PHYSICAL REVIEW VOLUME 165, NUMBER 3 15 JANUARY 1968

Properties of Crystalline Argon and Neon in the Self-Consistent Phonon Approximation

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(Received 7 August 1967)

The self-consistent phonon theory of anharmonic lattice dynamics, devised independently by several authors using varying techniques and implemented computationally by Koehler, is here applied to the crystals of neon and argon. A Lennard-Jones 6-12 interatomic potential is assumed. The quantities calculated are the phonon spectrum and the bulk thermodynamic properties of thermal expansion, compressibility, and specific heat, all as a function of temperature at zero pressure. Although the computations are intended primarily to explore in detail the content of the self-consistent phonon approximation preparatory to incorporating the more elaborate expressions of the next higher approximation, comparison is made with the existing experimental data.

I. INTRODUCTION

IN the past several years, the theory of the lattice dynamics of insulating crystals has undergone substantial revision, a development which seems all the more radical since the approach initiated by Born and von Karman[1] had continued to be the traditional standard[2] for such a long period of time. Finally, however, the failure of the traditional approach when applied to the case of crystalline helium[3] forced theorists to turn to the new techniques of many-body theory for an adequately generalized viewpoint.

Two distinct schemes have emerged, differing from each other in the basic picture of the crystal adopted as the zeroth approximation. Both schemes, however, contrast with the traditional theory by making no initial hypothesis of smallness for the amplitude of atomic vibrations, and hence no truncated Taylor-series expansion of the interatomic potential energy. One of the schemes[4,5] emphasizes the single-particle aspect of a crystal, focusing at first on the motion of an individual atom in the potential due to the self-consistent action of all the others. A lattice vibration, or phonon, is then found as a collective mode of response of the interacting array of atoms to a disturbance. The other scheme concentrates immediately on the collective aspects of the crystal, by regarding the equilibrium state as describable entirely in terms of phonons, or equivalently in terms of a fictitious set of harmonic oscillators, whose frequencies are to be determined self-consistently. Both schemes are approximations, each with its own strong and weak points, and in a sense the two pictures are complementary rather than contradictory.[5] But irrespective of conceptual validity, the latter scheme has the decided practical advantage of being more easily adapted to numerical evaluation and hence to a confrontation with experiment. In the present paper, we report on the first application of the self-consistent phonon scheme to the computation of various finite temperature properties, in this case of crystalline argon and neon.

The particular choice of argon and neon for this initial trial is dictated for several reasons. First, the appropriate fcc crystal structure is an especially simple one for computation. Also, the interatomic potential is generally felt to be better known for the rare gases than for any other substance, thus making theoretical predictions less ambiguous. Furthermore, out of the set of rare-gas crystals (excluding helium) argon and especially neon have a large zero-point motion and thus are a more severe test of the present theory in contrast to the traditional weak anharmonicity approach. For the same reason, these crystals have also received greater experimental attention, and a fair body of data concerning them is now available. Helium is ruled out here because its very large zero-point amplitude necessitates the additional complication of short-range correlation functions.[6] Besides, helium melts at such a low fraction of its Debye temperature that it is not a useful system for testing the temperature dependence of a theory.

We review in Sec. II the derivation of the self-consistent phonon theory, casting it into the form most suitable for numerical evaluation. Section III presents the results of the computation, in the particular forms of thermal expansion, compressibility, sound velocities,

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[1] M. Born and T. von Kármán, Phys. Z. 13, 297 (1912); 14, 15 (1913).

[2] See, e.g., M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1956).

[3] F. W. de Wette and B. R. A. Nijboer, Phys. Letters 18, 19 (1965).

[4] D. R. Fredkin and N. R. Werthamer, Phys. Rev. 138, A1527 (1965).

[5] N. S. Gillis and N. R. Werthamer, Phys. Rev. (to be published).

[6] L. H. Nosanow, Phys. Rev. 146, 120 (1966); J. H. Hetherington, W. J. Mullin, and L. H. Nosanow, *ibid.* 154, 175 (1967).

and specific heat, and compares with the existing experimental data. A critical evaluation is given in Sec. IV of the agreement between the computations and observation, and the possible sources for and implications of the residual discrepancies are discussed.

