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Thermal-Expansion Measurements and Thermodynamics of Solid Krypton*

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Accurate measurements of the lattice parameter of krypton versus temperature are reported. The measurements allow precise evaluation of the volume expansivity as a function of temperature. These results, together with recent measurements of specific heat, isothermal compressibility, and equilibrium vacancy concentration, provide enough information to allow tabulation and discussion of a number of thermodynamic properties of solid krypton. It is found that the thermal formation of atomic vacancies has a significant effect on all the thermodynamic functions of krypton at the higher temperatures. Entropy and isochoric specific-heat values are analyzed to obtain the leading anharmonic coefficient in the high-temperature expansion for the free energy of krypton. Additional explicit evidence for anharmonicity comes from the observed systematic decrease of Grüneisen parameter with increasing temperature. Finally, numerous published calculations of thermal properties of noble-gas solids are examined. It is concluded that no comprehensive model is presently available to predict the observed properties of krypton and argon within present experimental accuracy.

INTEREST in the noble-gas solids has stemmed from the belief that these crystals might be closely approximated by a system of particles interacting with simple pairwise-additive central forces. Numerous calculations have been performed for such model systems but detailed experimental information on noble-gas crystals has frequently not been available for comparison with such theory.

Here we report precise x-ray determinations of the lattice parameter of krypton crystals as a function of temperature. The thermal-expansion measurements have been made using two of the specimens prepared for the vacancy-concentration measurements reported in the preceding paper.[1] Specimen preparation and handling procedures have been described in that paper. They were generally similar to those employed in this laboratory in earlier work on argon,[2,3] neon,[4] and neon isotope[5] crystals.

Our measurements allow precise evaluation of the coefficient of volume-thermal expansion. These data together with recent specific-heat,[6] isothermal-compressibility,[7] and vacancy-concentration[1] measurements are then used to evaluate the isochoric entropy and specific heat. Analysis of these isochoric quantities yields values for the first few even moments of the harmonic phonon frequency spectrum and the leading anharmonic coefficient in the high-temperature expansion for the free energy. The importance of thermal vacancy effects at the higher temperatures is stressed.

The thermal expansivities of a number of noble-gas solids are then compared on the basis of two laws of corresponding states. Finally, some comparisons between experiment and existing theories of thermal properties are made. No single model appears to describe fully the behavior of krypton or argon within the accuracy of existing measurements.

I. EXPERIMENTAL METHOD AND RESULTS

A. X-Ray Camera

A large, orientable, rotating x-ray camera[8] served to measure the specimen lattice parameter a and lattice-parameter changes Δa. The ability to interchange the directions of the incident and diffracted x-ray beams permitted an absolute determination of the lattice parameter.

Back-reflection Laue diagrams made with the specimen at 4.2°K were used to determine the crystallographic orientation and structural properties of each specimen. A combination of x-ray wavelength and lattice planes which would result in a high-angle Bragg reflection could then be selected. By oscillation of the camera at a uniform rate about the Laue-Bragg maximum and by subsequent measurement of the position of the peak of the film darkening, an accurate determination of the lattice parameter is obtained, even for specimens having considerable subgrain structure.[9]

With a helium path, the exposure times for Ilford "G" x-ray film ranged from only a few minutes for low specimen temperatures to nearly 1 h for temperatures near the triple point. The films were measured on a linear comparator and linearly corrected for shrinkage.

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[1] D. L. Losee and R. O. Simmons, preceding paper, Phys. Rev. **172**, 934 (1968).

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

[3] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).

[4] D. N. Batchelder, D. L. Losee, and R. O. Simmons, Phys. Rev. **162**, 767 (1967).

[5] D. N. Batchelder, D. L. Losee, and R. O. Simmons, Phys. Rev. (to be published).

[6] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1462 (1961).

[7] A. O. Urvas, D. L. Losee, and R. O. Simmons, J. Phys. Chem. Solids **28**, 2269 (1967).

[8] D. N. Batchelder and R. O. Simmons, J. Appl. Phys. **36**, 2864 (1965).

[9] D. N. Batchelder, D. L. Losee, and R. O. Simmons, in *Crystal Growth*, edited by H. S. Peiser (Pergamon Press, Inc., New York, 1967), p. 843.

TABLE I. Lattice parameters of krypton crystals at 4.25°K.

Specimen	Diffracting planes	X [a] deg	Radiation[b]	Refraction correction Å*	Lattice parameter Å*
1[c]	622	13	Ni $K\alpha_1$	0.00006	5.64593
			Ni $K\alpha_2$		5.64595
2	640	9	Cu $K\alpha_1$	0.00005	5.64589
			Cu $K\alpha_2$		5.64585
4[c]	422	½	Cr $K\alpha_1$	0.00011	5.64583
Average value					5.64589

[a] Angle between diffracting planes and specimen cylinder axis.
[b] Wavelengths used according to Ref. 10: Ni $K\alpha_1$, 1.657910 Å*; Ni $K\alpha_2$, 1.661747 Å*; Cu $K\alpha_1$, 1.540562 Å*, Cu $K\alpha_2$, 1.544398 Å*; Cr $K\alpha_1$, 2.28970 Å*.
[c] See Ref. 9; specimen 4 used for compressibility measurements of Ref. 7.

Corrections to account for the finite depth of penetration of the x-ray beam into the specimen are negligible for krypton because of the large specimen-to-film distance of the x-ray camera. The x-ray wavelengths used are those given by Bearden[10] in Å* units. From consideration of camera geometry and the uncertainties in measurements of the x-ray films and camera dimensions, we estimate that the maximum possible error in the value of the lattice parameter at 4.25°K is 0.00010 Å*.

B. Lattice Parameter at 4.25°K

Table I summarizes the krypton lattice parameter determinations made on three specimens at 4.25°K using five different x-ray wavelengths. The range of scatter of the results from the average is less than the estimated maximum possible error. One previous determination of the lattice parameter of krypton with which the present value may be compared is 5.645 Å, with a stated experimental uncertainty of about 0.001 Å.[11] The agreement is satisfactory.

C. X-Ray Thermal Expansion

Determination of relative changes in the lattice parameter of a given specimen can be made with considerably higher precision than the accuracy with which the lattice parameter itself can be determined. In this case, errors such as those due to uncertainty in the camera geometry or uncertainty in the x-ray wavelengths do not affect the $\Delta a/a$ values. The present temperature scale is referred to Internl.-1948 above 90°K,

TABLE II. Smoothed values of some thermodynamic functions of solid krypton versus temperature. All values apply to the solid at the saturated vapor pressure. Linear expansion $\Delta a = a - a_0$, where a_0 is the lattice parameter extrapolated to $T = 0$°K; V, molar volume; β, volume coefficient of thermal expansion; χ, isothermal compressibility; C_P, isobaric specific heat; C_V, isochoric specific heat; S, entropy.

T °K	$10^4 \Delta a/a_0$	V_x [a] cm³ mole⁻¹	$10^5 \beta_x$ [a] °K⁻¹	$10^5 \beta$ [b] °K⁻¹	$10^{11} \chi_x$ [c] cm² dyn⁻¹	C_P [d] J mole⁻¹ °K⁻¹	C_V [e] J mole⁻¹ °K⁻¹	$S(V,T)$ [f] J mole⁻¹ °K⁻¹
4	0.04±0.05	27.097	1.5±0.5	···	2.9_0	0.403	0.403	0.134
6	0.22	27.099	5.1	···	2.9_0	1.557	1.555	0.481
8	0.74	27.103	10.3	···	2.9_2	3.587	3.579	1.19_2
10	1.74	27.112	16.8	···	2.9_3	5.933	5.907	2.24_2
15	5.87	27.145	33.4	···	2.9_5	11.70_7	11.55_3	5.76_3
20	12.8 ±0.1	27.202	47.1	···	2.9_7	15.95_8	15.55_1	9.74_9
25	21.7	27.273	57.7	···	3.0_3	18.89_1	18.14_3	13.64_4
30	32.0	27.357	65.4	···	3.1_0	20.88_7	19.75_4	17.27_6
35	43.4_5	27.452	71.2	···	3.1_8	22.36_8	20.83_6	20.61_0
40	55.7_5	27.552	75.4_5	···	3.3_1	23.48_9	21.59_4	23.67_5
45	68.7	27.659	79.2	···	3.4_3	24.28_8	22.01	26.48_8
50	82.3	27.771	82.6_5	···	3.5_7	25.01_2	22.35	29.08_6
55	96.5	27.888	86.5	···	3.7_8	25.69_4	22.62	31.50_1
60	114.4	28.012	90.4_5	···	3.9_1	26.35_1	22.83	33.76_7
65	127.0	28.142	94.5	···	4.1_2	26.95_7	22.99	35.89_9
70	143.3	28.279	98.7	99.1	4.3_5	27.51_0	23.05	37.91_9
75	160.4	28.421	103.0	103.7_5	4.6_0	28.03_7	23.07	39.83_4
80	178.2	28.571	107.2_5	108.7	4.8_7	28.56_0	23.07	41.66_1
85	196.8	28.727	111.7	114.1	5.1_7	29.19_2	23.13	43.40_9
90	216.3	28.893	116.5_5	120.5	5.4_3	29.90_3	23.12	45.09_8
95	236.6	29.067	121.8	127.8	5.7_7	30.74_0	23.21	46.73_6
100	257.8	29.246	129.0	137.6	6.1_5	31.71_9	23.18	48.33_8
105	280.5	29.441	137.7_5	149.7	6.5_8	32.81_5	23.01	49.91_0
110	305.1	29.654	148.0_5	164.0_5	7.0_5	34.05_4	22.70	51.46_5
115	331.7 ±0.15	29.884	159.9±1.0	180.8	7.5_3	35.79_0	22.53	53.01_4
(115.78)	···	(29.923)[g]	···	···	···	···	···	···

