively, at zero pressure, where they differ from the values given in Table I.

T (deg)	$10^4 v_t$ (cm sec^{-1})	$10^4 v_l$ (cm sec^{-1})	σ_s	$10^{11}\chi_s$ (cm^2 dyn^{-1})	$10^4\Delta a/a_0$	$10^4\beta$ (deg^{-1})
0	9.44	16.40	0.253	3.75[a]	...	...
10	9.4	16.4	0.25	3.7_6	...	...
20	9.4	16.3	0.25	3.8_2	...	...
30	9.2	16.1	0.25	3.9_4	...	...
40	9.0	15.8	0.26	4.1_2	...	...
50	8.8	15.4	0.26	4.3_7	...	...
60	8.4	14.8	0.26	4.7_2	...	...
70	8.0	14.2	0.27	5.1_9	206.74	17.00
80	7.6	13.5	0.27	5.8_0	270.21	20.36
83	7.4	13.2	0.27	6.0_4	291.72	21.55

[a] Present work.

The velocities estimated by this method and the resulting compressibilities are listed in Table II. A possible error in χ of up to 10% should be assumed at the higher temperatures consistent with the $\frac{1}{2}$ to 4% uncertainties estimated for the measured wave velocities. We note that the compressibilities do not agree with the 77°K value obtained by Stewart[25] or with any of the values reported by Smith and Pings.[26] Stewart obtained his isothermal value from an extrapolation of data taken at 325 atm and higher. Smith and Pings, who used an optical method, were hampered by conflicting data on the density variation of the Lorentz-Lorenz function. It is not clear, however, why these compressibility discrepancies exist which are larger than stated experimental uncertainty.

The deduced values for the Poisson ratio σ in Table II suggest an apparent slight deviation from $\sigma=\frac{1}{4}$ at 0°K, and an apparent increasing σ with increasing temperature. The value of σ at 0°K is close to that of the Barron and Klein[21] all-neighbor model. Poisson's ratio should be $\frac{1}{4}$ for a solid that has central forces and obeys the Cauchy relations.[27]

C. Empirical Relations

Although the calorimetric measurements of Flubacher and co-workers[10] were made on condensed argon having an unknown state of aggregation, we assume that their results can be correlated with the present work on argon crystals. The values for the density, the coefficient of thermal expansion, and adiabatic compressibility obtained above may then be used to obtain improved values for the isothermal compressibility as well as for the entropy S_0 and the specific heat C_v at constant volume. In particular, we find that the present C_v and S_0 values differ significantly from previous expectation.

Table I shows the results. In constructing it we have neglected the difference between C_P at zero pressure and the measured values at the saturated vapor pressure; the difference rises at most to 0.1% even at 83°K at which quoted error is ±0.5%.[10] On the other hand, we note, considering the accuracy of the present x-ray data, that an analogous correction for the lattice expansion is significant. The appropriate values are given in Table II.

Throughout Table I we have indicated appropriate experimental errors with the following important exception. Consistent treatment of the various thermodynamic relations requires that bulk volume values be used. Because of thermal vacancy formation these may be somewhat different from the present x-ray values at the highest temperatures. While an upper limit of 0.2% mole fraction vacancies can be set at the triple point,[28] direct experimental evidence about the vacancy content and its temperature dependence is not yet available. Very tentatively one may estimate the influence of thermal vacancies by using calculations of Nardelli and Terzi.[29] At 83°K the effect on Table I of correcting from x-ray to bulk values for their predicted vacancy content is to decrease ρ by about 0.0005 g cm^{-3}, to increase β by about 6×10^{-5} deg^{-1}, to reduce S_0 by about 0.13 J mole^{-1} deg^{-1}, to reduce C_v by about 0.55 J mole^{-1} deg^{-1}, and to increase the Grüneisen parameter γ by about 0.09. At the highest temperatures, therefore, this kind of uncertainty still exists in the tabulated values. Further, although we shall not mention it again in each case, corresponding uncertainty due to possible vacancy effects is also present for $T\gtrsim75$°K in each of the correlations mentioned below.

From an empirical standpoint, we note that the Lindemann-Nernst ratio

$$K=(C_p-C_v)/TC_p^2 \tag{2}$$

is remarkably constant for argon. In the entire temperature range above 15°K it has the value $(1.11\pm0.04)\times10^{-4}$ mole J^{-1}.

