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Calculation of the Temperature Dependence of the Second-Order Elastic Constants of fcc Ar, Kr, and Xe Using a Two-Body Short-Range Interatomic Potential*

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The temperature dependence of the second-order elastic constants of fcc Ar, Kr, and Xe have been studied using phenomenological (m-6) Lennard-Jones potentials acting between nearest neighbors and fitted to the zero-temperature zero-pressure lattice constant and the sublimation energy. The theory of the second-order elastic constants is briefly reviewed, and the second-order strain dependence of the quasiharmonic free-energy density is derived using perturbation theory. The resulting expressions for the temperature dependence of the elastic constants involve both third- and fourth-order force constants, and require a single scan of the Brillouin zone, which is carried out to give an accuracy of about 1%. We find that the contribution of the third-order force constants is comparable to that of the fourth-order ones and in some cases predominates. Adiabatic and isothermal results are presented both for constant volume (0°K M volume) and for the experimentally observed equilibrium M volume. We did not solve the equation of state. Wave velocities derived from our elastic constants are compared with recent experiments on crystals of Ar and Kr. Our results show that there are large anharmonic contributions to the temperature dependence of the elastic constants. Consequently, our Ne results are quantitatively unreliable (except at $T=0$) and we omit them. For $T>\sim\Theta_\infty/2$ there are indications of the breakdown of perturbation theory. The way our results may be affected by including higher-order anharmonic terms is illustrated by considering the temperature dependence of the zero-pressure bulk modulus of Ar.

1. INTRODUCTION

In a recent paper[1] the thermodynamic properties of solid fcc Ar, Kr and Xe were investigated using a short-range central force and the conventional perturbation expansion of the partition function. Here we present a study of the second-order elastic constants of the same solids in an essentially similar order of approximation. This means that we shall mostly work with a quasiharmonic partition function and hence speak of quasiharmonic elastic constants (i.e., second-order strain derivatives of the quasiharmonic free-energy density). Because the quasiharmonic frequencies are a function of strain, these elastic constants contain a contribution from both cubic and quartic force constants. They reduce, at $T=0$°K, to the elastic constants of Barron and Klein[2] and, when suitably averaged, yield the $\Theta_0{}^c$ (anharmonic) first studied by Flinn and Maradudin.[3] The present work represents a rederivation of Barron and Klein's results by a different and, in principle, more accurate method as well as an extension of their work to nonzero temperatures. Previous work on the elastic constants of the fcc lattice has been reviewed in a thesis by one of us (C.F.).[4] We shall, therefore, make only brief reference to earlier work.

Since it is now possible to grow large-grained single crystals in these solids that are either free standing or under pressure, quantitative measurements of the elastic constants are now within reach. Indeed, some preliminary data have already been reported and these provide an additional motive for our investigation.

There has been much speculation about the interatomic forces in the heavier rare-gas solids. In addition to the two-body central interatomic potential familiar in the theory of rare-gas crystals, Chell and Zucker and others[5] have suggested that the triple-dipole dispersion force plays an important role in the thermodynamic and elastic properties of heavier inert-gas solids, especially with regard to the Cauchy relations. However, Lucas[6] has argued that for the heavier rare-gas solids the dipole-dipole perturbation series is slowly convergent (implying that calculations based solely on the triple-dipole term may be misleading). Other authors[7] have argued that at least for Ar the triple-dipole term is dominant. Jansen[8] has claimed that the exchange interactions give even more important contributions, although Swenberg[9] appears to have refuted this claim. While there is no doubt many-body forces are present in the heavier rare-gas solids, their exact nature is still very contraversial. Thus in spite of certain obvious deficiencies, we have chosen to work with heuristic

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[1] M. L. Klein, G. K. Horton, and J. L. Feldman (to be published).

[2] T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. (London) **82**, 161 (1963); **85**, 533 (1965).

[3] P. A. Flinn and A. A. Maradudin, Ann. Phys. (N. Y.) **22**, 223 (1963).

[4] C. Feldman, Ph.D. thesis, Rutgers University, 1967 (unpublished).

[5] G. G. Chell and I. J. Zucker, Proc. Phys. Soc. (London) **1C**, 35 (1968); J. C. Rossi and F. Dannon, Discussions Faraday Soc. **40**, 97 (1965); M. L. Klein and R. J. Munn, J. Chem. Phys. **47**, 1035 (1967).

[6] A. A. Lucas, Physica **35**, 353 (1967); Phys. Rev. Letters **21**, A16 (1968).

[7] D. A. Copeland and N. R. Kestner, J. Chem. Phys. **49**, 5214 (1969); J. A. Barker, D. Henderson, W. R. Smith, Phys. Rev. Letters **21**, 134 (1968); J. A. Barker and A. Pompe, Australian J. Chem. **21**, 1683 (1968).

[8] L. Jansen, Phys. Rev. **135A**, 1292 (1964).

[9] C. E. Swenberg, Phys. Letters **24A**, 163 (1967).

two-body interatomic potentials of the type

$$\phi(R)=[6m\epsilon/(m-6)][(1/m)(R_0/R)^m-\tfrac{1}{6}(R_0/R)^6],$$

with $m=11$, 12, and 13. There is no *a priori* reason to believe that allowing $\phi(R)$ to act between all neighbors in the crystal lattice is superior to restricting it to nearest neighbors only.[10] Moreover, this latter assumption, in addition to simplifying some of the numerical work, allows us to compare with previous studies on the elastic properties of the fcc lattice with nearest-neighbor forces. We have chosen the parameter ϵ and R_0 in the potential to fit the sublimation energy and the zero-temperature zero-pressure lattice constant.[11]

Recent developments in lattice dynamics of rare-gas crystals have centered on the application and extension of Born's self-consistent phonon theory. For example, Gillis, Werthamer, and Koehler[12] have calculated (among other things) the temperature dependence of wave velocities in Ne and Ar using the lowest-order self-consistent scheme, i.e., in the Hartree approximation. These calculations omit the explicit contribution of odd-order anharmonic force constants and so temperature dependencies found by Gillis, Werthamer, and Koehler have little to do with the properties of the real crystals. Horner[13] has derived expressions for the elastic constants that include the leading odd-order force constants in a self-consistent fashion. While this paper is mostly concerned with the results of conventional perturbation theory including both cubic and quartic anharmonic force constants, we have devoted a section of this paper to a comparison of the conventional perturbation theory and the method of selfconsistent phonons using the temperature dependence of the isothermal bulk modulus of Ar for illustration.

In Sec. 2 of this paper, we briefly recall the various definitions of elastic constants and hence establish our notation. The strain dependence of the quasiharmonic free energy density is derived in Sec. 3, and in Sec. 4 we present expressions for the elastic constants based upon two-body central forces. Details of the calculation are outlined in Sec. 5 and specific application to Ar, Kr, and Xe and the comparison with experiment are given in Sec. 6. Section 7 contains the comparison between conventional perturbation theory and the method of selfconsistent phonons. The paper concludes with a summary.