[a] Present x-ray work.
[b] Bulk β was computed using the relation $n = \exp[2.0 - 895°\mathrm{K}/T]$, Eq. (4), to represent the fraction of atomic vacancies (Ref. 1) with $v^f = v_a$.
[c] Smoothed x-ray values of Ref. 7. Error is estimated to be ±1% at $T = 4$°K, rising to ±3% at $T = 78$°K, to ±5% at $T = 90$°K, and to about ±10% at higher temperatures. The effect of vacancies is considered here in Sec. II B and is shown in the present Fig. 3.
[d] Smoothed values obtained from Ref. 6, data listed in Appendix, p. 1481. Error is estimated by those authors to be ±2% at the lowest temperatures, decreasing to ±0.2% for $T > 20$°K, but increasing to ±0.5% at the highest temperatures. The effect of vacancies is considered in the present text in Sec. II C and is shown in the present Fig. 4.
[e] These bulk values depend at high temperatures upon the assumption $v^f = v_a$.
[f] $S(V,T) = \int_0^T C_P T^{-1} dT$. Error is estimated to be less than 0.2% for $T > 20$°K. The effect of vacancies is considered here in Sec. II D.
[g] Extrapolated value. Estimated error including uncertainty in the temperature is ±0.002 cm³.

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[10] J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

[11] L. H. Bolz and F. A. Mauer (unpublished), value given in Fig. 2 of G. L. Pollack, Rev. Mod. Phys. 36, 748 (1964).

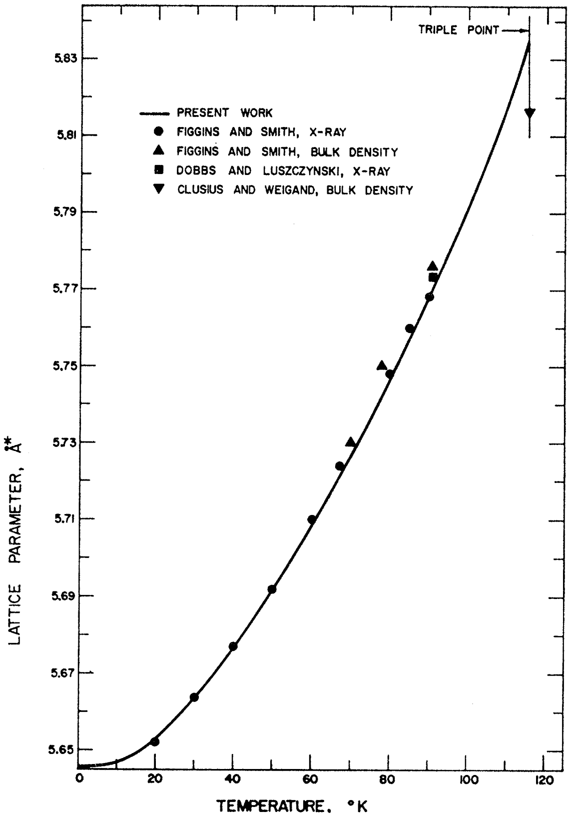

FIG. 1. The x-ray lattice parameter of solid krypton, compared to the results of previous investigators.

to NBS-1955 platinum between 90 and 20°K, and to NBS Provisional 2-20 below 20°K.[12] Observation of the onset of gross melting at the triple point of the krypton specimens provided an independent calibration point for the temperature scale, indicating that thermometer temperatures corresponded to specimen temperatures to better than 0.05°K near the triple point. The excellent agreement, over broad regions, of x-ray lattice-parameter data for different specimens indicates that relative temperatures on independent runs are known somewhat more accurately.

The smoothed values of $\Delta a/a_0$ versus temperature are listed in Table II along with several other thermodynamic functions of krypton which will be discussed below. A value of $a_0 = 5.64587 \pm 0.00010$ Å* has been obtained by extrapolation of the observed values of a to 0°K. The $\Delta a/a_0$ data are the result of measurements made on two different specimens (Nos. 1 and 2). The $\Delta a/a_0$ data for the two sets of measurements at the measured temperatures are given in the Appendix. The agreement between the two sets of measurements is generally excellent; the only discrepancies appearing are three points measured in the temperature range 20 to 30°K on specimen No. 2, which appear to be too small by an amount equivalent to approximately 0.5°K temperature offset.

The $\Delta a/a_0$ values listed in Table II have been taken from the averaged values of low-order polynomials least-squares-fitted to the data. For this smoothing, the three questionable points noted above were omitted. The average deviation of the data from the smooth curve is only about 12 ppm, and is of a fairly random nature. Uncertainties in the specimen temperature of the order of 0.02°K and in the film measurements, noted above, combine to account for the point scatter.

In order to maintain a high degree of precision in the $\Delta a/a_0$ measurements, a change in x-ray wavelengths and diffracting planes was effected at an elevated temperature for each specimen. The $\Delta a/a_0$ values for all such radiations and diffracting planes smoothly follow the adopted curve. The particular combinations used are noted in the Appendix.

In Fig. 1, we show the variation of the lattice parameter with temperature. The results of previous investigators are indicated by points in the graph. The results of the present work are contained well within the width of the solid line. Differences in temperature scale may be one cause of disagreement between the previous x-ray measurements[11,13,14] and the present work. In some cases there is agreement within the rather large estimated error limits of previous workers. The bulk density measurements from which lattice-parameter values have been inferred in the past are unreliable, probably because of microporosity of the specimens.[15] The triple-point value inferred from melting-curve[16] and liquid-density measurements and use of the Clausius-Clapeyron equation is clearly in error.

II. THERMAL PROPERTIES

A. Thermal Expansivity

The coefficient of volume thermal expansion, β, is defined by the equation

$$\beta = V^{-1}(\partial V/\partial T)_P, \qquad (1)$$

where T is temperature, P is pressure, and V is the bulk molar volume. A lattice-parameter expansivity β_x was obtained by differentiation of low-order polynomials fitted to the observed $\Delta a/a_0$ values from the relation

$$\beta_x = 3a^{-1}(\partial a/\partial T)_P. \qquad (2)$$

This lattice-parameter expansivity differs from the value of β appropriate for the bulk solid when vacancies are present, the relation between the two quantities

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[12] H. H. Plumb and G. Cataland, Metrologia 2, 127 (1966).

[13] B. F. Figgins and B. L. Smith, Phil. Mag. 5, 186 (1960).

[14] E. R. Dobbs and K. Luszczynski, Bull. Inst. Intern. Froid, Annexe Suppl. 3, 439 (1955).

[15] A discussion of this problem under usual conditions is given by V. G. Manzhelii and A. M. Tolkachev, Fiz. Tverd. Tela 5, 3413 (1964) [English transl.: Soviet Phys.—Solid State 5, 2506 (1964)].

[16] K. Clusius and K. Weigand, Z. Physik. Chem. B46, 1 (1940).

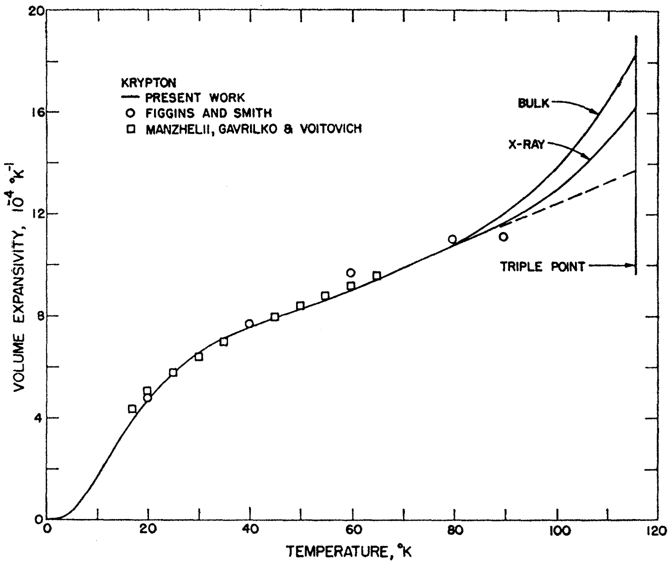

FIG. 2. The coefficient of volume thermal expansion of solid krypton at its saturated vapor pressure. The bulk curve was obtained using Eqs. (3) and (4). The estimated error in the x-ray expansivity is too small to be shown clearly on the figure. Accuracy for the bulk expansivity is dependent on the accuracy of the expression chosen to represent the vacancy content n. The straight dashed line is an arbitrary extrapolation used in the text, Sec. II A.

being

$$\beta=\beta_x+nh^f/kT^2. \tag{3}$$

Equation (3) neglects the possible formation of vacancy clusters and the possible variation of h^f, the vacancy enthalpy of formation, with temperature. Here n is the atomic fraction of monovacancies and k is the Boltzmann constant.