More significantly, one may compare the thermodynamic functions compiled here with an empirical Grüneisen equation of state[30]

$$(V_T-V_0)/V_0=E_T/(Q-bE_T)\,, \tag{3}$$

where V_T is the molecular volume at temperature T, $E_T=\int_0^T C_v dT$, and Q, b, and V_0 are parameters. Figure 4 shows the good agreement between this equation of

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[26] B. L. Smith and C. J. Pings, J. Chem. Phys. **38**, 825 (1963).

[27] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, Inc., New York, 1944), p. 104.

[28] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phil. Mag. **12**, 1193 (1965).

[29] G. F. Nardelli and N. Terzi, J. Phys. Chem. Solids **25**, 815 (1964).

[30] E. Grüneisen, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Julius Springer-Verlag, Berlin, 1926), Vol. X, p. 1.

state and experimental values at the given temperatures. The figure also yields E_T as a function of temperature.

The value of V_0 is taken to be the observed molar volume in the low-temperature limit. The values thus determined for the other two parameters, $Q=23$ kJ mole^{-1} and $b=5.6$, may be compared with those given by Mie-Grüneisen analysis[30]

$$Q=V_0\gamma_0^{-1}\chi_0^{-1}, \tag{4a}$$

and

$$b=(m+n+3)/6. \tag{4b}$$

Here γ is the Grüneisen parameter ($\gamma_0 \sim 2.4$, see below), the subscripts denote evaluation in the limit of low temperature, and m and n are the exponents in the interatomic potential function

$$\phi(r)=-Ar^{-m}+Br^{-n}. \tag{5}$$

The value of $Q \simeq 25$ kJ mole^{-1}, given by Eq. (4a), may be slightly larger than that obtained from the equation of state over the whole temperature range. However, the value of $(m+n) \simeq 31$ given by $b=5.6$ and Eq. (4b) is up to 50% larger than the values corresponding to the customary Lennard-Jones potential functions used for argon.

Figure 5 shows the Grüneisen thermodynamic parameter, $\gamma=\beta\rho^{-1}C_v^{-1}\chi^{-1}$, as a function of temperature. Uncertainties in β prevented any previous experimental determination of this temperature dependence.[9] Unfortunately, the magnitude of γ at high temperature is still uncertain by as much as 10% because of the uncertainty in χ noted above in Sec. III B. However, the apparent variation of γ in the range 10 to 30°K should be independent of this difficulty because the variation of χ is small at low temperatures.

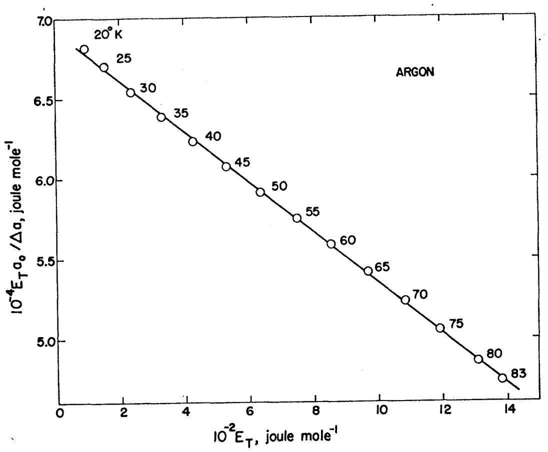

FIG. 4. Comparison of the measured properties of solid argon shown by points at the given temperatures, with an empirical Grüneisen equation of state, Eq. (3) of text, represented by the straight line. Agreement with the form of Eq. (3) is good, but the derived exponents in the Mie potential are much larger than the usual 6–12 assumption.

