

$$+\frac{1}{16} BB' \sum_{ijkl} \lambda_{1i} \lambda_{1j} \lambda'_{1k} \lambda'_{1l} \frac{\partial^4}{\partial x_i \partial x_j \partial x_k \partial x_l} \left( \frac{1}{r_0} \right). \quad (\text{A18})$$

For axially symmetric quadrupoles Eq. (A18) re-

duces to Eq. (A13). We have seen that any non-axial-symmetric quadrupole can be written as a combination of two axially symmetric quadrupoles  $A$  and  $B$ , with their symmetry axes along two different principal axes of the original quadrupole.

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## Properties of Crystalline Argon, Krypton, and Xenon Based upon the Born and Huang Method of Homogeneous Deformations. I. Zero-Pressure Thermal and Elastic Data \*

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The thermodynamic properties of solid argon, krypton, and xenon have been calculated for a two-body central force potential. Anharmonic contributions due to thermal expansion have been taken into account via a quasiharmonic calculation based upon the Born and Huang method of homogeneous deformations. The nonarbitrarily adjustable parameters of the Morse potential have been obtained from the solid-state bulk properties in a recursive refinement procedure. For those thermal properties sensitivity dependent upon the dilatation of the lattice the calculations become valid only for temperatures less than  $\frac{1}{3} T_M$ .

### I. INTRODUCTION

Born and Huang<sup>1</sup> (BH), via a perturbation expansion of the partition function, have developed the thermodynamics of a stressed harmonic lattice. The lattice potential energy is expressed as a double expansion in terms of the normal modes of the harmonic Hamiltonian and the parameters of a homogeneous deformation. For strains taken to be homogeneous deformations, the Helmholtz free energy is obtained as a series expansion (to second

order) in the Lagrangian strain parameters,  $\bar{u}_{\alpha\beta}$ . The free energy is given by Eq. 43.1 of BH. We have made explicit the formulas of BH applicable to our model of the noble-gas solids.<sup>2</sup>

Our quasiharmonic calculation hence includes the effect of anharmonicity due only to thermal expansion. Truly anharmonic effects due to three- and four-phonon processes have not been considered.

Several workers have developed perturbation theory descriptions of anharmonic phonon interactions.<sup>3-8</sup> More recent advances include the "self-

consistent phonon" approximation.<sup>9-11</sup> For the most recent advances in the theory of highly anharmonic crystals, one is referred to the work of Choquard<sup>12</sup> and Werthamer.<sup>13</sup> The experimental and theoretical status of the noble-gas solids has been periodically reviewed, and such comparisons can be found in Dobbs and Jones (1957),<sup>14</sup> Horton and Leech (1963),<sup>15</sup> Pollack (1964),<sup>16</sup> and Horton (1968).<sup>17</sup>

In this investigation, the nonarbitrarily adjusted parameters of a central force potential are determined completely from the zero-temperature zero-pressure experimental sublimation energy, density, and bulk modulus of the solid in a recursive refinement procedure. The theoretical zero-pressure thermal and elastic properties of our quasi-harmonic calculation are compared with the experimental data.

## II. THEORY

For large lattice dilatation, static lattice terms (in the energy density expansion) larger than second order in the strain begin to contribute significantly to the determination of the equilibrium strain parameters. Since the static lattice potential coefficients in the free-energy expansion are given explicitly by simple lattice sums of the two-body potential, contributions to seventh order in the static lattice strain have been included. [Terms to this order are not always significant (for zero pressure); however, they have been included to preclude any possibility of numerical rounding off errors.] If one assumes that the third- and higher-order elastic constants are independent of temperature, then the free energy (BH 43.1) for isotropic expansion ( $\bar{u}_{11} = \bar{u}_{22} = \bar{u}_{33} = U$ ;  $\bar{u}_{12} = \bar{u}_{13} = \bar{u}_{23} = 0$ ) is given by

$$F(V, T) = \Phi(V) + F_s(V_0, T) + \sum_{\alpha} F^{(\alpha\alpha)} U + \frac{1}{2} \sum_{\alpha\beta} F^{(\alpha\alpha)(\beta\beta)} U^2, \quad (1)$$

where

$$\Phi(V) = \Phi(V_0) + (1/3!) \Phi_3(V_0) U^3 + \dots + (1/7!) \Phi_7(V_0) U^7, \\ \Phi_n(V_0) = \left( \frac{\partial^n \Phi(V)}{\partial U^n} \right)_{U=0}.$$

For the lattice in static equilibrium ( $a = a_0$ ),  $\Phi_1(V_0) = 0$ . Since  $a = a_0(1 + 2U)^{1/2}$ , the coefficients may be expressed as derivatives with respect to the nearest-neighbor distance  $a$ . The second-order contribution (BH 40.10) has been included in  $F^{(\alpha\alpha)(\beta\beta)}$ . The coupling coefficients  $F^{(\alpha\alpha)}$ ,  $F^{(\alpha\alpha)(\beta\beta)}$  (BH 43.1) are appropriate wave-vector sums of products of eigenvectors, eigenfrequencies, thermal functions, anharmonic force constants, and phase factors.