The expansivity β_x resulting from the present data is tabulated as a function of temperature in Table II. The maximum possible error in β_x is estimated to be 5 ppm °K^{-1}; this estimate was obtained from the range of β_x values derived by fitting over different overlapping temperature intervals with different-order polynomials. Table II also lists the values of β obtained when the relation

$$n=\exp(2.0-895°\mathrm{K}/T) \tag{4}$$

is used to represent the vacancy concentration as a function of temperature. The uncertainty in the value of β at the highest temperatures is rather strongly dependent on the uncertainty in the parameters used to represent n. Both β and β_x are plotted in Fig. 2. There comparison is made with the results of previous workers.[13,17]

We observe that at the highest temperatures β_x rises sharply. At least two kinds of possible effects may contribute. This rapid increase with increasing temperature may be due simply to the relaxation of the lattice as additional vacancies are created or it may be due to higher-order anharmonic effects in the vibrating lattice.

First, if a vacancy is created in an otherwise perfect crystal, the lattice will undergo a distortion, thus changing the volume of the crystal by a certain amount. The thermodynamic volume of formation of a vacancy, $v^f=-(\partial g^f/\partial P)_T$, is the sum of two contributions, a term due to the creation of an additional substitutional atomic site and a lattice-relaxation term. We write this as

$$v^f=v_a(1+x). \tag{5}$$

The number x may be either positive or negative; v_a is the volume per atom $\frac{1}{4}a^3$. Now the lattice expansivity β_x includes the contribution of the relaxation term xv_a. Thus β_x may be imagined to be the sum of two terms

$$\beta_x=\beta_0+xnh^f/kT^2, \tag{6}$$

where β_0 is the expansivity of an hypothetical perfect crystal. If one had some idea about the expansivity of the hypothetical perfect crystal, then the volume of formation of the vacancy might be deduced.[18] In Sec. III E below, however, we find that no quantitative prediction about the perfect-crystal expansion of krypton is yet available. For purposes of discussion, we therefore make the tentative guess of a straight-line extrapolation of β_0 at moderate temperatures ($T \gtrsim \Theta$) to the highest temperatures. This guess is shown as a dashed line on Fig. 2. The use of Eq. (6) then leads to a value of x greater than +1, or $v^f \gtrsim 2v_a$. The vacancy volume of formation obtained in this arbitrary manner is much larger than most existing theoretical considerations have predicted.[1]

Second, higher-order anharmonic effects may contribute to an increase in β_0 above a linear temperature dependence. Without an independent experimental determination of v^f, one is without really firm evidence about the magnitude of such a possible increase.

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[17] V. G. Manzhelii, V. G. Gavrilko, and E. I. Voitovich, Phys. Status Solidi **17**, K139 (1966); Fiz. Tverd. Tela **9**, 1483 (1967) [English transl.: Soviet Phys.—Solid State **9**, 1157 (1967)].

[18] We note that *all* vacancy contributions to thermal expansion are included in the vacancy free volume of formation, even those which involve frequency shifts in the lattice made imperfect or otherwise stressed by vacancy formation. We are indebted to Professor C. P. Flynn and Professor A. V. Granato for discussions about this point.

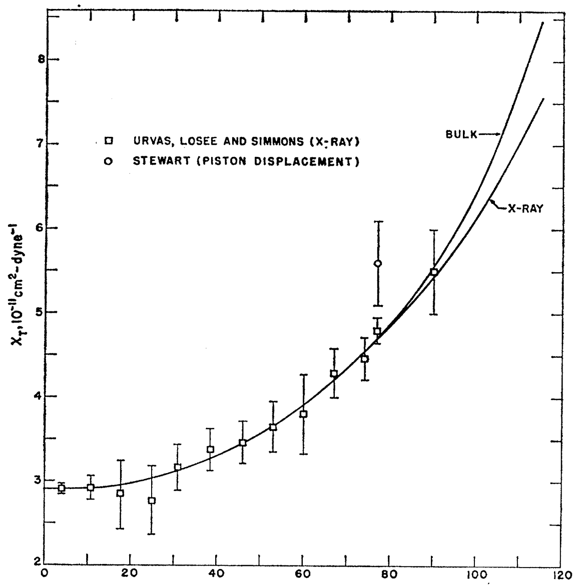

FIG. 3. The isothermal compressibility of solid krypton, determined for 90°K and below by x-ray measurements in the range below 20 bar (Ref. 7). Above 90°K, the values are chosen by a corresponding-states treatment, to follow the behavior of argon and xenon. The difference between bulk and x-ray values follows Eqs. (4) and (7), with the vacancy free volume of formation set equal to one atomic volume.

B. Isothermal Compressibility

The isothermal-compressibility measurements of Urvas and co-workers[7] are plotted in Fig. 3. These results were obtained by comparison of lattice-parameter values measured at various pressures applied hydrostatically by helium. We designate the values of isothermal compressibility so obtained as χ_x. Extrapolation to zero pressure of recent isothermal-compression measurements in the kbar range[19] is consistent with the values shown on Fig. 3.

If vacancies are present, the bulk compressibility χ differs from that of the hypothetical perfect crystal, χ_0:

$$\chi \equiv -V^{-1}(\partial V/\partial P)_T = \chi_0 + n(v^f)^2/v_a kT. \qquad (7)$$

Note that n in general depends upon the pressure. For an assumed $v^f = v_a$, χ_0 becomes the isothermal compressibility as determined by x-ray measurement, χ_x. The vacancy contribution to the bulk compressibility of krypton, if $v^f = v_a$, is of the order of 10% at the highest temperatures, and is also shown on Fig. 3. This isothermal contribution, arising from the pressure dependence of the vacancy enthalpy, appears much larger in krypton than a contribution calculated using elastic considerations alone.[20]

The possibility of thermal vacancy contributions to elastic properties needs to be considered individually for each type of experimental method employed. For example, ultrasonic measurements of the adiabatic compressibility at usual strain amplitudes would not be expected to include terms due to the creation or destruction of vacant sites. The correct bulk density would need to be used, however, in reducing data.

Because the measurements by Urvas and co-workers extend only to 90°K, an extrapolation procedure was adopted by these authors to estimate the high-temperature behavior of the compressibility. Examination of a law of corresponding states as discussed in Sec. III A below, and also in that paper,[7] permits a plausible extrapolation of the compressibility. We have selected the value $v^f = v_a$ for use with Eq. (7) because (a) it appears appropriate in view of the apparently small value of the entropy of formation for the vacancy,[1] (b) most of the theoretical calculations for argon predict rather small lattice relaxations x, and (c) such a value is not inconsistent with the high-temperature behavior of C_V noted in Sec. II C. The values adopted for χ_x are listed in Table II.

Daniels and co-workers[21] have reported results of inelastic neutron scattering by a krypton crystal at about 0.3 kbar and 79°K. The unknown pressure dependence of χ of krypton in the range below 0.5 kbar[7] and the appreciable statistical uncertainty in the phonon frequencies for small phonon wave vectors[21] prevent any detailed comparison between a χ value derived from the neutron work and the present Table II. However, we feel that there is no disagreement outside the uncertainties listed above.

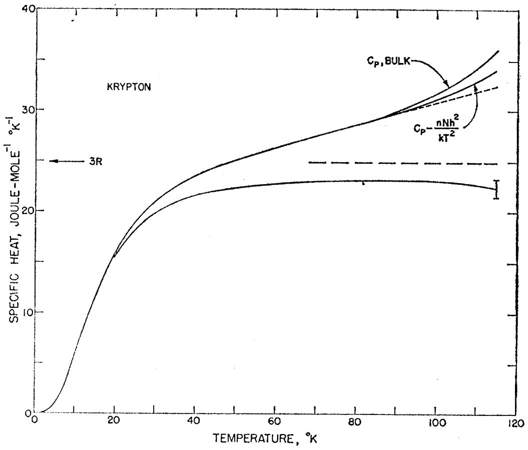

FIG. 4. Specific heats of solid krypton. The isobaric values of Ref. 6 were converted to isochoric values through the use of Eq. (10) with the "bulk" values of β and χ from Figs. 2 and 3 which depend upon Eq. (4). The vertical bar on the C_V curve indicates the uncertainty due to a possible 5% uncertainty in χ. The high-temperature C_V is consistent with a vacancy contribution near zero [Eq. (9)] and a relation $3Nk(1+AT)$, with A about -7×10^{-4} deg^{-1}; compare with Table IV.

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[19] J. W. Stewart, J. Phys. Chem. Solids **29**, 641 (1968).

[20] J. K. Mackenzie [Proc. Phys. Soc. (London) **B63**, 2 (1950)] employs continuum elasticity theory. A lattice-dynamical analysis is given by W. Ludwig, Natl. Bur. Std. (U. S.) Misc. Publ. **287**, 151 (1967).

[21] W. B. Daniels, G. Shirane, B. C. Frazer, H. Umebayashi, and J. A. Leake, Phys. Rev. Letters **18**, 548 (1967).

C. Specific Heats

Smoothed values of the specific-heat data of Beaumont, Chihara, and Morrison,[6] which include the heat of formation for the vacancies, are listed in Table II. The measurements were carried out on solid specimens in an unknown state of aggregation, but we shall assume the results to be comparable to the present work on krypton crystals. The formation of atomic monovacancies with increasing temperature leads to an increase in the specific heats C_P and C_V by amounts

$$\Delta C_P = nN(h^f)^2/kT^2 \tag{8}$$

and

$$\Delta C_V = \frac{nN}{kT^2}\left(h^f - \frac{\beta v^f T}{\chi}\right)\left(h^f - \frac{\beta_0 v^f T}{\chi_0}\right), \tag{9}$$

respectively,[22] where the specimen contains N atoms. For moderate vacancy content the ratios β/χ and β_0/χ_0 do not differ appreciably.