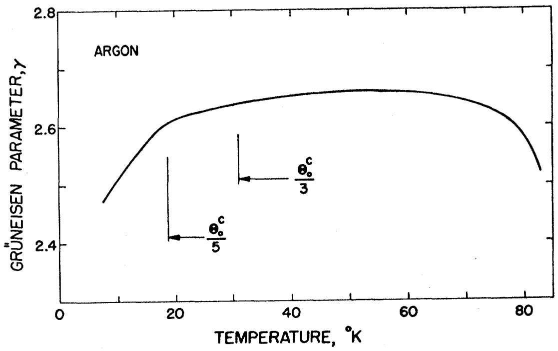

FIG. 5. Grüneisen's thermodynamic parameter, $\gamma=\beta\rho^{-1}C_p^{-1}\chi_s^{-1}$, for solid argon. The estimated error is ±0.02 or less in the range $\Theta_0/5$ to $\Theta_0/3$, but it increases at the highest temperatures (owing to uncertainty in χ_s) and at the lowest (owing to uncertainty in β). In the range below $\Theta_0/4$, values of γ drawn from Tables I and II actually show some small irregularities in their temperature dependence, but these are within possible experimental error and are not indicated in the graph.

At the highest temperatures, immediately below the triple point, the apparent temperature variation of γ may not be real or characteristic of a hypothetical perfect argon lattice. As noted above, a very tentative correction of γ for effects associated with thermal vacancy formation tends to increase the apparent γ by $\simeq 0.1$ at the highest temperatures,[28] but even such a difference would hardly be outside the present corresponding uncertainty in χ. The precise extrapolated temperature variation in χ is particularly uncertain, of course, near the end of the temperature range.

D. Comparison with Dynamical Theories

Predictions calculated from dynamical theories of crystal lattices may include dispersion curves and frequency distributions for phonons, and appropriate averages and strain dependences yielding temperature-dependent functions, such as the Grüneisen parameter and the (Debye) characteristic temperature Θ. Most such calculations for argon crystals have employed the quasiharmonic approximation,[3,31] although some workers have studied anharmonic models.[21,32–34]

In several cases for other types of crystals for which accurate single-crystal elastic data are available, reasonable self-consistency of these data with calorimetric and expansion measurements has been achieved.[35] On the other hand, theories starting on a more fundamental

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[31] J. Grindlay and R. Howard, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 129.

[32] D. C. Wallace, Phys. Rev. **139**, A877 (1965). Earlier references are given here and also in Refs. 21 and 33.

[33] A. J. E. Foreman and A. B. Lidiard, Phil. Mag. **8**, 97 (1963).

[34] J. L. Feldman, G. K. Horton, and J. B. Lurie, J. Phys. Chem. Solids **26**, 1507 (1965).

[35] J. G. Collins and G. K. White, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1964), Vol. IV, p. 450; D. E. Schuele and C. S. Smith, J. Phys. Chem. Solids **25**, 801 (1964); see also J. C. Phillips, Phys. Rev. **113**, 147 (1959).

atomic basis have generally shown only more qualitative agreement with experiment, at best.[36]

1. *Grüneisen's Parameter*

Barron[37] first used Born–von Kármán lattice dynamics to consider a temperature dependence of the Grüneisen parameter for a monatomic lattice. He showed from model-independent considerations that values of γ in the limits of high and of low temperatures, γ_∞ and γ_0, can be obtained from the 0 and -3 moments, respectively, of the lattice frequency distribution. He calculated these moments for a close-packed lattice with central forces and predicted for this model that the principal temperature variation of γ should occur at temperatures near $\frac{1}{5}\Theta$. Further approximate calculation with a Lennard-Jones 6–12 potential yielded a value of $\gamma_\infty = 3$ and a difference of $\gamma_\infty - \gamma_0 = 0.15$.[38]

The present work, Fig. 5, shows qualitative agreement with Barron's predictions. The observed γ varies by only ± 0.01 from a value 2.65 throughout the range 30 to 70°K (and possibly even above, see Sec. III C). γ is lower by 0.05 ± 0.02 at $\frac{1}{5}\Theta_0{}^c$, and decreases further at lower temperatures. Below $\frac{1}{10}\Theta_0{}^c$ the present experimental accuracy is insufficient to fix precisely the temperature variation of γ. The x-ray results hint of even further decrease in γ; the situation evidently deserves further experimental study.