## III. RECURSIVE POTENTIAL REFINEMENT AND THERMODYNAMIC FORMULAS

The Morse potential is given by

$$\phi(r) = \epsilon \{ -\exp[-2c(r - r_0)] + 2\exp[-c(r - r_0)] \}. \quad (2)$$

Define  $M_j^2 = (r_j/a)^2 = m_j^2 + n_j^2 + l_j^2$ , where  $m_j$ ,  $n_j$ ,  $l_j$  are the position coordinates of any atom in the lattice.

The potential energy for  $N$  atoms is given by

$$\Phi(a) = \frac{1}{2} N \epsilon (-B^2 \sum_j e^{-2cM_j a} + 2B \sum_j e^{-cM_j a}), \quad (3)$$

where

$$B = e^{cr_0}.$$

The parameters  $\epsilon$ ,  $a_0$ ,  $r_0$ , and  $c$  are calculated from the solid-state data by the following recursive procedure. If at absolute zero  $a_0$  is the value of  $a$  for the lattice to be in equilibrium then  $a_e = a_0 \times (1 + 2U)^{1/2}$ , where  $a_e$  is the experimental nearest-neighbor distance for zero temperature and zero pressure. Because of the zero-point energy,  $a_e > a_0$ . The isothermal bulk modulus is given by

$$K_T = \left( V \frac{\partial^2 F(V, T)}{\partial V^2} \right)_T.$$

The heat of sublimation at 0°K is  $L_0$ . Hence one iterates the equations

$$-L_0 = F(V, T=0), \quad a_e = a_0(1 + 2U)^{1/2}, \\ \left. \frac{\partial \Phi(V)}{\partial V} \right|_{V_0} = 0, \quad K_{\text{expt}} = V \left( \frac{\partial^2 F(V, T=0)}{\partial V^2} \right)_T. \quad (4)$$

The strain parameter  $U$  and contributions to  $F(V, T=0)$  from the preceding cycle are used in calculating the parameters of the static potential for the current cycle. The equations are iterated until there is no further change in the derived potential parameters.

For the first cycle

$$-L_0 = \Phi(V_0) + \frac{3}{8} R \Theta, \quad \left. \frac{\partial \Phi(V)}{\partial V} \right|_{V_0} = 0, \quad (5) \\ K_{\text{expt}} = V \left[ \frac{\partial^2 \Phi(V)}{\partial V^2} \right]_T \Big|_{V_0}, \quad U = \frac{3\gamma_I R \Theta}{V_0 K_{\text{expt}}}.$$

$\gamma_I$  is the low-temperature experimental Grüneisen parameter.  $\Theta$  is the 0°K calorimetric Debye temperature. The input data are given in Table I.

The calculated Morse potential parameters are shown in Table II. It is noted that these potential parameters are virtually the same as the Morse potential parameters given by Glyde<sup>27</sup> obtained by fitting the harmonic approximation at 0°K in a refinement procedure similar to ours.

The equilibrium value of  $U$  may be calculated from

$$-P = \left( \frac{\partial F}{\partial V} \right)_T \Big|_{U=U(T, P)}, \quad (6)$$

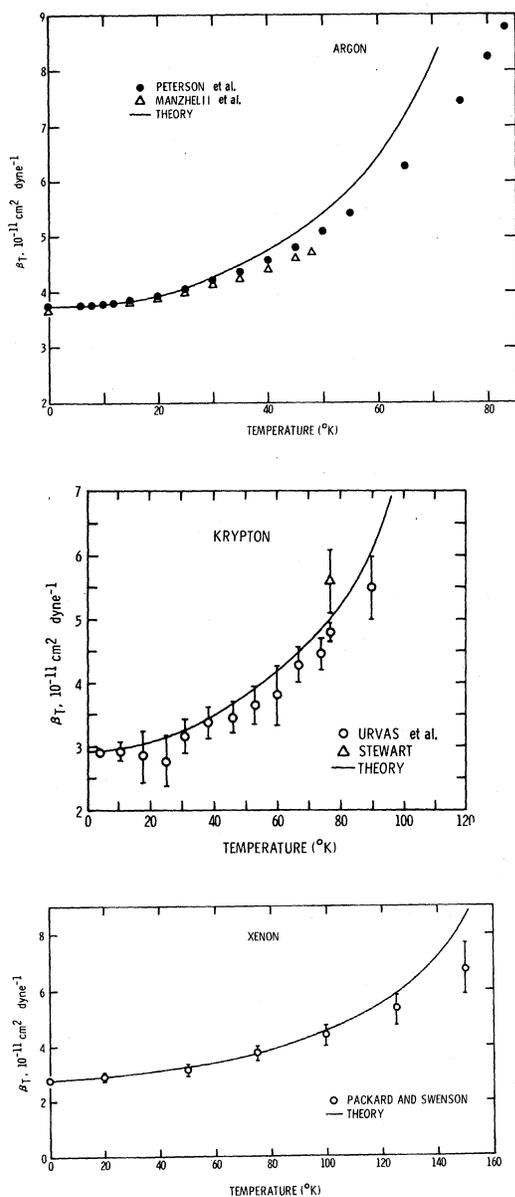


FIG. 1. Temperature dependence of the isothermal compressibility. Experimental data are from the following: argon, Ref. 18 (closed circles) and Ref. 26 (open triangles); krypton, Ref. 21 (open circles) and Ref. 29 (open triangles); xenon, Ref. 25 (open circles).

where  $V = V_0(1 + 2U)^{3/2}$ .