2. ELASTIC CONSTANTS: A BRIEF SURVEY

Elastic constants describe the strain dependence of W, the energy density of a solid. The theory of elastic constants has been thoroughly discussed recently[14] so that we shall only give a brief outline of the relevant results.

In terms of the $\{u_{\alpha\beta}\}$, the infinitesimal homogeneous deformation parameters of Huang,[15] the energy density of a solid can be written as

$$W-\hat{W}=H_{\alpha\beta}u_{\alpha\beta}+\tfrac{1}{2}H_{\alpha\beta,\sigma\tau}u_{\alpha\beta}u_{\sigma\tau}+\cdots.$$

Alternatively, we may use the $\{\eta_{\alpha\beta}\}$, the finite strain parameters of Leibfried and Ludwig,[16]

$$W-\hat{W}=C_{\alpha\beta}\eta_{\alpha\beta}+\tfrac{1}{2}C_{\alpha\beta,\sigma\tau}\eta_{\alpha\beta}\eta_{\sigma\tau}+\cdots.$$

If the deformation is isentropic and W is the internal energy density, then the coefficients in the above Taylor series expansions are adiabatic elastic constants. On the other hand, if the deformation is isothermal, these coefficients are the isothermal elastic constants. The isothermal and adiabatic elastic constants are related thermodynamically. $\hat{W}$ is the energy density in the undeformed solid; $H_{\alpha\beta}$ and $C_{\alpha\beta}$ determine the initial stress while $H_{\alpha\beta,\sigma\tau}$ and $C_{\alpha\beta,\sigma\tau}$ are the second-order elastic constants. It follows from their definition that Huang's constants $H_{\alpha\beta,\sigma\tau}$, unlike the $C_{\alpha\beta,\sigma\tau}$, do not have the full symmetry of second-order elastic constants. However, the $H_{\alpha\beta,\sigma\tau}$ give a simple form for the equations of small vibrations of solids under stress.[17] The elastic constants defined above are related by the condition of rotational invariance,

$$C_{\alpha\beta}=H_{\alpha\beta},$$
$$C_{\alpha\beta,\sigma\tau}=H_{\alpha\beta,\sigma\tau}-H_{\beta\tau}\delta_{\alpha\sigma},\quad\text{etc.}$$

Thus if the $H_{\alpha\beta}$ and $H_{\alpha\beta,\sigma\tau}$ are known, we can derive $C_{\alpha\beta}$ and $C_{\alpha\beta,\sigma\tau}$.

It is sometimes convenient to use the elastic constants $c_{\alpha\beta,\gamma\delta}$ which are derived from the stress-strain relation. These elastic constants are particularly useful when the initial stress is isotropic, i.e., $H_{\alpha\beta}=-p\delta_{\alpha\beta}$. Thus for example, the isothermal compressibility is given by

$$3\chi_T=(-3/V)(\partial V/\partial p)_T=c_{xx,xx}{}^{\text{iso}}+2c_{xx,yy}{}^{\text{iso}},$$

and

$$H_{xx,xx}=C_{xx,xx}-p=c_{xx,xx},$$
$$H_{xx,yy}=C_{xx,yy}=c_{xx,yy}-p,$$
$$H_{xy,xy}=C_{xy,xy}-p=c_{xy,xy}.$$

Hence

$$(3/\chi)=c_{xx,xx}+2c_{xx,yy}=C_{xx,xx}+2C_{xx,yy}+p$$
$$=H_{xx,xx}+2H_{xx,yy}+2p.$$

For a cubic crystal the adiabatic and isothermal

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[10] E. A. Guggenheim and M. L. McGlashan, Proc. Roy. Soc. (London) **A255**, 456 (1960).

[11] G. K. Horton, Am. J. Phys. **36**, 93 (1968).

[12] N. S. Gillis, N. R. Werthamer, and T. R. Koehler, Phys. Rev. **165**, 951 (1968).

[13] H. Horner, Z. Physik **205**, 72 (1967).

[14] R. N. Thurston, *Physical Acoustics 1A* (Academic Press Inc., New York, 1964); R. A. Cowley, Advan. Phys. **12**, 421 (1963); D. C. Wallace, Rev. Mod. Phys. **37**, 57 (1965).

[15] K. Huang, Proc. Roy. Soc. (London) **203A**, 178 (1950).

[16] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275; Z. Physik **160**, 80 (1960).

[17] T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. (London) **85**, 523 (1965).

elastic constants are related by

$$H_{xx,xx}{}^{\mathrm{ad}}-H_{xx,xx}{}^{\mathrm{iso}}=H_{xx,yy}{}^{\mathrm{ad}}-H_{xx,yy}{}^{\mathrm{iso}}=\gamma^2TC_V/V\,,$$
$$H_{xy,xy}{}^{\mathrm{ad}}-H_{xy,xy}{}^{\mathrm{iso}}=0\,,$$

where C_v is the heat capacity, V the volume, and γ the thermodynamic Grüneisen parameter

$$\gamma=(V/C_v)(\partial S/\partial V)_T=(V/C_v)(\beta/\chi_T)\,,$$

where S is the entropy and β the volume expansivity. Thus in order to calculate the adiabatic-isothermal correction we need, in addition to the elastic constants themselves, β and C_v. We recall that for a cubic solid $\beta=(\partial H_{xx}/\partial T)$.

3. STRAIN DEPENDENCE OF THE QUASIHARMONIC HELMHOLTZ FREE ENERGY

We have seen how the various elastic constants are related to the strain derivatives of the free-energy density. If we adopt the adiabatic hypothesis, the Helmholtz energy of a solid under strain $\{u_{\alpha\beta}\}$ can be written

$$F=F_0+\sum_{qj}a+\text{higher-order terms};$$

except in Sec. 7, we shall ignore the higher-order terms. F_0 is the static lattice energy of the deformed solid and

$$a\equiv a_{qj}=\tfrac{1}{2}\hbar\omega_{qj}+k_BT\ \ln[1-\exp(-\hbar\omega_{qj}/k_BT)]\,.$$