Horton and Leech[20] carried out extensive machine calculations in the harmonic approximation using interatomic potentials of the type given in Eq. (5). They investigated the effects (1) of taking different numbers of interacting neighbors, (2) of using different values of m, (3) of including zero-point energy, and (4) of taking limited account of anharmonicity in the calculations. Generally, γ values for their models are larger than present experimental values. Their γ_∞ values range about 2.8 ± 0.2, the smaller values corresponding to repulsive energy terms with lower values of m and to all-neighbor interactions. The observed temperature variation in γ, on the other hand, favors their nearest-neighbor calculations. We find, therefore, qualitative agreement but quantitative inconsistency between quasiharmonic models and the present experimental results.

2. *Characteristic Temperatures*

Several workers have studied the influence of anharmonic terms in the free energy of crystal models by various means. The work of Barron and Klein[21] for $T = 0$°K has already been mentioned in Sec. III B.1. Of course the present thermal expansion data do not alter their detailed discussion of many points. Of particular interest is the question of the sign and magnitude of the first anharmonic correction to the value of the appropriate Θ in the limit $T = 0$°K, for different assumed interatomic potentials. Their (positive) correction for most potentials results in Θ values in significantly better agreement with experiment than those given by quasiharmonic calculations alone.

Our expansion data do, however, suggest possible modification of the conclusions of Kuebler and Tosi.[39] Their inferences were drawn primarily from the apparent temperature dependence of the Debye temperatures for the entropy (Θ^{s_0}) and for the specific heat (Θ^c) using the thermodynamic functions for argon adopted by Beaumont and co-workers.[19] On the other hand, from our Table I one may obtain revised values of (Θ^{s_0}). Above the temperature of the minimum, (Θ^{s_0}) rises smoothly to a value near 84.4°K in the temperature range above 70°K. The total apparent rise above the minimum value is about 2.7% which is less than that supposed by Kuebler and Tosi. Unfortunately, we note that the existing uncertainty in χ leads to an error in (Θ^{s_0}) which might be as large as 2% near 80°K. Exhaustive analysis is not yet merited. One may conclude, however, that (1) at finite temperatures the first anharmonic correction to the entropy is most likely negative and may lie within the range indicated by Kuebler and Tosi, but (2) the anharmonic correction is possibly smaller than these authors anticipated. Wallace's[32] approximate calculations using a 6–12 potential generally predict a rather larger anharmonic correction than the existing data for argon suggest, but earlier models, for example Foreman and Lidiard,[33] had seriously overestimated the anharmonicity.

Because of its more marked temperature variation above 10°K, in Fig. 6 we show (Θ^c) as obtained from the C_v values in Table I. Also shown is (Θ^c), approximately corrected to the volume at 0°K by means of the relation of Paskin[40]

$$\Theta(V_0) = \Theta(V_T)(\rho_0/\rho_T)^\gamma . \tag{6}$$

The Θ values thus obtained agree within 3% or less with ones calculated using an approximate correction devised by Zener and Bilinsky,[41] the Θ values obtained from the Paskin relation being the smaller.

Again, as evidence for anharmonicity in argon due to thermal vibrations, one may compare Fig. 6 to the quasiharmonic calculations of Horton and Leech.[20] The

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[36] See, for example, A. S. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963); W. Cochran, Rept. Progr. Phys. **26**, 1 (1963).

[37] T. H. K. Barron, Phil. Mag. **46**, 720 (1955).

[38] A similar calculation by G. M. Graham [Can. J. Phys. **42**, 563 (1964)], considered zero-point effects and used a different method for obtaining the necessary sums over the frequency modes. The resulting difference, $\gamma_\infty - \gamma_0 = 0.025$, is much smaller than Barron's.

[39] J. Kuebler and M. P. Tosi, Phys. Rev. **137**, A1617 (1965). We note that these authors' entropy values differ from ours above 65°K, because in integrating, they used a different means of treating the experimental scatter in the original C_p data (Ref. 10). We are grateful to Dr. Tosi for comments on this matter.

[40] A. Paskin, Acta Cryst. **10**, 667 (1957).

[41] C. Zener and S. Bilinsky, Phys. Rev. **50**, 101 (1936).