Use of the relation Eq. (4) yields the effect of vacancy formation on C_P as indicated in Fig. 4. Previous workers have attempted to deduce the vacancy content of solid argon[6,22,23] and krypton[6] by making some extrapolation of C_P and attributing the differences between the measured C_P and the extrapolation to the formation of vacancies. Clearly such a procedure is arbitrary and may be misleading as the linear extrapolation shown in Fig. 4 indicates.

The isochoric specific heat C_V, calculated using the usual relation

$$C_V = C_P - \beta^2 VT/\chi, \tag{10}$$

is also shown in Fig. 4. The error in C_V which would result from a 5% error in χ at the highest temperature is indicated by the error bar at the end of the C_V curve. We note that ΔC_V [Eq. (9)] for the present adopted values of h^f, $v^f = v_a$, β, and χ is probably very small. For all apparently reasonable assumptions on the behavior of β and χ, the resulting C_V curves remain remarkably flat and stay well below the classical Dulong-Petit value, a fact which indicates appreciable anharmonicity in the lattice vibrations. A quantitative analysis can be carried out for temperatures below which vacancy effects enter. It appears below in Sec. III C.

D. Entropy

Entropy values obtained by a Simpson's-rule integration of the C_P/T data[6] as smoothed by us are also listed in Table II. The formation of atomic monovacancies leads to a contribution to the entropy of an amount[24]

$$\Delta S = nNk(h^f/kT + 1). \tag{11}$$

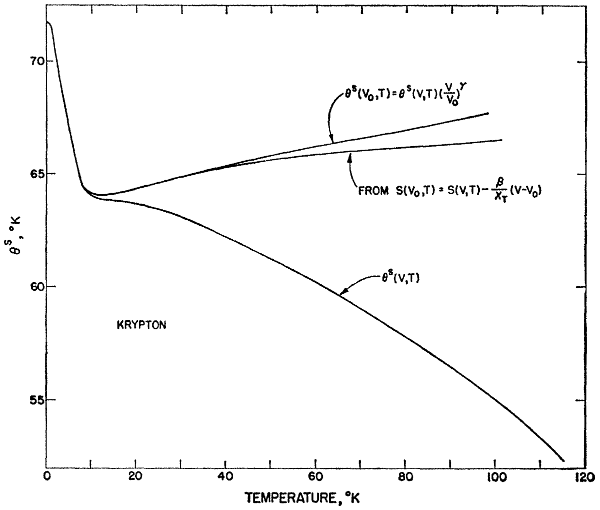

FIG. 5. Equivalent Debye temperatures for the entropy of solid krypton. According to Ref. 6, $\Theta^s(T\to 0°\mathrm{K}) = 71.7\pm0.7$°K. The temperature dependence above the minimum is analyzed for anharmonic effects in the text, Sec. III C.

Use of the relation Eq. (4) yields an entropy contribution of 0.22 J mole^{-1} °K^{-1} at 115°K, about twice the estimated experimental error in the calorimetry at this temperature. Figure 5 shows the corresponding temperature variation of the equivalent Debye temperature for the entropy, $\Theta^s(V,T)$, where V is the volume at temperature T. Also shown in this figure is the variation of $\Theta^s(V_0,T)$, the Debye temperature for the entropy referred to the volume at $T = 0$°K, V_0. $\Theta^s(V_0,T)$ has been computed using both of the formulas

$$\Theta^s(V_0,T) = \Theta^s(V,T)(V/V_0)^\gamma \tag{12a}$$

and

$$S(V_0,T) = S(V,T) - (\beta/\chi)(V - V_0), \tag{12b}$$

where γ is the experimental Grüneisen parameter $\beta V\chi^{-1}C_V^{-1}$. Equation (12a) is an approximate relation,[25] while Eq. (12b) is a series expansion of $S(V,T)$ to first order in $(V - V_0)$.[26] The rather large volume change at the higher temperatures casts doubt on the accuracy of results obtained through use of either formula. Equation (12a) is particularly suspect because γ depends upon temperature and/or volume. An exact calculation, which could be performed if additional data were available on the P-V-T surface of krypton, might result in $\Theta^s(V_0)$ values lying between the two curves shown in Fig. 5.

III. DISCUSSION

A. Law of Corresponding States

de Boer formulated a quantum-mechanical law of corresponding states[27] which has been applied to the

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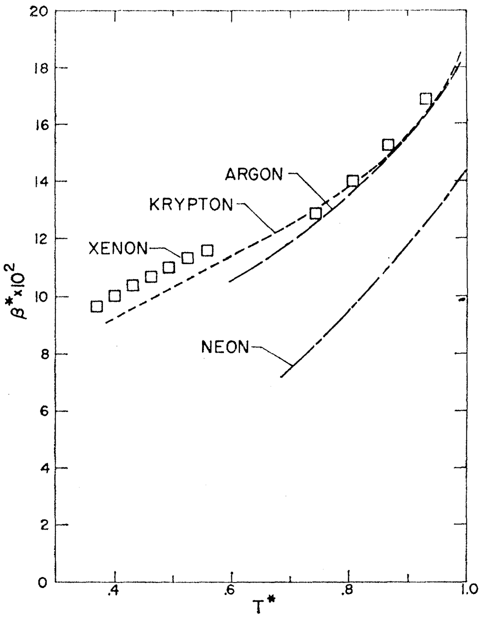

FIG. 6. Classical reduced coefficient of volume thermal expansion, β^*, versus reduced temperature, T^*. x-ray measurements on krypton, argon, and neon crystals are shown by lines. Bulk values for xenon (Refs. 17 and 31) are shown by squares. The respective Debye temperatures occur at T^* values of about 0.4 (xenon), 0.6 (krypton), 1.0 (argon), and 3 (neon).

noble-gas solids by several authors.[23,28] If a two-body two-parameter interatomic potential is sufficient, it will have the form $\phi(r)=\epsilon f(r/\sigma)$, where ϵ and σ are a characteristic energy and length, respectively, associated with each substance. The universal equation of state is given by

$$P^*=P^*(V^*,T^*,\Lambda^*), \tag{13}$$

where $P^*=P\sigma^3/\epsilon$, $V^*=V/N\sigma^3$, $T^*=kT/\epsilon$, and Λ^* is a dimensionless parameter, $h/[\sigma(m\epsilon)^{1/2}]$, which is a measure of the importance of quantum effects. Leadbetter and Thomas[29] have examined the density and surface tension of the noble gases in the liquid phase in an attempt to detect deviations attributable to many-body forces. No such deviations were found outside an experimental error of several percent. If many-body forces are present, their effect might be largely compensated in the choice of effective two-body parameters.

When the reduced volume coefficient of thermal expansion, β_x^*, is plotted against T^*, good agreement is obtained for the heavier solids argon[3] and krypton. Here $T^*=T/T_{\text{tr}}$, where T_{tr} is the triple-point temperature and $\beta_x^*=\beta_xT_{\text{tr}}$. Results of such a reduction of variables are shown for the higher values of T^* in Fig. 6. Though highly accurate data are not available for the high-temperature expansivity of xenon, published values of β[30,31] yield β^* values rather close to the curves for argon and krypton. Similar good agreement between the reduced compressibilities has been found by Urvas and co-workers.[7]

We expect that the classical scaling procedure $\beta^*=\beta T_{\text{tr}}$ would not be valid at the lower temperatures, $T<\Theta$, or for the lighter substances such as neon,[4] because of the increasing importance of quantum effects. Examination of Fig. 6 indeed verifies that the β^* for each substance falls below the common curve for temperatures below the characteristic Θ for the substance.

Manzhelii and co-workers[17] have considered the coefficients of thermal expansion of noble-gas solids as a function of the reduced temperature T/Θ_0, where Θ_0 is the equivalent Debye temperature for the specific heat in the limit $T\rightarrow0$. They propose that at sufficiently low temperatures, the ratios of the coefficients should obey the relation

$$\frac{\beta_1}{\beta_2}=\frac{C_{V_1}}{C_{V_2}}\frac{\gamma_1V_2\chi_1}{\gamma_2V_1\chi_2}=R, \tag{14}$$

where the subscripts 1 and 2 denote different members of a pair of substances. (In the comparisons which follow, we let substance 1 be krypton.) These workers assume that the ratio of specific heats, C_{V_1}/C_{V_2}, at a common reduced temperature is unity. This assumption has been approximately justified, at least up to T/Θ_0

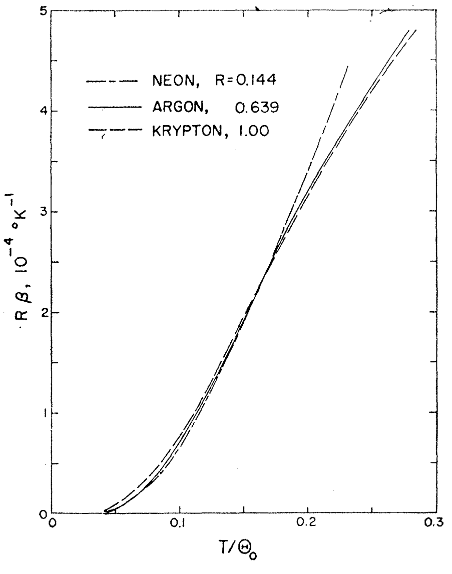

FIG. 7. Reduced coefficients of volume thermal expansion, $R\beta$, versus reduced temperature, T/Θ_0, for x-ray measurements on neon, argon, and krypton at low temperature. The reducing relation is Eq. (14) of the text.