The various thermodynamic functions of interest here are given by

$$C_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V, \quad \beta_T^{-1} = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T, \quad \alpha = \beta_T \left( \frac{\partial P}{\partial T} \right)_V,$$

$$C_p - C_V = \frac{TV\alpha^2}{\beta_T}, \quad \gamma = \frac{V\alpha}{C_V\beta_T}, \quad (7)$$

$$C_{11}^S - C_{11}^T = C_{12}^S - C_{12}^T = \gamma^2 TC_V/V, \quad C_{44}^S - C_{44}^T = 0.$$

#### IV. RESULTS

Using the Born and von Kármán cyclic boundary conditions we have obtained the normal modes on a mesh of points evenly distributed throughout the portion of the Brillouin zone which cannot be further reduced by the symmetry operations of the lattice point group. The coupling coefficients for the full zone have been obtained for the secular determinant of nearest neighbors.

In the root sampling technique for a small but finite mesh a relative overweighting of the long-wavelength phonons give rise to an anomalous rise in the specific heat at low temperatures. Consequently, in the calculation of low-temperature properties, the frequency interpolation routine of Gilat and Raubenheimer<sup>28</sup> has been used to obtain a satisfactory harmonic spectrum. This permits a more definitive discussion of the thermal data in the low-temperature limit.

Since the observed zero-temperature zero-pressure bulk modulus was used in the potential determination our 0°K compressibilities shown in Fig. 1 agree with the experimental results; however, above about  $\frac{1}{2} T_M$  the theoretically predicted isothermal compressibilities are too high, being outside the large experimental error limits. For krypton the theoretical  $\beta_T$  is also higher above 40°K than the experimental data of Coufal, Veith, Korpiun, and Lüscher<sup>30</sup> (not shown).

The volume expansivities are shown in Fig. 2. For  $T \geq \frac{1}{3} T_M$  (a temperature range corresponding to rms displacements greater than 4% of the nearest-neighbor distance—see Fig. 3), our theoretical expansivity deviates seriously from measured values, as does that obtained by Klein, Hor-

TABLE I. Experimental input data for potential parameters determination.

Solid	$a_e$ (Å)	$L_0$ (cal mole <sup>-1</sup> )	$\theta_0$ (°K)	$\beta_T$ (10 <sup>-11</sup> cm <sup>2</sup> dyn <sup>-1</sup> )	$\gamma_T$
Argon	3.7555 <sup>a</sup>	1846 <sup>b</sup>	93.3 <sup>b</sup>	3.75 <sup>a</sup>	2.4 <sup>a</sup>
Krypton	3.992 <sup>c</sup>	2666 <sup>b</sup>	71.7 <sup>b</sup>	2.91 <sup>d</sup>	2.5 <sup>c</sup>
Xenon	4.336 <sup>e</sup>	3830 <sup>f</sup>	64.0 <sup>g</sup>	2.77 <sup>h</sup>	2.3 <sup>i</sup>

<sup>a</sup>See Ref. 18.

<sup>b</sup>See Ref. 19.

<sup>c</sup>See Ref. 20.

<sup>d</sup>See Ref. 21.

<sup>e</sup>See Ref. 22.

<sup>f</sup>See Ref. 23.

<sup>g</sup>See Ref. 24.

<sup>h</sup>See Ref. 25.

<sup>i</sup>See Ref. 26.