For two-body central forces, our only concern in this paper,

$$F_0=\frac{N}{2}\sum_l\phi(l)\,,$$

where the l summation is over the N lattice sites of the crystal under strain $\{u_{\alpha\beta}\}$. The ω_{qj} and their associated eigenvectors $\mathbf{e}_{qj}$ are obtained from solutions of the secular equation

$$\mathfrak{D}_{\alpha\beta}{}^qe_\beta=\omega^2e_\alpha\,,$$

where $\mathfrak{D}_{\alpha\beta}{}^q$ is the dynamical matrix of Born and von Kármán. For the special case of central forces,

$$\mathfrak{D}_{\alpha\beta}{}^q=\frac{2}{M}\sum_l\phi_{\alpha\beta}(l)\mathcal{S}_q(l)\,,$$

where

$$\phi_{\alpha\beta}(l)=\partial^2\phi(l)/\partial x_\alpha(l)\partial x_\beta(l)\,,$$

and

$$\mathcal{S}_q(l)=\sin^2(\tfrac{1}{2}q_\alpha x_\alpha(l))\,.$$

The $\phi_{\alpha\beta}(l)$ are the harmonic (strain-dependent) force constants, M is the atomic mass, and $x_\alpha(l)$ is the αth Cartesian component of the position vector of the lth atom in the strained lattice:

$$x_\alpha(l)=\hat{x}_\beta(l)(\delta_{\alpha\beta}+u_{\alpha\beta})\,.$$

The caret denotes a quantity in the undeformed solid. If we expand F as a Taylor series about the undeformed lattice sites and ignore the higher-order terms, we find

$$\hat{v}H_{\alpha\beta}{}^{\mathrm{iso}}=\tfrac{1}{2}\sum_l\hat{\phi}_\alpha(l)\hat{x}_\beta(l)+\frac{1}{N}\sum_{qj}\hat{a}_{\alpha\beta}\,,$$

$$\hat{v}H_{\alpha\beta,\sigma\tau}{}^{\mathrm{iso}}=\sum_l\hat{\phi}_{\alpha\sigma}(l)\hat{x}_\beta(l)\hat{x}_\tau(l)+\frac{1}{N}\sum_{qj}\hat{a}_{\alpha\beta,\sigma\tau}\,,$$

where $\hat{v}$ is the atomic volume in the undeformed lattice and, for example,

$$\hat{\phi}_\alpha(l)=[\partial\phi(l)/\partial\hat{x}_\alpha(l)]_{\{u_{\alpha\beta}\}=0}\,,$$
$$\hat{a}_{\alpha\beta}=(\partial a/\partial u_{\alpha\beta})_{\{u_{\alpha\beta}\}=0}\equiv(\partial a/\partial u_{\alpha\beta})_0\,,\quad\text{etc.}$$

After some rearrangement we find

$$\hat{a}_{\alpha\beta}=(\hat{u}/2\hat{\omega}^2)(\partial\omega^2/\partial u_{\alpha\beta})_0\,,$$

$$\hat{a}_{\alpha\beta,\sigma\tau}=\left(\frac{\hat{u}}{2\hat{\omega}^2}\right)\left(\frac{\partial^2\omega^2}{\partial u_{\alpha\beta}\partial u_{\sigma\tau}}\right)_0-\left(\frac{\hat{u}+T\hat{C}_v}{4\hat{\omega}^4}\right)\left(\frac{\partial\omega^2}{\partial u_{\alpha\beta}}\frac{\partial\omega^2}{\partial u_{\sigma\tau}}\right)_0,$$

where $\hat{\omega}\equiv\hat{\omega}_{qj}$, $\hat{\mu}\equiv\hat{\mu}_{qj}=\hbar\hat{\omega}(n+\frac{1}{2})$, with

$$n=[\exp(\hbar\hat{\omega}/kT)-1]^{-1}\quad\text{and}\quad\hat{C}_v=(\partial\hat{\mu}/\partial T)_v\,.$$

The term $\hat{a}_{\alpha\beta,\sigma\tau}$ shows clearly how the strain dependence of the individual normal modes contribute to the temperature dependence of the elastic constants. To proceed further we must relate the strain dependence of the individual normal modes to anharmonic force constants, and this we do by following Feldman[18] and developing the dynamical matrix as a Taylor series in the strains $\{u_{\alpha\beta}\}$,

$$\mathfrak{D}_{\alpha\beta}{}^q=\hat{\mathfrak{D}}_{\alpha\beta}{}^q+\Delta_{\alpha\beta}\,.$$

To second order

$$\Delta_{\alpha\beta}=\left[\frac{2}{M}\sum_l\phi_{\alpha\beta\sigma}(l)x_\tau(l)\mathcal{S}_q(l)\right]u_{\sigma\tau}$$
$$+\left[\frac{1}{M}\sum_l\phi_{\alpha\beta\sigma\mu}{}^{(l)}x_\tau(l)x_\gamma(l)\mathcal{S}_q(l)\right]u_{\sigma\tau}u_{\mu\nu}\,.$$

The strain dependence of the individual normal modes follows by treating $\Delta_{\alpha\beta}$ as a perturbation (details are given in Feldman's paper).

4. QUASIHARMONIC ELASTIC CONSTANTS FOR CENTRAL FORCES

The procedure outlined in the previous section leads to the following expressions for the elastic constants (for simplicity we have now suppressed the carets):

$$H_{\alpha\beta}{}^{\mathrm{iso}}=H_{\alpha\beta}{}^{(0)}+H_{\alpha\beta}{}^{(1)}\,,$$
$$H_{\alpha\beta,\sigma\tau}{}^{\mathrm{iso}}=H_{\alpha\beta,\sigma\tau}{}^{(0)}+H_{\alpha\beta,\sigma\tau}{}^{(3)}+H_{\alpha\beta,\sigma\tau}{}^{(4)}\,,$$

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[18] J. L. Feldman, Proc. Phys. Soc. (London) 84, 361 (1964).

where

$$vH_{\alpha\beta}{}^{(0)}=\tfrac{1}{2}\sum_{l}\phi_{\alpha}(l)x_{\beta}(l)\,,$$

$$vH_{\alpha\beta,\sigma\tau}{}^{(0)}=\tfrac{1}{2}\sum_{l}\phi_{\alpha\sigma}(l)x_{\beta}(l)x_{\tau}(l)\,,$$

and

$$vH_{\alpha\beta}{}^{(1)}=(MN)^{-1}\sum_{qj}\,(ue_{\gamma}e_{\delta}/\omega^{2})\sum_{l}\phi_{\gamma\delta\alpha}(l)x_{\beta}(l)\mathcal{S}_{q}(l)\,.$$

The term $dH_{\alpha\beta}{}^{(1)}/dT$, required in the calculation of expansivity, is obtained by simply replacing u by c_v in the above expression:

$$vH_{\alpha\beta,\sigma\tau}{}^{(4)}=(MN)^{-1}\sum_{qj}\,(ue_{\gamma}e_{\delta}/\omega^{2})\times\sum_{l}\phi_{\gamma\delta\alpha\sigma}(l)x_{\beta}(l)x_{\tau}(l)\mathcal{S}_{q}(l)\,,$$

$$vH_{\alpha\beta,\sigma\tau}{}^{(3)}=-\frac{h}{NM^{2}}\sum_{qjj'}\left(\frac{1+n+n'}{\omega+\omega'}+\frac{n'-n}{\omega-\omega'}\right)\frac{e'_{\gamma}e_{\delta}e'_{\mu}e_{\nu}}{\omega\omega'}\times\sum_{lk}\phi_{\gamma\delta\alpha}(l)\phi_{\mu\nu\sigma}(k)x_{\beta}(l)x_{\tau}(k)\mathcal{S}_{q}(l)\mathcal{S}_{q}(k)\,.$$

In this form[19] it is tempting to think of $H_{\alpha\beta,\sigma\tau}{}^{(3)}$ as the long-wavelength limit of the usual cubic anharmonic frequency shift.[20] However, the point has been discussed in detail by Cowley,[21] and we note that at finite temperatures the limiting slopes of phonon dispersion curves $[\Omega(Q)$ versus $Q]$ $(\Omega\rightarrow 0,\ Q\rightarrow 0)$ yield *neither* isothermal nor adiabatic elastic constants.