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[28] J. de Boer and B. S. Blaisse, Physica 14, 149 (1948); N. Bernardes, Phys. Rev. 120, 807 (1960); G. Boato and G. Casanova, Physica 27, 571 (1961).

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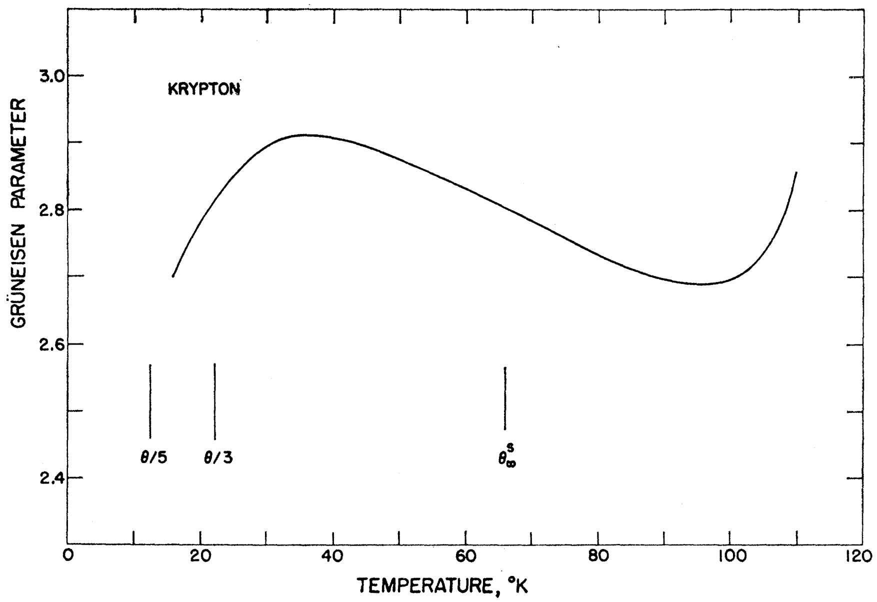

FIG. 8. Thermal Grüneisen parameter γ [Eq. (16)] for solid krypton. The systematic decrease in γ in the range 40 to 80°K is well outside experimental uncertainty and can be attributed to volume-dependent anharmonic contributions to the free energy of the solid.

~ 0.07, by Fenichel and Serin,[32] who examined data for Θ^c in a form equivalent to

$$(\Theta^c/\Theta_0)=1-B\Theta_0{}^c(T/\Theta_0)^2. \tag{15}$$

For neon, argon, krypton, and xenon, values of $B\Theta_0{}^c$ all lay within the range 18 to 22.

Unfortunately, the test of Eq. (14) for argon, krypton, and xenon in the region $0.2<T/\Theta_0<0.9$ that is shown in Fig. 4 of Manzhelii and co-workers[17] appears to be of *ad hoc* character. The values of γ are assumed constant and are not independent of the β values being tested. The ratio of specific heats probably varies in this broad range. Further, temperature variation of χ is neglected in a region where we expect the various noble-gas solids to differ because of different zero-point energy effects.

Our test of Eq. (14) as a consistency relation is shown in Fig. 7. The values of reducing quantities used are given in Table III. For values of γ, independent of β measurements, we used (12-6) nearest-neighbor (1N) model calculations.[33] Experimental values of the low-temperature limit of γ are uncertain, but appear to be somewhat smaller than these calculated values. The low-temperature expansion coefficient of xenon appears to be known with limited accuracy, so we have omitted xenon from Fig. 7.[34]

TABLE III. Quantities adopted for testing the corresponding-states relation [Eq. (14)] for the low-temperature coefficient of thermal expansion in Fig. 7. The ratio R is arbitrarily set at unity for krypton.

Substance	V cm^3 mole^{-1}	Θ °K^a	χ^{-1} kbar^a	γ^b	R
Ne	13.391^c	74.6	11.2	3.12	0.144
Ar	22.557^d	93.3	26.7	2.83	0.639
Kr	27.097^e	71.7	34.4	2.80	1.000
Xe	34.717^f	64.0	36	2.78	1.35

[a] References for these values are given in Ref. 7.
[b] See Ref. 33.
[c] See Ref. 4.
[d] See Ref. 3.
[e] Present work.
[f] See Ref. 34.

Examination of Fig. 7 reveals that neon, argon, and krypton indeed follow the proposed behavior at low temperatures. The small apparent differences below $T/\Theta_0\sim 0.1$ are within experimental uncertainty. Above a temperature $T/\Theta_0\sim 0.18$ the value $R\beta$ for neon rises sharply; we note that the compressibility of neon begins its sharp variation at about this temperature.[4] Where the curves are similar, one may guess that any variation of γ with temperature either is weak or is similar for these substances as a function of T/Θ_0.

B. Grüneisen Parameter

The thermal Grüneisen parameter is defined by

$$\gamma=\beta V/\chi C_V. \tag{16}$$

The parameters $\gamma(-3)$ and $\gamma(0)$, the values of γ in the limits of low and high temperature, respectively, are related to the -3 and 0 moments of the harmonic phonon spectrum, μ_{-3} and μ_0. The major variation in γ with temperature occurs in the neighborhood of $T=\frac{1}{5}\Theta$ for a harmonic model,[33,35] with an estimated difference of $\gamma(0)-\gamma(-3)\simeq 0.1$, using a Mie-Lennard-Jones ($m-6$) potential. The present work, shown in Fig. 8, indicates qualitative agreement with the prediction of the rapid

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[34] Use of the x-ray data of D. R. Sears and H. P. Klug [J. Chem. Phys. **37**, 3002 (1962)] yields $R\beta$ values lying below the curves in Fig. 7.

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

TABLE IV. Leading anharmonic coefficient A and characteristic temperatures Θ for solid krypton. Quantities are defined in the text, Sec. III C. The first four lines were obtained by analyzing data points above 20°K. A value of $A=-7\times10^{-4}$ °K^{-1} can also be obtained by visual inspection of Fig. 4, if vacancies contribute little to C_V.

Function	$\Theta(-3)$ °K	$\Theta(0)$ °K	$\Theta(2)$ °K	$\Theta(4)$ °K	10^4A °K^{-1}
$S(V_0,T)$ [a]	···	64 ± 2	69 ± 3	77 ± 5	-5 ± 0.5
$S(V_0,T)$ [b]	···	65 ± 2	72 ± 3	83 ± 5	-2 ± 0.5
$C_V(V_0,T)$ [c]	···	···	64 ± 5	63 ± 10	-8 ± 1
$C_V(V_0,T)$ [d]	···	···	70 ± 5	80 ± 10	-5 ± 1
Vapor pressure	···	66 ± 3	···	···	(-5 assumed)
$C_P(V_0,T\rightarrow0)$	71.7 ± 0.7 [e]	···	···	···	(-10)[f]

[a] Corrected from $S(V,T)$ using Eq. (12a).
[b] Corrected from $S(V,T)$ using Eq. (12b).
[c] Corrected from $C_V(V,T)$ using $\Theta^c(V_0,T)=\Theta^c(V,T)(V/V_0)^\gamma$.
[d] Corrected using $C_V(V_0,T)=C_V(V,T)-\gamma TV^{-1}(V-V_0)(\partial C_V/\partial T)$.
[e] See Ref. 6. This value of $\Theta(-3)=\Theta_0{}^c$ from Ref. 6 applies to the real (anharmonic) crystal. In Ref. 41, a (12-6) $1N$ model for krypton yields an anharmonic to quasiharmonic correction for $\Theta(-3)$ of -1.6 deg.
[f] Crude estimate using an assumption of Ref. 40 and a model of Ref. 41.

variation in γ near $\frac{1}{5}\Theta$. The high- and low-temperature limits of γ, however, are too uncertain to allow an estimate of $\gamma(0)-\gamma(-3)$. The uncertainty in $\gamma(-3)$ is due to the relatively large uncertainty in β at extreme low temperatures.[36]

The downward trend in γ with increasing temperature can be attributed to volume-dependent anharmonic contributions to the free energy of the solid. Such a calculation of γ for the range 40–80°K [37] indeed shows close agreement with the present work, but this close agreement may be fortuitous. The calculations employed experimental values for the thermal expansion in an intermediate step and also employed a calculated value for the anharmonic coefficient A which appears significantly larger than most values we find experimentally for the same temperature range (Sec. III C below).

The subsequent rise in γ at the highest temperatures is not strongly dependent on the choice of parameters used to characterize the vacancy content of the solid, if Eqs. (3), (7), and (9) are used. The rise might therefore be associated with error in the extreme high-temperature values of χ or with higher-order anharmonic effects.