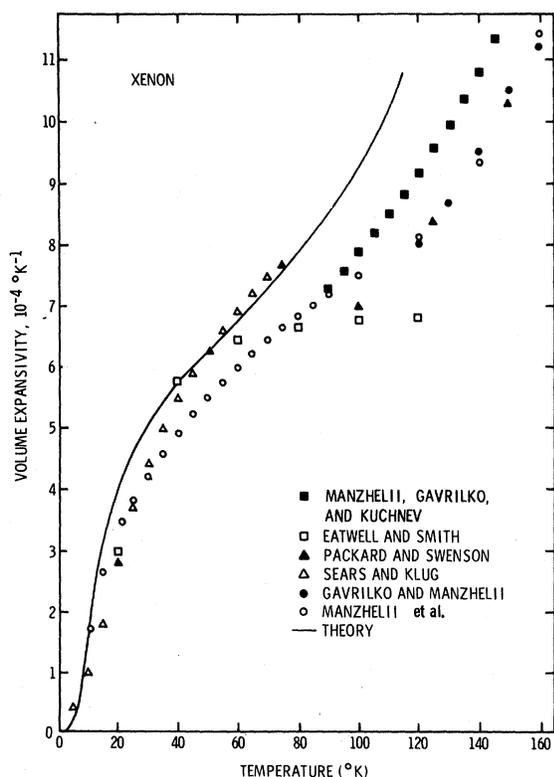
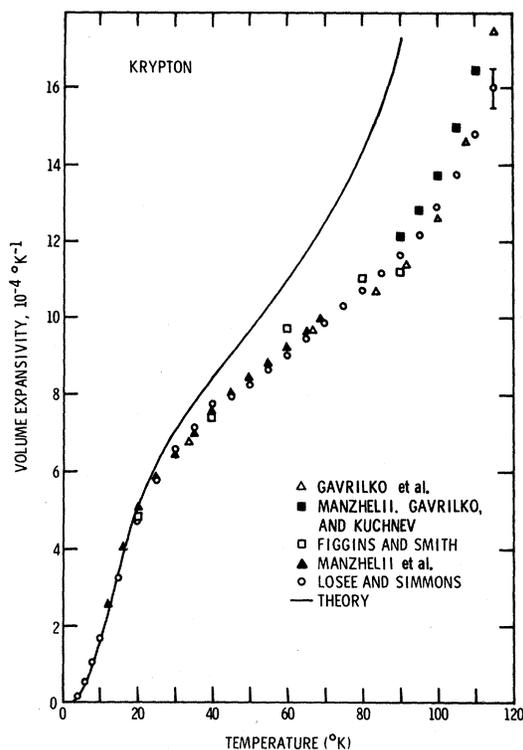
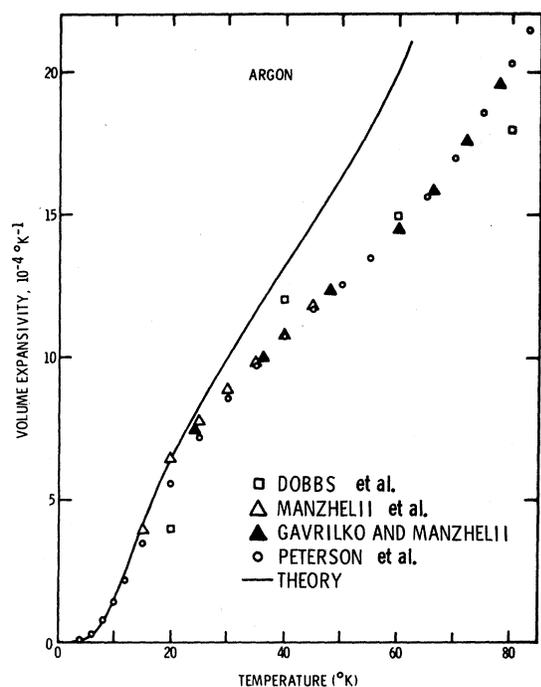


FIG. 2. Temperature dependence of the volume expansivity. Experimental data are from the following: argon, Ref. 18 (open circles), Ref. 26 (open triangles), Ref. 31 (open squares), and Ref. 32 (closed triangles); krypton, Ref. 20 (open circles), Ref. 26 (closed triangles), Ref. 32 (open triangles), Ref. 33 (closed squares), and Ref. 34 (open squares); xenon, Ref. 22 (open triangles), Ref. 25 (closed triangles), Ref. 26 (open circles), Ref. 33 (closed squares), Ref. 35 (open squares), and Ref. 36 (closed circles).

ton, and Feldman<sup>37</sup> in a quasiharmonic calculation. Both calculations drastically *overestimate* the expansivity. Klein, Horton, and Feldman<sup>37</sup> also performed a low-order anharmonic calculation using conventional perturbation theory. Their anharmonic

result seriously *underestimates* the expansivity. This overestimation of anharmonic effects signals the breakdown of perturbation theory in this temperature range.

The specific heats at constant pressure ( $C_p$ )

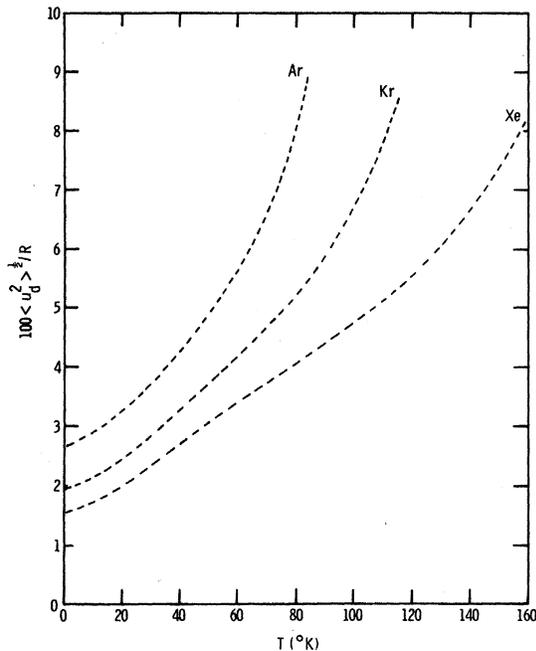


FIG. 3. Temperature dependence of the rms displacements as a percentage of the nearest-neighbor distance.

shown in Fig. 4 also seriously deviate from the experimental results above  $\frac{1}{3} T_M$ . This overestimation is due to the effect of  $\alpha^2/\beta_T$  in Eq. (7). Owing to a negative anharmonic contribution to  $C_V$  together with too low a theoretical expansivity,  $C_p$  for the anharmonic calculation<sup>37</sup> is too low above  $\frac{1}{2} T_M$ .