Our force constants are defined as follows:

$$\phi_{\alpha}(l)=Ax_{\alpha}(l)\,,\quad \phi_{\alpha\gamma}(l)=Bx_{\alpha}(l)x_{\gamma}(l)+A\delta_{\alpha\gamma}\,,$$

$$\phi_{\sigma\tau\alpha}(l)=CX_{\sigma}(l)x_{\tau}(l)x_{\alpha}(l)+B[x_{\sigma}(l)\delta_{\tau\alpha}+x_{\tau}(l)\delta_{\sigma\alpha}+x_{\alpha}(l)\delta_{\sigma\tau}]\,,$$

$$\begin{aligned}\phi_{\sigma\tau\alpha\gamma}(l)=Ex_{\sigma}(l)x_{\tau}(l)x_{\alpha}(l)x_{\gamma}(l)&+C[X_{\sigma}(l)x_{\tau}(l)\delta_{\alpha\gamma}+x_{\tau}(l)x_{\alpha}(l)\delta_{\sigma\gamma}\\&+x_{\sigma}(l)x_{\alpha}(l)\delta_{\tau\gamma}+x_{\sigma}(l)x_{\gamma}(l)\delta_{\tau\alpha}\\&+x_{\tau}(l)x_{\gamma}(l)\delta_{\sigma\alpha}+x_{\alpha}(l)x_{\gamma}(l)\delta_{\sigma\tau}]\\&+B[\delta_{\alpha\gamma}\delta_{\tau\alpha}+\delta_{\tau\gamma}\delta_{\sigma\alpha}+\delta_{\alpha\gamma}\delta_{\sigma\tau}]\,,\end{aligned}$$

with $A=D\phi$, $B=D^{2}\phi$, $C=D^{3}\phi$, $E=D^{4}\phi$, $D\equiv \mathrm{d}/\mathrm{rdr}$, and r the nearest-neighbor distance.

We now restrict ourselves to the nearest-neighbor model. The parameters A, B, C, and E are then unique and the l and k summations become trivial. We stress that this restriction is made for computational convenience and from our lack of enthusiasm for the *all neighbor* Lennard-Jones potential.

5. OUTLINE OF THE CALCULATIONS AND RESULTS FOR THE GENERAL NEAREST-NEIGHBOR MODEL

We omit most of the tedious but straightforward work required to reduce the sums defined in Sec. 3. to a convenient form for computation. The necessary transformation properties of the coordinates and polarization vectors for the fcc lattice are well-known. We introduce the parameters of Feldman and Horton[22]

$$a_{1}=A/r^{2}B\,,\quad a_{3}=r^{2}C/B\,,\quad a_{4}=r^{4}E/B\,,$$

$$\lambda=\hbar/r^{3}(BM)^{1/2}\,,\quad\text{and}\quad T_{R}=kT/\lambda r^{4}B\approx 2.6T/\Theta_{\infty}\,.$$

In terms of these parameters, one finds

$$\begin{aligned}vH_{\alpha\beta}{}^{(0)}&=(r^{4}B)F_{\alpha\beta}{}^{(0)}\,,\\ vNH_{\alpha\beta}{}^{(1)}&=(\lambda r^{4}B)F_{\alpha\beta}{}^{(1)}(a_{3},a_{1},T_{R})\,,\\ vN\partial H_{\alpha\beta}{}^{(1)}/\partial T&=(r^{2}B/Mk_{B})F_{\alpha\beta}{}^{(2)}(a_{3},a_{1},T_{R})\,,\\ vH_{\alpha\beta,\sigma\tau}{}^{(0)}&=(r^{4}B)F_{\alpha\beta,\sigma\tau}{}^{(0)}(a_{1})\,,\\ NvH_{\alpha\beta,\sigma\tau}{}^{(4)}&=(\lambda r^{4}B)F_{\alpha\beta,\sigma\tau}{}^{(4)}(a_{4},a_{3},a_{1},T_{R})\,,\\ NvH_{\alpha\beta,\sigma\tau}{}^{(3)}&=(\lambda r^{4}B)F_{\alpha\beta,\sigma\tau}{}^{(3)}(a_{3},a_{1},T_{R})\,.\end{aligned}$$

The $F^{(m)}$'s for $m\neq 0$ can be expressed readily in terms of single sums over the first Brillouin zone. For example,

$$F_{xx,yy}{}^{(4)}=\tfrac{1}{2}a_{4}I_{21}+a_{3}(2I_{21}+I_{1})+2(I_{21}-2I_{2})\,,$$

with

$$I_{21}=\sum_{\tau j}\frac{u_{R}}{\omega_{R}{}^{2}}\,(e_{x}+e_{y})^{2};\quad \sin^{2}\pi(\tau_{x}+\tau_{y})\,.$$

I_1 and I_2 are obtained by replacing $(e_x+e_y)^2$ by unity and $e_x{}^2$, respectively. The $F^{(3)}$ sums are somewhat more complicated. Here, $2\pi\boldsymbol{\tau}=(2^{-1/2}r)\mathbf{q}$, $u_R=u(\boldsymbol{\tau}j)/\lambda r^4B$, and $\omega_R=\hbar\omega(\boldsymbol{\tau}j)/\lambda r^4B$. The reduced frequencies ω_R and their associated eigenvectors $e_\alpha(\boldsymbol{\tau}j)$ are the solutions of the reduced secular equations

$$(\omega_{R}{}^{2}-2a_{1}L)e_{\alpha}=L_{\alpha\beta}e_{\beta}\,,$$

with

$$L=\sum_{l}\mathcal{S}(l)\,,$$

and

$$L_{\alpha\beta}=2r^{-2}\sum_{l}x_{\alpha}(l)x_{\beta}(l)\mathcal{S}(l)\,.$$

The complete expressions for the $F^{(m)}$'s in terms of sums over the Brillouin zone can be found in Ref. 4. We note that sums like I_{21} are functions of T_R and a_1. To evaluate these sums we first choose a reduced wave vector $\boldsymbol{\tau}$ from the irreducible element of the Brillouin zone and then use Jacobi's method to solve the reduced secular equation for $\omega_R(\tau j)$ and $e_\alpha(\boldsymbol{\tau}j)$, $j=1, 2, 3$. Fortunately, a single diagonalization is sufficient to determine $\omega_R(a_1)$. We then compute the lattice sums for six different values of $a_1(-0.02<a_1<0.1)$ while holding T_R fixed. T_R is then cycled through the desired range of values. The whole procedure is then repeated for all the selected reduced wave vectors in the irreducible element

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[19] Our expression for $H_{\alpha\beta,\sigma\tau}{}^{(3)}$ is closely related to Eq. (58) of Ref. 13. However, it differs from it by factors of 2 in the leading terms.