C. Characteristic Temperatures and Anharmonicity

In the harmonic approximation the value of $\Theta^s(V_0,T)$ is expressible as a power series in T^{-2} for $T\geq\Theta/2\pi$. This may be written[38]

$$\Theta_h{}^s(V_0,T)=\Theta(0)\left[1+\sum_{n=1}^{\infty}a_nT^{-2n}\right],\tag{17}$$

where

$$\Theta(0)=e^{1/3}\left(\frac{h}{k}\right)\left[\prod_{j=1}^{3N}\nu_j\right]^{1/3N}\equiv e^{1/3}\left(\frac{h}{k}\right)\nu_g,\tag{18}$$

the ν_j being phonon frequencies, ν_g the geometric mean frequency, and h the Planck constant. The coefficients a_n are given by polynomial expressions in the even moments of the phonon spectrum, μ_{2n}. One further defines, for $n>0$,

$$\Theta(2n)=(h/k)\left[\tfrac{1}{3}(2n+3)\mu_{2n}\right]^{1/2n}.\tag{19}$$

The leading anharmonic coefficient in the entropy, A, may be defined in the limit of high temperature by[39]

$$A=[S(V_0,T)-S_h]/3NkT,\tag{20}$$

where S_h is the harmonic entropy as determined by Eq. (17). By first fitting Eq. (17) to the experimental values of $\Theta^s(V_0,T)$ over a moderate temperature interval and then comparing S and S_h at a higher temperature using Eq. (20), one may then obtain successive approximations for the values of $\Theta(2n)$ and A. Because of the uncertainty in the values of Θ^s at the highest temperatures, we applied this procedure to krypton only over a temperature range below 75°K.

Table IV summarizes the present computer calculations of A and $\Theta(2n)$ using both Eq. (12a) and Eq. (12b) to find the values of $\Theta^s(V_0,T)$. We also analyzed the isochoric specific heat in a similar manner[38] but with considerably less accuracy because of greater uncertainty in referring C_V to the volume at $T=0$. The two different correction schemes used are given in Refs. c and d of Table IV. Usually about 12 iterations were sufficient to produce satisfactory convergence of the fitting to the experimentally observed $\Theta(V_0,T)$ values. Errors listed in Table IV are estimated only from the range of values obtained by choosing different fitting ranges and different high-temperature test points.

A quite crude but rather independent estimate of A may be made by using Barron's assumption[40] that the observed low-temperature limit of the characteristic temperature, 71.7°K,[6] may be approximated by $\Theta(-3)\times(1-\frac{3}{8}A\Theta(2))$, where $\Theta(-3)$ is the corresponding

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[36] A crude empirical estimate of $\gamma_0=\gamma(-3)$ is obtained by fitting the observed thermal behavior of krypton to a Mie-Grüneisen equation of state [E. Grüneisen, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Julius Springer-Verlag, Berlin, 1926), Vol. X, p. 1]

$$(V-V_0)/V_0=E_T/(Q-bE_T),$$

where $E_T=\int_0^TC_VdT$. The parameters Q and b according to the Mie-Grüneisen analysis are $Q=V_0\gamma_0{}^{-1}\chi(0)^{-1}$ and $b=\frac{1}{6}(m+n+3)$, where the numbers m and n are the exponents in the Mie potential function. A good fit to the present data is obtained with $Q=34$ kJ and $b=5.6$. This yields a value $\gamma(-3)=2.7$. We note that this $\gamma(-3)$ appears to be only a few percent high, judging from the behavior of the present values of γ shown in Fig. 8. Similar, probably slightly high, estimates of $\gamma(-3)$ result from this form of analysis applied to argon (Ref. 3) and to neon (Ref. 4). For all three solids the value of b obtained by such fitting is very much larger than the value corresponding to the use of a (12-6) potential.

[37] C. Feldman, J. L. Feldman, G. K. Horton, and M. L. Klein, Proc. Phys. Soc. (London) **90**, 1182 (1967).

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TABLE V. Summary of selected theoretical models for anharmonic or quasiharmonic fcc crystals at finite temperature, compared to the present experimental values for krypton in Table II and for argon by Peterson and co-workers (Refs. 2 and 3). $\Delta a/a_0$, relative x-ray lattice expansion from zero up to the melting point [at $\sim 1.6\Theta(-3)$ for Kr, at $\sim 0.9\Theta(-3)$ for A]; $\beta(T)$, coefficient of volume thermal expansion; $\chi(T)$, isothermal compressibility; $\gamma(T)$, Grüneisen parameter; A, leading anharmonic coefficient Eq. (20) and Table IV; F, Helmholtz free energy; μ_n, nth moment of phonon spectrum. Unless otherwise specified, in all models additivity of a pair-potential interaction alone is assumed and the potential parameters are fixed from crystal data at low T (H_0, latent heat of sublimation; M-L-J, Mie-Lennard-Jones).

Ref.	(Substance)	Year	Model studied; remarks	$\Delta a/a_0$	$\beta(T)$	$\chi(T)$	$\gamma(T)$	A
[a]	(Kr)	1958	Lattice-wave calculation of (F_3+F_4) by perturbation theory, M-L-J (12-6) 1N potential; strain dependence of μ_2 used; predictions of elastic constants.	···	···	$\chi(0)$ large; T variation large by factor ~ 2 up to $T/\Theta \sim 2$	···	Somewhat large
[b]	(Ar)	1958	Anharmonic Einstein model including only fourth-derivative terms, M-L-J (12-6) potential fitted to P-V isotherms at $T/\Theta \sim 0.8$; C_P very low at low T.	Good agreement	Fair agreement, $0.2 \lesssim T/\Theta \lesssim 0.8$	Fair agreement	···	Large
[c]	(Ar)	1959	Quasiharmonic model of generalized Grüneisen type, M-L-J (12-6) AN potential with harmonic ϵ, σ.	High	Fair agreement up to $T/\Theta \sim 0.3$, then high	$\chi(0)$ good, but $\chi(T)$ large by $\sim 20\%$	···	Assumed zero
[d]	(Kr)	1960	Einstein model for krypton via corresponding-states principle from fitting of 6-parameter potential to S, H, and V for argon at two temperatures; potential inconsistent with low T anharmonicity (see Ref. 41 and Ref. 60, p. 117).	$\sim 15\%$ low	Especially low near $T=0$	Too large	···	Assumed zero
[e]	(Ar)	1961	Lattice-wave calculation of (F_3+F_4) in the limits $T \rightarrow 0$ and high T by perturbation theory; M-L-J (12-6) AN potential with ϵ, σ from gas data; includes extension of Ref. 39.	Low	Low, especially for $T/\Theta > 0.3$	$\chi(0)$ good, but too large for $T > 0$	···	Somewhat large
[f]	(Ar)	1963	Classical Einstein anharmonic model, which neglects correlation, includes only A_4. Deduction of vacancy content therefore suspect.	···	···	···	···	Large by factor ~ 2
[g]	(Ar)	1964	Debye approximation and Grüneisen equation, model parameters fitted to experimental $S(T)$ and $V(T)$.	See remarks	Low at low T; within 5% for $T/\Theta > 0.4$	Large, especially for $T/\Theta > 0.3$	Too low	Assumed zero
[h]	(Ar)	1964	Cellular model, M-L-J (12-6) potential with hard core added, ϵ, σ from Ref. 45; some account of correlation.	$\sim 80\%$ high	High, especially below $T/\Theta > 0.4$	···	···	···
[i]	(Kr)	1964	Calculation of F_2 phonon sums using Houston's method, M-L-J (12-6) ?N potential; minimizes F at each T for $P=0$ to obtain $V(T)$.	$\sim 30\%$ high at $T/\Theta \sim 1$	Fair agreement for $0.3 < T/\Theta < 1$	···	···	···
[j]	(fcc)	1965	Direct evaluation of lattice wave (F_3+F_4) in the Brillouin zone; M-L-J (m-n) potential, AN for equilibrium and second-derivative terms, 2N otherwise; here value of $\kappa \sim$ for krypton.	About correct at $T/\Theta \sim 2$	Qualitative agreement except near $T/\Theta \sim 2$	F_3+F_4 contribution to $\chi(T)$ is small	Too high, but correct T variation to $T/\Theta \sim 1.5$	Within experimental uncertainty; $\partial \lvert A \rvert / \partial V > 0$
[k]	(Ar)	1965	Extension of Ref. 51 to evaluation of (F_3+F_4) at high T by perturbation theory, M-L-J (12-6) 1N potential fitted to H_0, a_0. For subsequent argon calculation, see Ref. 60, p. 123.	$\sim 30\%$ high	···	···	···	Factor $\gtrsim 2$ too large
[l]	(Ar)	1965	Calculation of F_2 phonon sums using Houston's method, (12-8-6) AN potential fitted to H_0, a_0, and shear modulus	$\sim 25\%$ high	$\gtrsim 25\%$ high, no upturn at high T	$\chi(0) \sim 5\%$ low	···	Assumed zero
[m]	(Kr)	1965	Lattice-wave calculation of strain dependence of μ_2, μ_4, and μ_6 used; (m-6) 1N and AN potentials ($m=12$, 13); anharmonic zero-point properties also calculated.	···	···	$\chi(0)$ excellent, T variation large by factor 2	···	Within experimental uncertainty

TABLE V. (*continued*).