II. SELF-CONSISTENT PHONON FORMALISM

The self-consistent phonon theory has been derived by several different authors using various techniques. The earliest appearance in the published literature is due to Boccara and Sarma,[7] who used a variational approach. [*Note added in proof.* We have since found an even earlier derivation: D. J. Hooton, Phil. Mag. **3**, 49 (1958).] They proposed to approximate the true Hamiltonian by an effective trial Hamiltonian of the harmonic-oscillator form, in which the entire set of spring constants linking the fictitious atoms are variational parameters to be determined by minimizing the trial free energy. This technique is a particularly elegant one, but is difficult to generalize. A derivation published by Ranninger,[8] but attributed by him to Choquard,[9] adopts the more fundamental approach of diagrammatic perturbation theory. Although the interatomic potential is expanded in Taylor series about the equilibrium atomic positions, resulting in a well-known diagrammatic development,[10] a simple selection of graphs involving all orders of derivatives of the potential can be resummed into closed form yielding equations equivalent to those of Boccara and Sarma. This theory has already been extended by Ranninger and Choquard to take account of a more complicated set of graphs, which result in expressions for the phonon lifetime, but we have not implemented these more elaborate formulas in the present work.

A derivation close in spirit to that of Boccara and Sarma has been given independently by Koehler.[11] Working exclusively at zero temperature, he adopted a trial ground-state wave function of the correlated Gaussian form, with correlation matrix to be determined variationally. Since *any* suitable such wave function is the true ground state of *some* fictitious harmonic Hamiltonian, Koehler's approach gives identically the $T=0$ limit of Boccara and Sarma.

Recent work of Horner[12] interconnects the variational and the diagrammatic perturbation techniques, by appealing to the sophisticated renormalization theorems of de Dominicis and Martin.[13] Horner shows that if the interatomic potential is Taylor series expanded to all orders, then the full vertex function renormalization merely replaces the various derivatives of the potential by new coefficients. Renormalization of the second-order (harmonic) vertex and truncation of the potential energy at that point yields just the effective harmonic Hamiltonian of the self-consistent phonon approximation. However, since the self-consistent phonon diagrams are topologically of the Hartree type, their equivalence to a variational approach occurs in just the manner well known in other standard many-body systems, such as the BCS superconductivity theory and the random-phase-approximation (RPA) theory of the electron gas.

In reviewing the self-consistent phonon approximation, we give essentially the Boccara-Sarma derivation, but with some elaborations and extensions to adapt it for implementation on the computer. We begin by assuming that the true Hamiltonian of the crystal is of the form

$$\mathcal{H}=\sum_i -\frac{1}{2M}\nabla_i^2+\tfrac{1}{2}\sum_{i,j} v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\,, \tag{1}$$

where $\mathbf{R}_{ij}$ are the vectors joining the mean positions of the atoms in the lattice, and $\mathbf{u}_i$ are the dynamical displacement variables. As an approximation, we adopt a trial harmonic Hamiltonian of the form

$$\mathcal{H}_h=\sum_i -\frac{1}{2M}\nabla_i^2+\tfrac{1}{2}\sum_{i,j} \tfrac{1}{2}(\mathbf{u}_i-\mathbf{u}_j)\cdot\mathbf{\Phi}_{ij}\cdot(\mathbf{u}_i-\mathbf{u}_j)\,, \tag{2}$$

where the $\mathbf{\Phi}_{ij}$'s are to be determined variationally. From $\mathcal{H}_h$, we construct a trial harmonic density matrix

$$\rho_h=\exp(-\beta\mathcal{H}_h)/\mathrm{Tr}\{\exp(-\beta\mathcal{H}_h)\}\,. \tag{3}$$

The resulting trial free energy is

$$F_{\mathrm{trial}}=\mathrm{Tr}\{\rho_h(\mathcal{H}+\beta^{-1}\ln\rho_h\}\equiv\langle\mathcal{H}+\beta^{-1}\ln\rho_h\rangle\,. \tag{4}$$

Using the notation

$$F_h\equiv\langle\mathcal{H}_h+\beta^{-1}\ln\rho_h\rangle \tag{5}$$

for the free energy corresponding to the harmonic Hamiltonian, and

$$\mathbf{D}_{ij}\equiv\langle(\mathbf{u}_i-\mathbf{u}_j)(\mathbf{u}_i-\mathbf{u}_j)\rangle \tag{6}$$

for the displacement-displacement correlation function, we can rewrite F_{trial} as

$$F_{\mathrm{trial}}=F_h+\tfrac{1}{2}\sum_{i,j}\langle v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\rangle-\tfrac{1}{2}\sum_{i,j}\tfrac{1}{2}\mathbf{D}_{ij}:\mathbf{\Phi}_{ij}\,. \tag{7}$$

Furthermore,

$$\begin{aligned}\langle v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\rangle&=\langle\exp(\mathbf{u}_i-\mathbf{u}_j)\cdot\nabla)\rangle v(\mathbf{R}_{ij})\\&=\exp(\tfrac{1}{2}\mathbf{D}_{ij}:\nabla\nabla)v(\mathbf{R}_{ij})\,,\end{aligned} \tag{8}$$

using Taylor's theorem and a well-known property of harmonic oscillators.