[20] A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).

[21] R. A. Cowley, Proc. Phys. Soc. (London) **90**, 1127 (1967).

[22] J. L. Feldman and G. K. Horton, Proc. Phys. Soc. (London) **92**, 227 (1967).

TABLE I. An example of the convergence of the calculation.

No. of points in $\frac{1}{2}$ zone	$I_1(T_R=0.1291,\ a_1=0.015)/N$
128	0.383464
1024	0.383379
3456	0.383372
11 664	0.383371

of the Brillouin zone. Calculations were carried out using the equivalent of 128, 1024, 3456, and 11 664 points in the half zone. The convergence of the sum I_1 is shown in Table I; certain less important sums do not converge quite as well, but in any case are determined to about $\frac{1}{3}\%$.

There are various internal checks and test sums in the calculation. Some of these are generalizations of an identity used by Stern.[23] Others are internal consistency relations; one of these is

$$\left(\frac{\partial(-p)}{\partial \ln v}\right)_T=\left(\frac{\partial H_{xx}}{\partial \ln v}\right)_T=H_{xx,xx}{}^{\text{iso}}+2H_{xx,yy}{}^{\text{iso}}+2p.$$

Near $T=0°$K this is satisfied to about 0.1%, and at high T the accuracy falls to a little better than 1%. We have also found very good agreement with the elastic constants obtained by Barron and Klein from the strain dependence of the zero-point energy. To illustrate this agreement, $\Delta\Theta_0$, the anharmonic contribution to Θ_0 for a general nearest-neighbor model with central forces, was found by Barron and Klein to be

$$\Delta\Theta_0{}^c/\Theta^c\propto[\tilde{a}_4-\tilde{a}_3{}^2(0.31\pm0.04)+\tilde{a}_3(10\pm0.7)+(21.8\pm1.3)],$$

whereas we find

$$\Delta\Theta_0{}^c/\Theta_0\propto[\tilde{a}_4-\tilde{a}_3{}^2(0.2977)+\tilde{a}_3(10.68)+20.0].$$

Flinn and Maradudin, who only retained the leading terms, found 0.2997 for the coefficient of $\tilde{a}_3{}^2$. In this comparison we restricted ourselves to the special case of $a_1=0$, i.e., the equilibrium volume of the static lattice. Quantities referring to this volume were denoted by a tilde.

Finally, we refer to the work of Lloyd[24] who studied elastic constants of the fcc lattice with nearest-neighbor central forces using the molecular field approximation of Bethe. For the high-temperature limit he found

$$(24\tilde{v})H_{xx,xx}{}^{\text{iso}}/3k_BT=2\tilde{a}_4-(5/3)\tilde{a}_3{}^2+\text{other terms},$$

$$(24\tilde{v})H_{xx,yy}{}^{\text{iso}}/3k_BT=\tilde{a}_4-(7/6)\tilde{a}_3{}^2+\text{other terms},$$

$$(24\tilde{v})H_{xy,xy}{}^{\text{iso}}/3k_BT=\tilde{a}_4-(5/8)\tilde{a}_3{}^2+\text{other terms},$$

whereas for $\Theta_\infty{}^c/T=0.3$ we find -1.669, -1.55, and -0.636, respectively, for the coefficients of $\tilde{a}_3{}^2$, and exact agreement for the coefficients of $\tilde{a}_4$.

Our calculations, therefore, are in good agreement with the previous studies on the fcc lattice with short-range central forces. A complete tabulation, as a function of temperature (T_R) and volume (a_1), of the various sums over the Brillouin zone that contribute to the elastic constants are given elsehwere.[4]

6. APPLICATION TO RARE-GAS CRYSTALS AND COMPARISON WITH EXPERIMENT

In the Appendix, we have tabulated selected values of the elastic constants of Ar, Kr, and Xe based upon Lennard-Jones (m-6) nearest-neighbor potentials with $m=11, 12, 13$. We give the temperature dependence for both the experimentally observed molar volumes (approx $p=0$) and the zero-temperature M volumes. Results for Ar are also shown in Fig. 1. One interesting aspect of our calculation is that at constant volume our theoretical elastic constants show little temperature variation, even with the inclusion of the strain dependence of the individual normal modes. Thus the isochoric bulk modulus also shows only a small temperature variation. The temperature variation of the isochoric bulk modulus of solid Xe is in good accord with the experimental findings of Packard and Swenson.[25] We always find

$$(d\ln c_{11}{}^{ad}/dT)_v>0 \quad\text{and}\quad (d\ln c_{44}/dT)_v<0,$$

which implies, for example, that transverse and longitudinal first-sound propagation in the [001] direction,

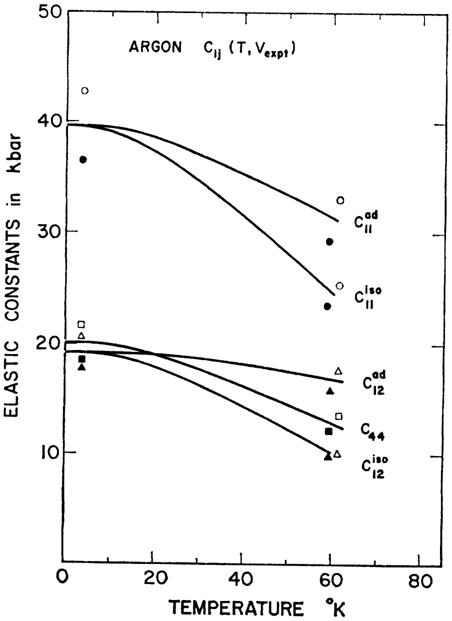

FIG. 1. Temperature dependence of the quasiharmonic elastic constants of Ar. The solid lines refer to the (12-6) Lennard-Jones potential. Open and full circles, triangles and squares refer, respectively, to (13-6) and (11-6).

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[23] E. A. Stern, Phys. Rev. **111**, 786 (1958).

[24] P. Lloyd, Australian J. Phys. **17**, 269 (1964); **17**, 524 (1964).