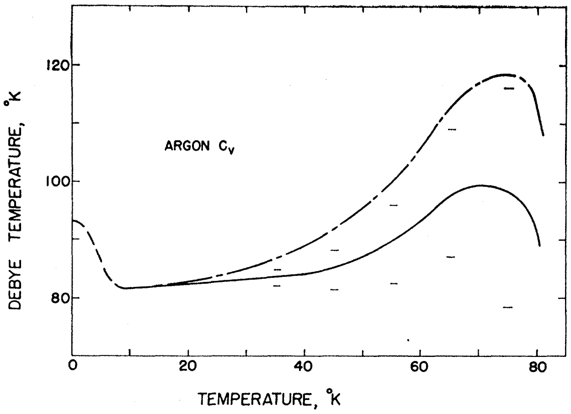

FIG. 6. Variation with temperature of the Debye temperature for the specific heat at constant volume of solid argon, based upon Refs. 10, 19, and the present work. Error ranges marked on one curve show the consequences of an estimated 10% uncertainty in the compressibility. Dashes—Beaumont *et al.*; solid line—present work; broken line—referred to $V(0°\text{K})$.

quantitative values of Θ calculated by Horton and Leech are in all cases lower than the experimental ones. These disagreements are from 3 to 13% in the temperature range 0 to 16°K. In addition, the experimental value of $\Theta(T)/\Theta(0)$ at the temperature of the minimum, 10°K, disagrees by 5% with a value from their all-neighbor calculation with the repulsive term exponent m equal to 12. The qualitative shape of the calculated and experimental curves is similar in the temperature range 10 to 18°K. But above 18°K the experimental curve continues to rise, while the (harmonic) theoretical one levels off to zero slope at 40°K.

As discussed for γ in Sec. III C, the apparent observed drop in (Θ^c) at extreme high temperatures may not be real or it may be a lattice effect. It is clear that extrapolation schemes as applied earlier for (Θ^{s_0}) [39] and for C_v [33] are at present quite inconclusive means of investigating the magnitude and, in particular, the temperature dependence of possible thermal vacancy effects in argon.

IV. CONCLUSION

In summary, there are a number of satisfactory qualitative agreements between the present work and existing detailed lattice calculations. However, a considerable number of quantitative discrepancies and uncertainties remain. Further theoretical work, particularly at finite temperatures and with anharmonic contributions included, therefore appears worthwhile. At the same time, new and more precise experimental data for the elastic properties and thermal vacancy content of argon crystals are required. The present work has shown that it should be possible to prepare and to manipulate crystal specimens suitable for such investigations.

ACKNOWLEDGMENTS

W. E. Schoknecht helped us with some of the calculations. One of us (R.O.S.) wishes to thank Professor S. Amelinckx and the Solid State Physics Department of S.C.K.-C.E.N., Mol, Belgium, for their stimulation and hospitality during the first half of 1965. He is also indebted to the U. S. National Science Foundation for support during the same period.

APPENDIX

TABLE III. X-ray lattice parameter thermal expansion data for argon, referred to the extrapolated value at 0°K.

T(°K)	$10^4\Delta a/a_0$	T(°K)	$10^4\Delta a/a_0$	T(°K)	$10^4\Delta a/a_0$
2.36	0.02	5.92	0.18	27.80	30.35
2.75	0.08	6.24	−0.03	28.34	31.76
2.75	−0.12	6.67	0.25	31.22	39.96
3.28	0.03	7.10	0.07	33.05	45.59
3.34	−0.08	7.74	0.40	37.40_1	59.82
3.78	−0.01	8.48	0.51	43.82_0	82.98
3.78	−0.05	8.54	0.56	46.23_5	92.44
4.25	0.07	8.56	0.56	49.03_1	103.84
4.25	−0.03	9.17	0.62	52.19_0	117.31
4.25	0.05	10.24	1.05	55.21_0	130.89
4.25	0.07	11.85	2.20	57.51_5	141.56
4.25	−0.13	13.65	3.58	60.24_4	154.71
4.25	−0.09	14.13	4.18	62.53_3	166.42
4.25	0.01	15.84	5.99	63.97_7	173.66
4.26	−0.04	16.74	7.27	70.38_8	208.98
4.26	0.05	18.57	10.08	72.99_1	224.42
4.26	0.08	20.71	13.71	75.15_0	237.60
4.26	0.05	21.00	14.77	77.14_2	250.53
4.27	0.05	22.38	17.49	80.02_3	270.27
5.24	0.15	23.82	20.53	81.90_6	283.58
5.81	−0.11	25.08	23.50	83.17_6	292.83