Ref.	(Substance)	Year	Model studied; remarks	$\Delta a/a_0$	$\beta(T)$	$\chi(T)$	$\gamma(T)$	A
[n]	(Ar)	1965	Minimizes F for $P=0$, with (F_3+F_4) from Ref. 61(c), evaluated approximately for M-L-J (12-6) $1N$ potential, with ϵ, σ from Ref. 45.	Low by factor ~ 2	···	···	···	···
[o]	(Ar)	1965	Quantum Einstein anharmonic model, M-L-J (12-6) used for cell potential; model includes only A_4; correlation neglected; $S(T)$ too low; deduction of vacancy content suspect.	Good agreement	High near $T\sim 0$; low near $T/\Theta\sim 0.9$	Good agreement	$\gamma(\Theta/2)$ $\sim 5\%$ high; $\gamma(0°\mathrm{K})$ very high	Large; C_V low by 3% at T/Θ ~ 0.6
[p]	(Ar)	1966	Phonon field model, anharmonic Hamiltonian, third-derivative terms only, evaluated in Debye approximation; M-L-J (12-6) potential with harmonic ϵ, σ.	Neglected in calculation of $\gamma(T)$	···	$d\chi/dT$ neglected in calculation of $\gamma(T)$	Agreement near T/Θ ~ 0.4	···
[q]	(Kr)	1967	Lattice-wave calculation of F_2 only, (exp-6) $4N$ potential with parameters from H_0, a_0, and an incorrect $\chi(0)$.	Unstable above $T/\Theta\sim 1.3$	High by factor ~ 2; expecially poor at low T	$\chi(0)$ large, T variation large by factor 2	···	Assumed zero
[r]	(Kr)	1967	Lattice-wave calculation of (F_3+F_4) in limits $T\rightarrow 0$ and high T, central $1N$ potential; examples of M-L-J (m-6) $1N$ potential results; comparison with Refs. 39, 52, 61(c), 61(d).	···	···	···	···	Within experimental uncertainty; $\partial\|A\|/\partial V>0$
[s]	(Kr)	1967	Lattice-wave calculation for M-L-J (12-6) $1N$ potential with self-consistent potential parameters from Ref. 33 and J. S. Brown (see Ref. 62).	Uses experiment (see text, Sec. III B)	···	Uses Ref. 58	$\sim 4\%$ high; correct T variation for 0.6 $<T/\Theta<1.5$	Uses Ref. 42
[t]	(Kr)	1967	Lattice-wave calculation of quasiharmonic elastic constants (include third- and fourth-derivative terms), central $1N$ potential; example of M-L-J (m-6) results.	Uses experiment	···	Slightly high, but T variation good	···	···
[u]	(Ar)	1967	Self-consistent phonon approximation (sums all even-derivative anharmonic terms), M-L-J (12-6) $\sim AN$ potential, ϵ and σ from gas data; elastic-wave velocities also calculated.	$\sim 15\%$ low	Low, especially for $T/\Theta>0.3$	$\chi(0)$ excellent, but very weak T variation	···	C_P very low at high T

[a] Reference 39.
[b] Reference 45.
[c] Reference 46.
[d] Reference 47.
[e] Reference 48.
[f] Reference 22.
[g] Reference 49.
[h] Reference 50.
[i] Reference 51.
[j] Reference 52.
[k] Reference 53.
[l] Reference 54.
[m] Reference 41.
[n] Reference 55.
[o] Reference 23.
[p] Reference 56.
[q] Reference 57.
[r] Reference 42.
[s] Reference 37.
[t] Reference 58.
[u] Reference 59.

temperature calculated for a harmonic model. The value of $\Theta(-3)=69.9°\mathrm{K}$ for a (12-6) $1N$ model of krypton[41] leads to a value $A\simeq -10^{-3}$ deg^{-1}.

It is clear from Table IV that accurate data on the P-V-T surface of krypton is needed before $\Theta^s(V_0,T)$ or $\Theta^c(V_0,T)$ may be known well enough to deduce A with an accuracy much better than about 30%. Furthermore, such P-V-T data appear necessary before it will be possible to make meaningful statements about possible higher-order anharmonic contributions to the free energy. A calculated value of $A=-11\times 10^{-4}$ deg^{-1} from the leading contributions (A_3 and A_4, third order and fourth order, respectively) to the free energy of a (12-6) $1N$ model of krypton[42] appears larger than most present values in Table IV. Uncertainty arising from the volume corrections and from use of the high-temperature expression Eq. (20) is large enough, however, that we have summarized this situation in the last column of Table V as agreement "within experimental uncertainty."

It is interesting to inquire whether the present deductions are consistent with the measured equilibrium vapor pressure p of krypton. The analysis depends upon equating the Gibbs free energy of a lattice-dynamical model for an anharmonic crystal containing thermal vacancies to that of an imperfect vapor.[24,43] The resulting expression can be simplified in the case of krypton because the temperature range of interest is well above $\Theta(2)$. By neglecting gas imperfection and the mean atomic volume in the crystal relative to that in the

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vapor, one then obtains the expression

$$\ln[p(8\pi^3kT/m^3)^{1/2}/\Omega^3]+n \\ =\Phi_0/NkT+3\ln(2\pi\nu_g/\Omega)-3AT, \quad (21)$$

where m is the atomic mass, Ω a frequency, Φ_0 the static lattice energy, ν_g the frequency defined in Eq. (18), and A the leading anharmonic coefficient defined in Eq. (20).

From the measurements reported in the preceding paper[1] one finds that the term n (always smaller than 3×10^{-3}) is negligible compared to variations in the other term on the left side of Eq. (21), because of estimated error in existing vapor-pressure measurements. On the other hand, our analysis for anharmonic effects given above indicates that the size of the term $-3AT$ in the region below the melting temperature is significant, but uncertain as to precise magnitude. In Fig. 9, the data of Beaumont and co-workers[6] are plotted in order to test for agreement with the form of Eq. (21). The frequency Ω is set at 10^{10} sec^{-1}. The agreement is good. The slope of the straight line through the data points yields $\Phi_0=-11.06\pm0.07$ kJ mole^{-1}. If one makes the simple assumption[40] that in the limit of high temperature

$$\nu_j^a=\nu_j(1-AT), \quad (22)$$

where ν_j^a are the (anharmonic) phonon frequencies in the actual crystal, then the intercept of the straight line yields $2\pi\nu_g^a=(5.08\pm0.06)\times10^{12}$ sec^{-1}. These values for Φ_0 and ν_g^a apply to the crystal in the high-temperature range, say, at $\simeq104$°K.

In order to compare these results with the previous analysis, which was applied to krypton at its 0°K molar volume, one must correct them. Salter[24] has worked out a correction to obtain $\Theta(1)$ from Φ_0 and enthalpy data; the result, however, is rather uncertain because of the subtraction of large but nearly equal quantities. The frequency correction is more straightforward; there are corrections for explicit anharmonicity and for volume change. For the first, one has an average value $-AT=0.051$ in the range 90 to 115°K, which leads to a value $2\pi\nu_g=5.00\times10^{12}$ sec^{-1}. For the volume correction, one may write

$$\Delta\nu_g/\nu_g\simeq-\gamma\Delta V/V\simeq(2.9)(0.24\pm0.05), \quad (23)$$

where a "harmonic" value of $\gamma(0)\sim2.9$ has been chosen by inspection of Fig. 8 and the effective relative volume change is $(-8.0\pm1.7)\%$ from Table II. From Eq. (18), the resulting $\Theta(0)$ is 66 ± 3°K. This value is entered in Table IV, where it is in satisfactory agreement with values from the earlier analysis at lower temperature.

In principle, one might use such an analysis of vapor pressure to furnish independent evidence about the possible higher-order anharmonic effects mentioned above in Sec. II A. But present data, including P-V-T values, are insufficiently precise for this purpose.

A measurement of the temperature dependence of the ^{83}Kr 9.3-keV γ resonant absorption[44] has given $\Theta(-1)$ about 37°K. This value appears rather small when compared to values for other $\Theta(n)$'s in Table IV.

D. Comparison with Theoretical Models

We attempt to summarize in Table V selected results of the many published calculations which it is claimed apply to the static thermodynamic properties of crystalline krypton or argon. Certain individual points have been discussed in previous sections, but a general summary is required to give a broad indication of the accuracy and limitations of published calculational schemes. Study of Table V shows that an interesting variety of methods and models has been proposed.[45–62]

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[61] Several other different calculations, not specifically applied to krypton or argon, should be mentioned. (a) E. A. Stern [Phys. Rev. **111**, 786 (1958)] worked out a three-parameter explicit anharmonic model. (b) J. Laval [J. Phys. Radium **22**, 451 (1961)] presented a quasiharmonic model showing a qualitatively correct form for $\beta(T)$. (c) A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsefall [Ann. Phys. (N. Y.) **22**, 223 (1963), and earlier work], with their leading-term approximation, stimulated quantitative study of explicit anharmonic effects. (d) P. Lloyd [Australian J. Phys. **17**, 269 (1964)] showed that a form of molecular field approximation might be used to simplify considerably the computation of third- and fourth-derivative terms.

[62] *Note added in proof.* Another quasiharmonic calculation has recently been reported by F. W. de Wette and R. M. J. Cotterill [Solid State Commun. **6**, 227 (1968)]. They fitted the parameters ϵ, σ, and m to data at 0°K, and calculated elastic wave velocities in argon and phonon dispersion in krypton. We note that (a) outdated experimental values of lattice constant and compressibility were used for neon and argon, (b) the "experimental" values of elastic wave velocities in argon from 0 to 80°K, given in their Table 3, with which comparisons are made, in fact were not measured for temperatures much below 80°K and moreover are inconsistent with the input values of the argon compressibility at 0°K, and (c) the calculations were fitted to experimental thermal expansions, rather than to values predicted by the model, thereby introducing inconsistency.