[25] J. R. Packard and C. A. Swenson, J. Phys. Chem. Solids **24**, 1405 (1963).

at constant volume, will have temperature dependences of opposite sign. For Ne, the temperature dependence of [001]L and [001]T phonon energies has been studied,[26] at constant volume, and an effect similar to the above has been observed. However, in view of our remarks in Sec. 4. we must enter a caveat concerning the relationship[21] between zero and first sound, etc.

Individual contributions to $C_{11}(V_{\text{expt}},T)$ for Kr based upon the (12-6) potential are shown in Fig. 2. The contribution of the quartic force constant term $H_{xx,xx}{}^{(4)}$ is comparable to, *or less than*, the term $H_{xx,xx}{}^{(3)}$. This result has the important consequence (see Fig. 2) that the sum $H^{(0)}+H^{(4)}$, unlike the total $H^{(0)}+H^{(4)}+H^{(3)}$, shows little temperature dependence. The change in $H^{(0)}$ through thermal expansion of the crystal is cancelled by the contribution of $H^{(4)}$. This suggests that self-consistent wave velocities or elastic constants that omit the explicit contributions of the type $H^{(3)}$ will show little temperature variation. Thus we have an explanation for the almost temperature-independent wave velocities predicted for Ne and Ar by Gillis, Werthamer, and Koehler.[12] Our work here indicates that the cubic term $H^{(3)}$ gives a significant (in some cases even dominant) contribution to the temperature dependence of the elastic constants.

There have been comparatively few experiments on wave propagation in solid Ar, only one in solid Kr, and none in Xe. The earlier work has been reviewed recently.[27] These reviews include comparisons of our calculations with the experiments of Moeller and Squire[28]; Gsänger, Egger, and Lüscher[29]; Peter, Korpiun, and Lüscher[30]; and with earlier studies on polycrystals. As an example, we show in Fig. 3 a comparison of our calculations of $\rho V_L{}^2[110]$ for solid Kr based upon (12-6) and (13-6) interatomic potentials with the experiments of Peter, Korpiun, and Lüscher. These simple models give a fair account of the magnitudes, but the predicted temperature dependences are too large (we shall return to this point in Sec. 7).

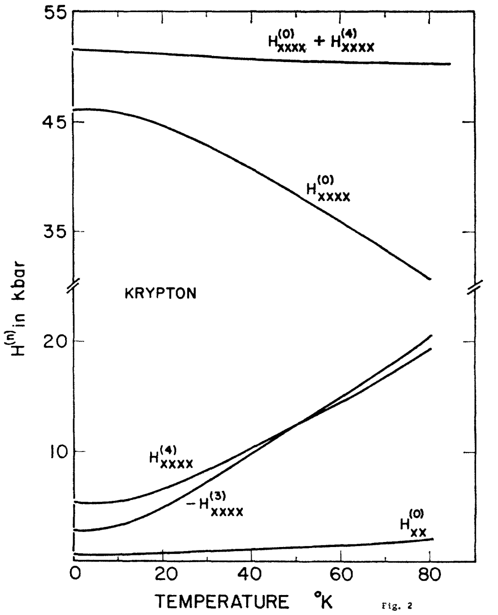

FIG. 2. Temperature dependence of component contributions to the H_{11} of Kr based upon the (12-6) Lennard-Jones potential.

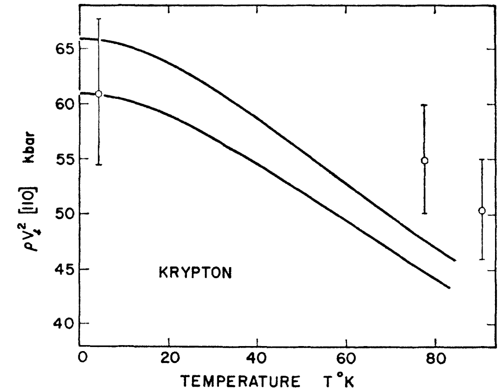

FIG. 3. Temperature dependence of the longitudinal wave velocity in [110] direction of Kr. The experimental data are from Ref. 28. The upper solid curve corresponds to $m=13$, the lower one to $m=12$.

Recently Gsänger, Egger, and Lüscher[31] have reported new measurements of longitudinal first sound for [100] and [110] directions. The experiments, which were carried out on separate crystals, are compared with our calculations in Fig. 4 and 5. The wave velocity for the [110] direction is in good agreement with our calculations, but the wave velocity in the [100] direction, which yields c_{11} directly, disagrees drastically with our simple models. In particular, the experimental result $V_L[110]<V_L[100]$ is very strange indeed. However, this could perhaps indicate substantial noncentral force contributions to the elastic constants.

Most recently, Keeler and Batchelder[32] have measured both L and T first sound in oriented single crystals of Ar, and a comparison of their work with ours will be of interest.

We have not mentioned the remarkable experiment of Simmons and his co-workers[33] on the isothermal compressibility of solid Ar, Kr, and Ne, because we have made detailed comparisons with this work elsewhere.[1]

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[26] J. A. Leake, W. B. Daniels, J. Skalyo, Jr., B. C. Frazer, and G. Shirane (to be published).

[27] J. Hingsammer and E. Lüscher, Helv. Phys. Acta **41**, 914 (1969) and Ref. 11.

[28] H. R. Moeller and C. F. Squire, Phys. Rev. **151**, 689 (1966).

[29] M. Gsänger, H. Egger, and E. Lüscher, Phys. Letters **24A**, 135 (1967).

[30] H. Peter, P. Korpiun, and E. Lüscher, Phys. Letters **24A**, 207 (1968).

[31] M. Gsänger, H. Egger, and E. Lüscher, Phys. Letters **27A**, 695 (1968).

[32] G. J. Keeler and D. N. Batchelder (private communication).

[33] V. V. Goldman, G. K. Horton, and M. L. Klein, Phys. Rev. Letters **21**, 1527 (1968); Phys. Letters **28**, 341 (1969).

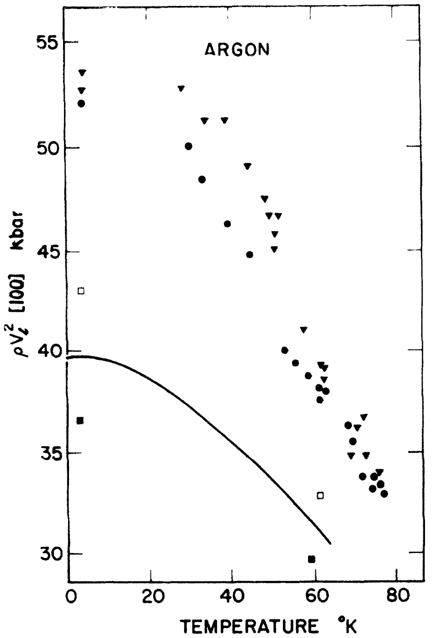

FIG. 4. Temperature dependence of the longitudinal wave velocity in the [100] direction of Ar. Experimental data are from Ref. 29.