Plots of the Debye temperature are shown in Fig. 5. The theoretical  $\theta(V_0, T)$  have been calculated from  $C_V(V_0)$  in Eq. (7). Using their measured volume expansivities, Peterson, Batchelder, and Simmons<sup>18</sup> (PBS) and Manzhelii, Gavrilko, and Voitovich<sup>26</sup> (MGV) have analyzed the  $C_p$  data of Flubacher, Leadbetter, and Morrison<sup>38</sup> to obtain  $\theta(T)$  of argon. Losee and Simmons<sup>20</sup> have reanalyzed the  $C_p$  data of Beaumont, Chihara, and Morrison<sup>19</sup> to obtain  $\theta(T)$  of krypton for their volume expansivity data. The xenon  $\theta(T)$  is that predicted from the  $C_p$  data of Fenichel and Serin<sup>24</sup> and Clusius and Riccoboni<sup>39</sup> for the  $\beta_T$  of Packard and Swenson<sup>25</sup> and the volume expansivities of MGV and Manzhelii, Gavrilko, and Kuchnev.<sup>33</sup>

The relative agreement of our 0°K  $\theta$  calculated

TABLE II. Morse potential parameters obtained by the recursive refinement procedure.

Solid	$-\epsilon/k$ (°K)	$a_0$ (Å)	$r_0$ (Å)	$c$ (Å <sup>-1</sup> )
Argon	149.41	3.7105	3.7746	1.6006
Krypton	209.25	3.9660	4.0259	1.5449
Xenon	289.52	4.3190	4.3950	1.3674

from the elastic constants<sup>43-45</sup> ( $\theta_0^{el}$ ) is anticipated from the potential refinement procedure which yields the correct zero-temperature elastic constants (or rather  $C_{11} + 2C_{12}$ ). The slight maximum in the  $\theta(T)$  curves for argon and krypton at low temperature is due to the negative  $T^5$  term in the  $C_V$  expansion<sup>17</sup> (see also Paper III of this series) which arises when  $\theta_0^{el}$  is used in the low-temperature fit. An analysis of the long-wavelength limit

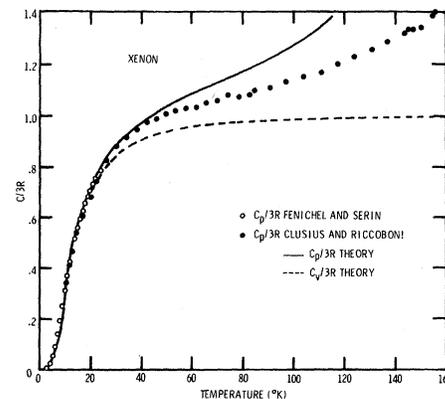
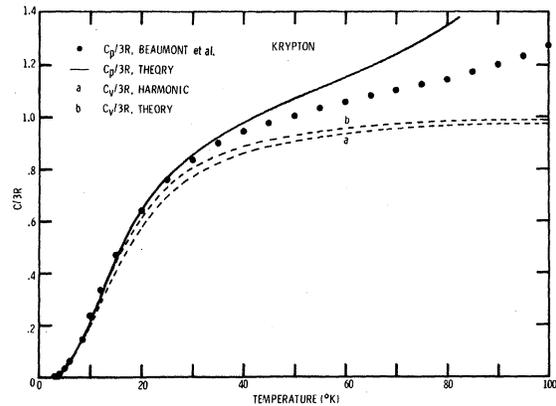
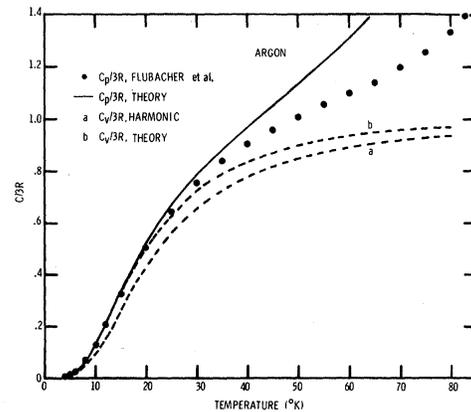


FIG. 4. Temperature dependence of the specific heats. (a)  $C_p/3R$  static lattice contribution, (b)  $C_V/3R$  quasi-harmonic. The experimental data are from the following: argon, Ref. 38; krypton, Ref. 19; and xenon, Ref. 24 (open circles) and Ref. 39 (closed circles).