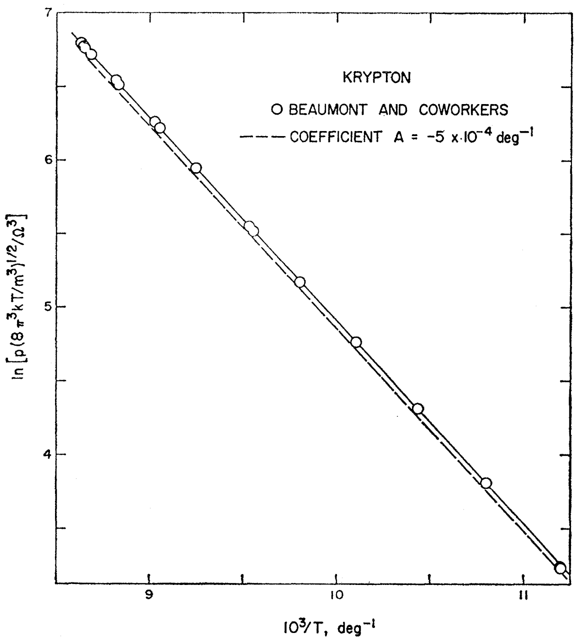

FIG. 9. Graph to determine the geometric mean lattice frequency $\nu_g{}^a$ and the static lattice energy Φ_0 of solid krypton from equilibrium vapor-pressure data. The relevant relation is Eq. (21) of the text, Sec. III C. Data are from Ref. 6. Contrary to Ref. 24, the effect of thermal vacancies on the graph is negligible. The dashed line shows the effective result for a quasiharmonic crystal, after subtraction of a term $-3AT$ with an assumed leading anharmonic coefficient $A=-5\times10^{-4}$ deg^{-1}.

Nearly all models for which extensive calculations have been carried out are central-force models, frequently employing a Mie-Lennard-Jones pair potential. Because of this, the derived properties, such as thermal expansion or the leading coefficient in T in the anharmonic free energy, A, are likely to be qualitative in nature. For example, the leading term in the anharmonic specific heat may lie within present experimental uncertainty for only three of the models listed in Table V.

In general, present experimental accuracy now suggests that calculations of temperature-dependent properties should take into account both the change in volume due to thermal expansion and explicit anharmonic effects. Choice of a given central pairwise potential, even just for nearest neighbors, then may secure agreement for a given quantity within present experimental accuracy. But no single model or potential yet fits all crystalline properties for which measurements are available. For example, the various Einstein models in Table V yield good agreement at intermediate or high temperature for at least one thermodynamic property. However, these models are generally suspect at low temperature; this deficiency may then be reflected at *all* temperatures, such as by $S(T)$ being too low.

Horton and co-workers[33,42] have stressed the importance of self-consistency in the choice of potential parameters when any precise comparison between models, or between models and experiment, is to be carried out. More than one-third of the models in Table V do not employ such self-consistent parameters.

The (m-6) nearest-neighbor (1N) and all-neighbor (AN) models of Barron, Klein, Horton, and co-workers have been studied for krypton in the greatest detail, with potential parameters appropriate to the present data. Separate calculations of $\Theta^c(0°\text{K})$,[41] $\Theta^c(T)$,[42] $\chi(0°\text{K})$,[41,63] $\chi(T)$,[58] $\gamma(T)$,[37] and of phonon dispersion[64] have individually shown fairly good agreement with experiment. In our opinion, however, there appear to be residual inconsistencies in this model description of the thermodynamic properties of krypton. On the one hand, (14-6)1N or (13-6)AN models appear to fit the krypton phonon-dispersion data and the $\Theta^c(0°\text{K})$-versus-Λ^* relationship for the family of noble-gas crystals. But such large m values yield (a) values for the anharmonic coefficient A which appear significantly larger than present inference from experiment and (b) values for $\gamma(T)$ near the maximum which are 10–15% larger than the measurements, Fig. 8.

Whether such possible disagreements with experiment depend upon the approximations employed, and not upon the force law assumed, might be judged to some extent by comparison with different computational methods. The most complete set of calculations seems to have been carried out by Wallace[52] but his results are not specialized to any particular noble-gas solid. Wallace's models appear to give the right qualitative behavior of all the anharmonic properties observed in krypton, with the exception of the observed increasing volume expansivity near the triple point. His work, that of Ludwig,[39] and that of Feldman and Horton[42] emphasize the importance of including *both* odd- and even-order derivative terms in calculations for finite temperature.

Inadequacies in existing theories might be of two sorts; first, it may be necessary to calculate a given property to all orders of perturbation theory,[65] and second, there may be no central two-body potential function which is appropriate to noble-gas atoms condensed into the solid phase.[1]

IV. CONCLUSION

A number of thermal properties of solid krypton are now known with sufficient accuracy to provide a stringent test of theories of static thermal and anharmonic properties of noble-gas solids. Further evidence for the applicability of laws of corresponding states has been given when the thermal expansions of the noble-gas solids are compared. It has been seen that the formation of atomic vacancies at the higher temperatures makes an important contribution to all the thermodynamic properties of krypton. Finally, comparisons with theory reveal qualitative agreement be-

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tween the observed properties of krypton and some calculations, but systematic agreement in detail for all thermal properties is lacking. For krypton, the situation can be considered good, however, when comparison is made to that for other classes of solids. For the latter, anharmonic effects being smaller are easier to approximate, and largely phenomenological theories with many adjustable parameters are generally employed.

APPENDIX

Complete lattice-thermal-expansion data for two different specimens of solid krypton are given in Table VI.

TABLE VI. X-ray lattice-parameter thermal-expansion data from specimens Nos. 1 and 2. $a_0=5.64587\pm0.00010$ Å*.

T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$
		Specimen No. 1						Specimen No. 2			
4.30	0.04[a]	35.92	45.77	76.01	163.84	2.5	0.01[d]	32.98	38.79	86.02	200.86
4.30	0.05	39.85	55.22	80.00	178.14	3.2	−0.01	35.98	45.57	90.00	216.20
4.30	0.03	39.87	55.50	83.98	192.73	4.25	0.04	38.99	53.28	94.04	232.75
8.45	0.95	43.97	65.92	88.01	208.48	4.25	0.04	42.01	60.85	94.15	233.00[e]
9.95	1.78	48.23	77.40	92.13	224.69	5.93	0.20	45.00	68.59	98.02	249.44
12.28	3.36	52.00	87.73	96.02	241.02	8.68	0.95	47.98	76.96	102.00	266.54
14.61	5.43	55.97	99.24	100.02	257.81	9.86	1.46	51.98	87.97	106.00	285.25
19.44	12.10	59.99	111.24	104.14	276.30	12.28	3.10	56.00	99.49	107.01	290.38
19.45	12.12	59.99	111.40[b]	108.05	295.52	15.14	6.13	59.97	111.46	107.07	290.60
24.28	20.23	59.99	111.49	111.98	315.31	18.00	9.63	63.99	123.33	108.87[c]	299.46
28.05	27.85	63.99	123.74	113.97	325.99	21.16	13.70	69.98	143.44	109.99[c]	305.38
31.97	36.26	67.99	136.72	···	···	24.02	19.03	74.00	156.90	110.03	305.39
35.92[c]	45.60	71.98	149.95	···	···	26.95	24.88	78.03	171.17	112.00	315.45
						29.96	31.93	82.00	185.73	114.04	326.34

[a] Ni $K\alpha_1$ radiation (1.657910 Å*) and (622) planes used on this and on succeeding data points, until otherwise specified.
[b] Co $K\alpha_1$ radiation (1.788965 Å*) and (620) planes used, as in Ref. a; refraction correction 0.00007 Å*.
[c] Measurement made after cooling.
[d] Cu $K\alpha_1$ radiation (1.540562 Å*) and (640) planes used, as above.
[e] Fe $K\alpha_1$ radiation (1.936042 Å*) and (531) planes used, as above; refraction correction 0.00008 Å*.

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Pressure Derivatives of Second-Order Elastic Constants of MgO*

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The deviations of the second-order elastic constants from the Cauchy relation for some representative alkali halides were successfully accounted for by Löwdin's theory of many-body forces of quantum-mechanical origin. In the present paper, this theory is extended to include second-nearest-neighbor (nearest anion-anion) interaction in MgO for the calculation of the pressure derivatives of the second-order elastic constants. The calculated values, $\partial c_{12}^*/\partial p=1.4$ and $\partial c_{44}^*/\partial p=0.5$, are compared with the empirical results. While the qualitative agreement tends to support the theory that the many-body character of interionic interactions is indeed responsible for the particularly large deviations observed in MgO, better quantitative agreement would require a more elaborate calculation.

I. INTRODUCTION

THE elastic constants of crystals and their dependence on pressure are of considerable interest because of the information on the interatomic forces which they provide. In particular, deviations from the Cauchy relations in ionic crystals indicate in certain cases the presence of many-body forces of quantum mechanical (QM) origin.

For cubic crystals under hydrostatic pressure p the six Cauchy relations reduce to the equation[1] $c_{12}-c_{44}=2p$, where c_{12} and c_{44} are the effective elastic constants of the compressed crystal that determine, for example, ultrasonic wave propagation. It is well established theoretically that the Cauchy relations hold for centrosymmetric crystal structures in the absence of thermal-

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