7. HIGHER-ORDER APPROXIMATIONS FOR THE BULK MODULUS

The bulk modulus is defined as $B_T = Vd^2F/dV^2$ and, hence, there are as many approximate ways of calculating B_T as there are for F. Even if we exclude cell models (Einstein approximation type of models, etc.) there are still many possible approximations for F to be found in the literature. In Fig. 6 we compare the zero-pressure bulk modulus of Ar derived from four approximate F's using a (12-6) $1N$ pair potential.

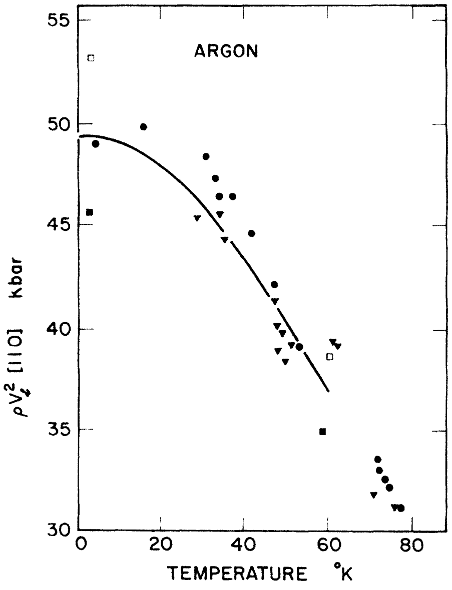

FIG. 5. Temperature dependence of the longitudinal wave velocity in the [110] direction of Ar. Experimental data are from Ref. 29.

The quasiharmonic bulk modulus, labeled QH, is derived from the quasiharmonic free energy, and we recall that this includes the contribution of third-and fourth-order force constants.

The perturbation theory bulk modulus labelled PT, includes the volume dependence of the conventional cubic and quartic anharmonic force constants and hence involves fifth- and sixth-order force constants as well.[1] The bulk modulus labeled SC was derived from the volume dependence of F_{SC}. This free energy contains certain dominant even-order force constants in a self-consistent fashion. This result is the one that corresponds to the approximation of Gillis, Werthamer, and Koehler.[12] The fourth approximation considered by us is labeled ISC, the improved self-consistent approximation. This last bulk modulus is obtained from a free-energy F_{ISC} which includes F_{SC} plus a contribution from odd-order self-consistent force constants.[33] In the figure we also show the two experimental points due to Simmons and co-workers.[34]

It is clear that the quasiharmonic approximation overestimates the temperature dependence of the bulk modulus (recall Fig. 3). However, for temperatures less than about half the melting temperature it is good to a few per cent. It is encouraging that the ISC bulk modulus which represents the most reliable prediction

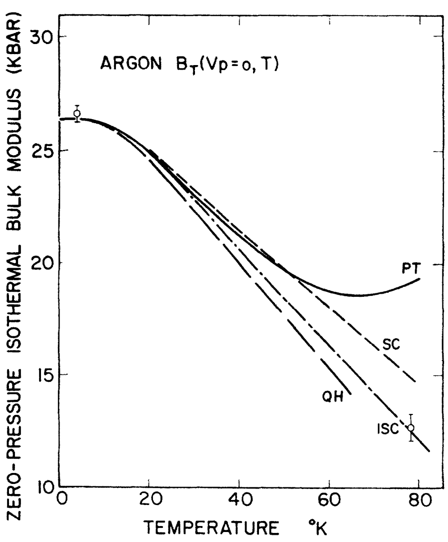

FIG. 6. Bulk modulus of Ar. The two experimental points are from Ref. 32. QH is the present quasiharmonic calculation; PT is the result of including fifth- and sixth-order force constants using perturbation theory and is quoted from Ref. 1; SC and ISC are the results of self-consistent and improved self-consistent calculations quoted from Ref. 31.

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[34] A. O. Urvas, D. L. Losee, and R. O. Simmons, Phys. Rev. **172**, 944 (1968); J. Phys. Chem. Solids **28**, 2269 (1967); O. G. Peterson, D. N. Batchelder and R. O. Simmons, J. Appl. Phys. **36**, 2682 (1965); Phys. Rev. **150**, 703 (1966); D. N. Batchelder, D. L. Losee, and R. O. Simmons, *ibid.* **162**, 767 (1967); D. L. Losee and R. O. Simmons, Phys. Rev. Letters **18**, 451 (1967).

of the model potential is also in the best accord with experiment. This gives us some added confidence in our model potential as a reasonable starting point.

Thus our quasiharmonic results must ultimately be supplemented by further work in which higher-order effects are properly considered. Such calculations are in progress and the results will be presented elsewhere.

8. SUMMARY

We have studied the temperature dependence of the quasiharmonic elastic constants of an fcc lattice with nearest-neighbor central forces. These results have been used to calculate both the isobaric and isochoric elastic constants of Ar, Kr, and Xe, assuming a Lennard-Jones (m-6) interatomic potential ($m=11$, 12, and 13) acting between nearest neighbors only. $m=12$ or 13 agrees with certain of the experimental data. Our results for Ne were not included here because large anharmonic effects in this solid make the quasiharmonic approximation unreliable. For the same reason our calculations on Ar, Kr, and Xe were not extended to their melting points. To illustrate the importance of higher-order anharmonic terms, the bulk modulus of Ar is calculated using the conventional perturbation theory and by the method of self-consistent phonons. Deviation from the quantitative predictions of our model potential can be understood as caused by the breakdown of the quasiharmonic approximation, except for the measurement of the longitudinal sound velocity in the [100] direction in an Ar crystal where there is a striking disagreement between theory and experiment that is at present unresolved. It is probably premature to expect a clear picture of the role of nonadditivity of interatomic forces to emerge from a comparison of our work with the available experimental information. There are indications, both from a comparison of our work with experiment and our own self-consistent calculations, that the QH approximation predicts temperature-dependent elastic constants correctly to a few percent below roughly half the melting temperature of inert-gas solids.

ACKNOWLEDGMENTS

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APPENDIX

Some results of the calculations are shown in Table II.

TABLE II. Selected values of the isochoric and isobaric quasiharmonic elastic constants of Ar, Kr, and Xe based upon Lennard-Jones (m-6) nearest-neighbor potentials with $m=11$, 12, and 13. The quantity $\rho V_{T1}^2[110]$ is the same as C_{44}.