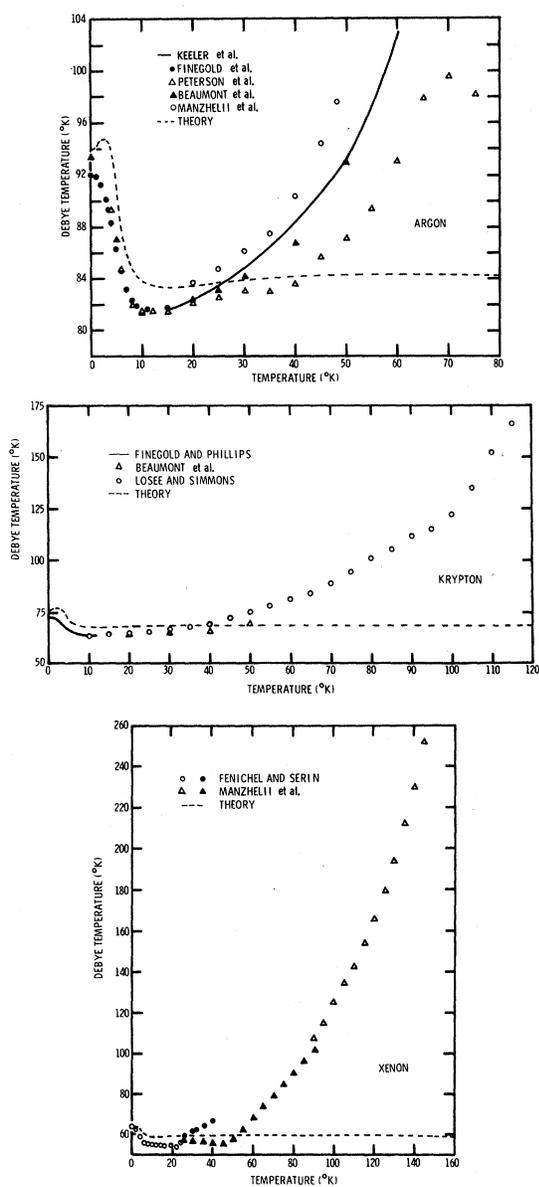


FIG. 5. Debye temperature  $\theta(V_0)$  plots. The analyses of the primary experimental data are from the following: argon, Ref. 18 (open triangles), Ref. 19 (closed triangles), Ref. 26 (open circles), Ref. 40 (closed circles), and Ref. 41 (solid curve); krypton, Ref. 19 (open triangles), Ref. 20 (open circles), and Ref. 40 (solid curve); xenon, Ref. 24 (open circles), Ref. 26 (open triangles), Ref. 33 (closed triangles), and Ref. 42 (closed circles).

of the frequency distribution spectrum  $[g(\omega) = a\omega^2 + b\omega^4]$  indicates the quartic coefficients to be positive. Hence, our (harmonic) spectrum would predict no maximum in the  $\theta(T)$  curve. This maximum in the  $\theta(T)$  curve is an artifact of the low-temperature fitting procedure and an inadequate sampling of the low-temperature volume-dependent contribution. However, for  $T < 20^\circ\text{K}$  our

theoretical  $\theta(V_0)$  are all larger than the experimental results. At high temperatures our  $\theta(V_0)$  plots exhibit the character of a quasiharmonic  $C_V$  calculation which approaches the classical limit of  $3R$  per mole.

The adiabatic elastic constants shown in Fig. 6 are the appropriate second derivatives of the free energy and as such are not just the  $F^{(\alpha\alpha)(\beta\beta)}$  coefficients but contain contributions from the third- and higher-order elastic coefficients. The adiabatic compressibility  $3/(C_{11}^S + 2C_{12}^S)$  for our model is compared in Fig. 6 with the analyses of PBS and MGW and the experimental results of Keeler and Batchelder<sup>41</sup> (KB). There is excellent agreement up to and above  $80^\circ\text{K}$  between the theoretical re-

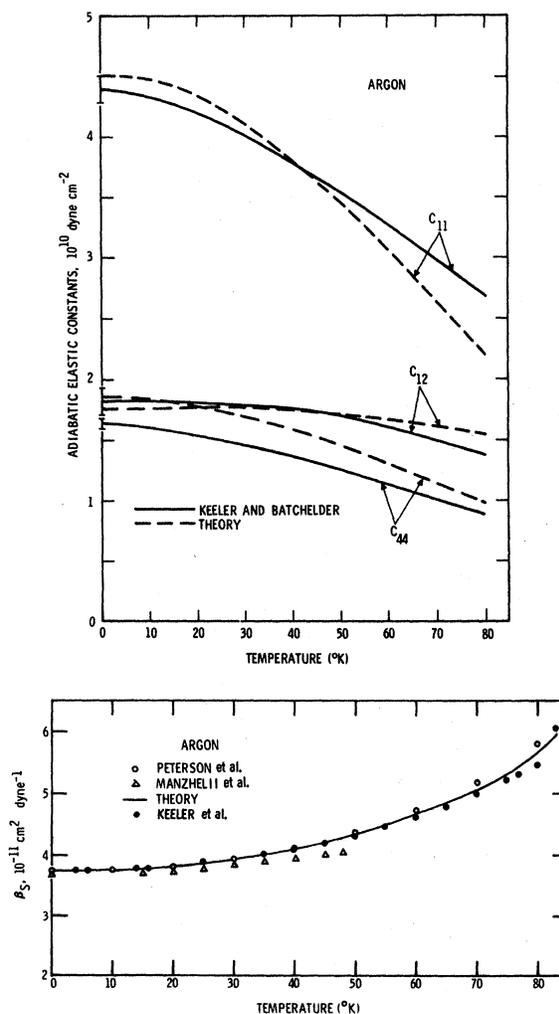


FIG. 6. Temperature dependence of the adiabatic elastic constants and of the adiabatic compressibility of argon. The experimental data are from Ref. 41 (closed circles). The adiabatic compressibilities derived from experimental data are from Ref. 18 (open circles) and Ref. 26 (open triangles).