				Argon $C_{ij}(V_{\text{expt}},T)$ in kbars					
T	C_{11}^{iso}	C_{11}^{ad}	C_{44}	C_{12}^{iso}	C_{12}^{ad}	B^{iso}	$\rho V_L^2[110]$	$\rho V_{T2}^2[110]$	m
3.54	36.5		18.4	17.7		24.0	45.5	9.43	11
3.68	39.7		20.0	19.2		26.0	49.5	10.3	12
3.80	42.8		21.6	20.6		28.0	53.3	11.1	13
7.35	39.6	39.7	20.0	19.1	19.2	25.9	49.4	10.3	12
16.19	38.3	39.0	19.4	18.3	19.1	25.0	48.4	10.0	12
39.79	31.6	35.5	16.2	14.4	18.1	20.1	43.0	8.69	12
59.27	23.5	29.4	12.2	10.0	15.9	14.5	34.9	6.76	11
60.49	24.5	31.3	12.9	10.1	16.9	14.9	37.0	7.23	12
61.45	25.4	33.1	13.6	10.0	17.8	15.1	39.0	7.67	13
				Argon $C_{ij}(V_{T=0^\circ\text{K}},T)$ in kbar					
7.36	39.6	39.7	20.0	19.2	19.3	26.0	49.4	10.2	12
16.35	39.0	39.7	19.6	18.9	19.6	25.6	49.2	10.0	12
73.57	35.7	43.5	17.4	18.0	25.8	23.9	52.0	8.87	12
118.1	31.9	43.5	14.8	17.3	28.8	22.2	50.9	7.34	11
122.6	34.5	48.0	16.1	18.3	31.7	23.7	56.0	8.12	12
126.8	37.0	52.5	17.5	19.1	34.7	25.1	61.1	8.92	13
				Krypton $C_{ij}(V_{\text{expt}},T)$ in kbar					
2.88	44.8		22.5	22.1		29.8	56.0	11.4	11
3.00	48.8		24.5	24.0		32.3	60.9	12.4	12
3.11	52.8		26.5	25.9		34.9	65.9	13.4	13
13.24	47.7	48.2	24.0	23.4	23.9	31.5	60.0	12.2	12
33.63	42.9	45.6	21.7	20.6	23.2	28.0	56.1	11.2	12
53.62	37.4	42.1	19.1	17.3	22.0	24.0	51.1	10.1	12
78.48	28.4	34.9	14.7	12.4	18.9	17.7	41.6	8.00	11
80.24	29.7	37.2	15.5	12.6	20.1	18.3	44.2	8.55	12
81.80	30.9	39.5	16.3	12.7	21.3	18.8	46.7	9.08	13

TABLE II (*continued*)

T	C_{11}^{iso}	C_{11}^{ad}	C_{44}	C_{12}^{iso}	C_{12}^{ad}	B^{iso}	$\rho V_L^2[110]$	$\rho V_{T2}^2[110]$	m
Krypton $C_{ij}(V_{T=0°\mathrm{K}},T)$ in kbar									
5.99	48.6	48.6	24.3	23.9	24.0	32.2	60.6	12.3	12
13.30	48.1	48.6	24.1	23.7	24.2	31.9	60.5	12.2	12
59.86	46.1	51.2	22.6	23.3	28.4	30.9	62.4	11.4	12
95.82	41.8	49.3	20.0	21.9	29.5	28.5	59.4	9.92	11
99.76	45.4	54.2	21.8	23.6	32.4	30.8	65.1	10.9	12
103.5	48.9	59.1	23.7	25.2	35.3	33.1	70.9	11.9	13
Xenon $C_{ij}(V_{\mathrm{expt}},T)$ in kbar									
2.57	50.4		25.2	24.9		33.4	62.8	12.7	11
2.68	54.9		27.5	27.2		36.4	68.6	13.9	12
2.78	59.2		29.7	29.3		39.3	74.0	15.0	13
11.91	54.4	54.7	27.3	26.9	27.2	36.1	68.2	13.7	12
21.25	53.0	54.1	26.6	26.1	27.2	35.1	67.2	13.4	12
30.81	51.2	53.1	25.7	25.1	26.9	33.8	65.7	13.1	12
50.26	46.9	50.3	23.7	22.5	25.9	30.6	61.8	12.2	12
77.66	40.2	45.6	20.5	18.4	23.9	25.7	55.3	10.9	12
103.91	31.7	38.4	16.3	13.9	20.7	19.9	45.9	8.90	11
106.3	33.2	41.0	17.3	14.2	22.0	20.5	48.8	9.50	12
108.3	34.4	43.3	18.1	14.3	23.2	21.0	51.4	10.1	13
Xenon $C_{ij}(V_{T=0°\mathrm{K}},T)$ in kbar									
5.37	55.0	55.0	27.5	27.3	27.3	36.5	68.6	13.9	12
11.94	54.6	55.0	27.3	27.1	27.5	36.3	68.6	13.8	12
53.73	53.3	56.8	26.3	26.8	30.4	35.7	69.9	13.2	12
63.21	53.1	57.3	26.2	26.9	31.1	35.6	70.4	13.1	12

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F Center in Ionic Crystals. II. Polarizable-Ion Models

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The states of the F center are considered on the basis of models which treat the movement of the nearest neighbors to the F center and the F electron in a self-consistent manner. The lattice is first described in terms of a classical ionic-crystal theory. The theory is then extended to treat the nearest-neighbor ions in a quantum-mechanical manner. The one defect electron (the F electron) is treated according to polarizable-ion models. The absorption energy, the emission energy, the lifetime of the first excited state, the zero-phonon transition energies, and the Huang-Rhys factors are evaluated for two models, which differ in the rigor used to compute the polarization of the nearest and next-nearest neighbors. It is found that the model that contains the more rigorous evaluation of the polarization agrees best with the experimental results for CaO and perhaps MgO. In addition, it is found that both these models are least successful for F centers in NaCl and KCl. Not enough data exist to make judgments about the agreement for CaF_2, SrF_2, and BaF_2.

I. INTRODUCTION

THE F center in ionic crystals consists of one electron (the F electron) localized about a vacant anion site, regardless of the valency. Even though the F center is one of the simplest defects which may occur in ionic crystals, calculations of its optical properties have been a challenge to theoreticians ever since Tibbs first undertook such calculations for the alkali halides.[1] Such calculations are even today unsatisfactory in many cases when one studies the lifetimes of the excited states, the phonon structure, and the spatial extent of the F-electron wave function. Two basic models from which we may calculate the electronic structure of the F center exist. For brevity, we refer to these models as Hartree (or Hartree-Fock) polarizable-ion models (HFPI) and semicontinuum (or semicontinuum-polaron) models (SCP). Both types of models reduce a many-electron problem to an effective one-electron (the F-electron) problem and treat the lattice polarization and the F electron in a self-consistent manner. They differ most profoundly in their treatment of the effective interaction between the F electron and the anion vacancy due to ionic polarization. We may view the vacancy as an infinite-effective-mass hole having a charge

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[1] S. R. Tibbs, Trans. Faraday Soc. 35, 147 (1934).