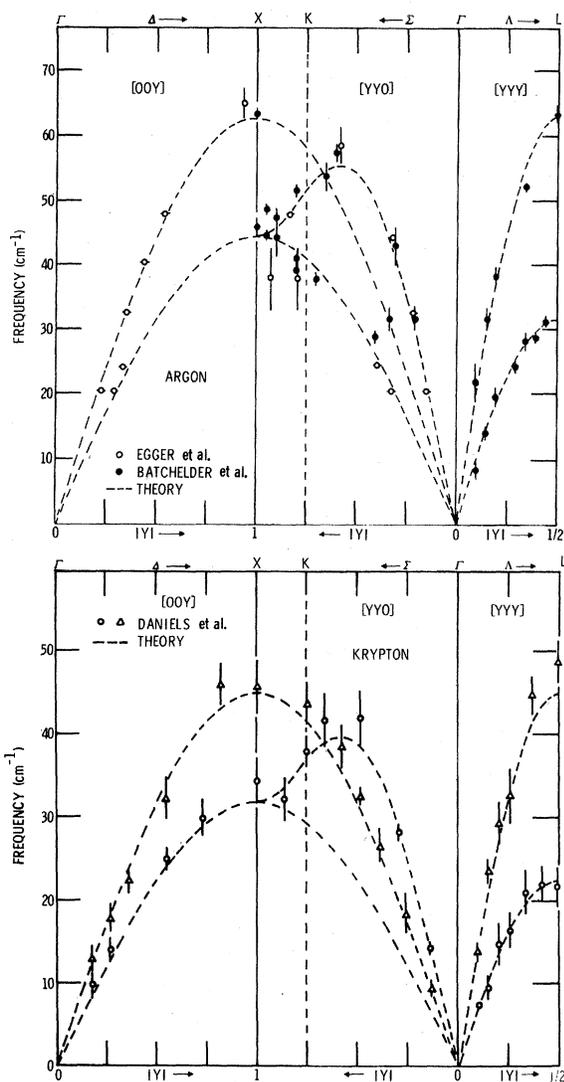


FIG. 7. Dispersion curves of argon at 4°K and krypton at 79°K. The experimental data are from the following: argon, Ref. 50 (open circles) and Ref. 51 (closed circles); krypton, Ref. 52.

sults and those of PBS and KB. Since the isothermal compressibilities of PBS and MGV shown in Fig. 1 involved a conversion from the adiabatic

data, it is perhaps more significant that our adiabatic results are in agreement than that our isothermal results disagree (above 40°K). This point can be clarified when the elastic data for krypton and xenon become available.

Our elastic data for argon are compared with other lattice dynamics models and the experimental data in Table III. The anisotropy factor  $A$  (unity for an elastically isotropic crystal) and the Cauchy relation relative deviation factor  $\delta$  are given by

$$A = 2C_{44}/(C_{11} - C_{12}), \quad \delta = (C_{44} - C_{12})/C_{12}.$$

Our model predicts solid argon to be 5% more anisotropic than the elastic constants measured by KB. We predict a positive Cauchy deviation comparable to the all-neighbor Lennard-Jones model of Barron and Klein<sup>46</sup> (BK). Zucker and Chell<sup>47</sup> (ZC) using essentially the same model as Barron and Klein included three-body triple-dipole-type interactions. These interactions yielded elastic constants resulting in a negative deviation from the Cauchy relation. This condition, in agreement with KB, gives evidence of the importance of such three-body interaction in argon. However, like other model calculations<sup>48,49</sup> the BK and ZC models seriously underestimate the low-temperature  $C_{11}$  elastic constant, and the Debye temperature calculated from these elastic constants is 4 and 8% lower, respectively, than the calorimetric  $\theta_0$  of Finegold and Phillips.<sup>40</sup>

The dispersion curves of argon and krypton are plotted in Fig. 7. Shown also are the argon neutron scattering relations of Egger *et al.*<sup>50</sup> and Batchelder *et al.*<sup>51</sup> (the latter's measurements on Ar<sup>36</sup> have been converted to a mass of 39.948). Since the experimental temperature was 4°K the theoretical results are for the quasiharmonic frequencies corresponding to the theoretically predicted 4°K volume. The quasiharmonic dispersion curves of krypton are calculated for the theoretical dilatation corresponding to the 79°K and 0.3 kbar data of Daniels *et al.*<sup>52</sup> The over-all agreement between theory and experiment seems very satisfactory, with the theoretical curves lying generally well within the experimental error.

TABLE III. Elastic data of crystalline argon at 0°K. The  $C_{ij}$  are in units of  $10^{10}$  dyn cm<sup>-2</sup>.

Ref.	$C_{11}$	$C_{12}$	$C_{44}$	$\frac{1}{3}(C_{11} + 2C_{12})$	$A$	$\delta \times 100$	$\theta_0^a$
Present results	4.48	1.76	1.84	2.67	1.35	+4.55	94.0
Keeler and Batchelder <sup>41</sup>	4.39	1.83	1.64	2.68	1.28	-10 ± 7	90.5
Barron and Klein <sup>46</sup>	3.71	2.07	2.15	2.62	2.62	+3.9	88.3
Zucker and Chell <sup>47</sup>	3.59	2.02	1.85	2.54	2.36	-8.4	84.2
Peterson <i>et al.</i> <sup>18</sup>				2.67			
Finegold and Phillips <sup>40</sup>							92.0 ± 0.3 <sup>a</sup>
Beaumont <i>et al.</i> <sup>19</sup>							93.3 ± 0.6 <sup>a</sup>

<sup>a</sup>Calorimetric values.

## V. CONCLUSIONS

An over-all consideration of the results of our quasi-harmonic and other truly anharmonic perturbation expansion calculations<sup>37</sup> indicates that for temperatures above  $\frac{1}{3}$ – $\frac{1}{2}$  of the melting temperature and rms displacements from 4 to 6% of the nearest-neighbor distance the apparent breakdown of the perturbation theory to the low orders considered results in large positive or negative deviations from experimental observations. This is aside from any contributions attributable to defects in the bulk solid. The following paper in this series is concerned with equation-of-state calculations of argon, krypton, and xenon. There we find that for pressures to 20 kbar the theoretical isotherms are in exceptional agreement with experiments for temperatures within 7, 2, and 11 °K of the zero-pressure melting points of argon, krypton, and xenon,

respectively. In addition, melting lines based upon Born's mechanical stability criteria<sup>53</sup> are in agreement with the experimental melting curves below 2 kbar.

Thus it is seen that even though the theory may yield too large a dilatation at temperatures greater than  $\frac{1}{2} T_M$  (for zero pressure), the theory is still capable of quantitatively correct predictions over a much wider range of temperature and strain for other specific bulk properties.

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## Properties of Crystalline Argon, Krypton, and Xenon Based upon the Born and Huang Method of Homogeneous Deformations. II. Equation of State and Melting Lines\*

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Pressure-volume-temperature relationships of solid argon, krypton, and xenon for a Morse potential calculation are compared to the static data of Stewart and Packard and Swenson. Theoretical melting lines based upon mechanical instability of the crystal lattice are presented. It is concluded that within the context of our model below 2 kbar the stability criteria alone are an adequate consideration in the melting line predictions for solid argon, krypton, and xenon.

### I. INTRODUCTION

In an earlier paper<sup>1</sup> (hereafter referred to as Paper I) the author described a stressed harmonic potential model calculation of solid argon, krypton, and xenon. Cubic and quartic stress terms in the crystal Hamiltonian were considered via Born and Huang's (BH) method of homogeneous deformations.<sup>2</sup> The parameters of a Morse potential (see Table II of Paper I) were determined completely from the 0°K solid-state data by a recursive refinement procedure [Eq. (4) of Paper I]. The purpose of this work is to examine the equation of state of solid argon, krypton, and xenon and compare with the static data (to 20 kbar). A study of properties along the "melting line" is also presented. (The "melting line" is based upon Born's mechanical stability criteria.<sup>3</sup>)

### II. EQUATION OF STATE

For our model of solid argon, krypton, and xenon (see Paper I) the Helmholtz free energy was given as a series expansion in the Lagrangian strain parameters (in this case,  $\bar{u}_{11} = \bar{u}_{22} = \bar{u}_{33} = u$ ,  $\bar{u}_{12} = \bar{u}_{13} = \bar{u}_{23} = 0$ ) by

$$F(V, T) = \Phi(V) + F_S(V_0, T) + \sum_{\alpha} F^{(\alpha\alpha)} u_{\alpha} + \frac{1}{2} \sum_{\alpha\beta} F^{(\alpha\alpha)(\beta\beta)} u_{\alpha}^2, \quad (1)$$

with

$$\Phi(V) = \Phi(V_0) + (1/3!) \Phi_3(V_0) u^3 + \dots + (1/7!) \Phi_7(V_0) u^7,$$

$$\Phi_n(V_0) = \left( \frac{\partial^n \Phi(V)}{\partial u^n} \right)_{u=0}.$$

The  $F^{(\alpha\alpha)}$ ,  $F^{(\alpha\alpha)(\beta\beta)}$  anharmonic coupling coefficients are given by Eq. 43.1 of BH. The pressure ( $P$ ) for volume ( $V$ ) or vice versa may be calculated from

$$-P = \left[ \left( \frac{\partial F}{\partial V} \right)_{T, u=u(T, P)} \right] = \left[ \left( \frac{\partial F}{\partial u} \right) \left( \frac{\partial u}{\partial V} \right) \right]_{u=u(T, P)}, \quad (2)$$

where

$$V = V_0(1 + 2u)^{3/2}, \quad (3)$$

The static equilibrium volume  $V_0$  (per atom) =  $\frac{1}{2}\sqrt{2} a_0^3$ . The values of  $a_0(P=0)$  are given in Table II of Paper I. The pressure (volume) dependence of all the thermodynamic quantities given in Eq. (17) can be obtained by evaluating Eq. (1) for the  $P \neq 0$  strains [see Eq. (2)]. All the coefficients in Eq. (1) are evaluated at the zero-temperature zero-pressure static volume. This means that in the equation-of-state (EOS) calculations no additional time-consuming computations of the  $F^{(\alpha\alpha)}$  or  $F^{(\alpha\alpha)(\beta\beta)}$  coupling parameters are required. The EOS data herein presented are for the Morse potential parameters of argon, krypton, and xenon given in Table II of Paper I.

Many analytical equations of state have been derived following the development of the theory of the finite strain of elastic solids by Murnaghan.<sup>4</sup> Some of the more commonly used are those developed by Birch,<sup>5</sup> Gilvarry,<sup>6</sup> Anderson,<sup>7</sup> and MacDonald.<sup>8</sup> However, it is not within the scope of this paper to analyze the theoretical results in terms of such EOS expressions. At this time, interpretation will be given only in terms of comparisons with the re-