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[7] N. Boccara and G. Sarma, Physics **1**, 219 (1965).

[8] J. Ranninger, Phys. Rev. **140**, A2031 (1965).

[9] P. Choquard, *Equilibrium Theory of Anharmonic Crystals* (W. A. Benjamin, Inc., New York, to be published).

[10] L. Van Hove, N. M. Hugenholtz, and L. P. Howland, *Problems in Quantum Theory of Many-Particle Systems* (W. A. Benjamin, Inc., New York, 1961).

[11] T. R. Koehler, Phys. Rev. Letters **17**, 89 (1966).

[12] H. Horner, dissertation, Technischen Hochschule München, 1966 (unpublished); Z. Physik **205**, 72 (1967).

[13] C. De Dominicis and P. C. Martin, J. Math. Phys. **5**, 31 (1964).

Now F_{trial} can be regarded as a functional of both $\boldsymbol{\Phi}$ and $\mathbf{D}$, which are to be varied separately. Since F_h is a functional of $\boldsymbol{\Phi}$ only, we obtain the pair of variational equations

$$0=\delta F_{\text{trial}}/\delta \boldsymbol{\Phi}_{ij}=\delta F_h/\delta \boldsymbol{\Phi}_{ij}-\tfrac{1}{4}\mathbf{D}_{ij}\,, \tag{9}$$

$$0=\delta F_{\text{trial}}/\delta \mathbf{D}_{ij}=\tfrac{1}{4}\langle\nabla\nabla v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\rangle-\tfrac{1}{4}\boldsymbol{\Phi}_{ij}\,. \tag{10}$$

Equation (9) expresses $\mathbf{D}$ in terms of $\boldsymbol{\Phi}$; Eq. (10) gives the result that the variationally optimum choice of $\boldsymbol{\Phi}$ is given by the *thermal average* of the second derivative of the potential.

We can go beyond the Boccara-Sarma derivation to obtain even more explicit formulas. We introduce a Fourier representation for $\boldsymbol{\Phi}$,

$$\boldsymbol{\Phi}_{ij}=N^{-1}\sum_{\mathbf{k}}\left[1-\exp(i\mathbf{k}\cdot\mathbf{R}_{ij})\right]\boldsymbol{\Phi}_{\mathbf{k}}\,, \tag{11}$$

noting that $\boldsymbol{\Phi}_{ii}=0$, and diagonalize $\boldsymbol{\Phi}_{\mathbf{k}}$ to give the harmonic phonon eigenvalues and eigenvectors,

$$\boldsymbol{\Phi}_{\mathbf{k}}-\boldsymbol{\Phi}_0=M\sum_{\lambda=1}^{3}\hat{\epsilon}_{\mathbf{k}\lambda}\hat{\epsilon}_{\mathbf{k}\lambda}\omega_{\mathbf{k}\lambda}{}^2\,. \tag{12}$$

Alternatively, the eigenvalue equation can be written in the more usual form,

$$\omega_{\mathbf{k}\lambda}{}^2\hat{\epsilon}_{\mathbf{k}\lambda}=(MN)^{-1}\sum_{j}\left[1-\exp(-i\mathbf{k}\cdot\mathbf{R}_{ij})\right] \times\langle\nabla\nabla v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\rangle\cdot\hat{\epsilon}_{\mathbf{k}\lambda}\,. \tag{13}$$

Then the harmonic free energy can be expressed simply in the phonon representation as

$$F_h=\sum_{\mathbf{k}\lambda}\beta^{-1}\ln(2\sinh\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda})\,, \tag{14}$$

and hence Eq. (9) demonstrates that the displacement-displacement correlation is

$$\mathbf{D}_{ij}=N^{-1}\sum_{\mathbf{k}\lambda}\left[1-\exp(i\mathbf{k}\cdot\mathbf{R}_{ij})\right] \times\hat{\epsilon}_{\mathbf{k}\lambda}\hat{\epsilon}_{\mathbf{k}\lambda}(M\omega_{\mathbf{k}\lambda})^{-1}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}\,. \tag{15}$$

Furthermore, we can employ Eq. (8) to show that

$$\begin{aligned}\langle v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\rangle&=\int d^3u\, v(\mathbf{R}_{ij}+\mathbf{u})\int d^3\mathbf{q}(2\pi)^{-3}\\&\qquad\times\exp(-i\mathbf{q}\cdot\mathbf{u}-\tfrac{1}{2}\mathbf{q}\cdot\mathbf{D}_{ij}\cdot\mathbf{q})\\&=\left[(2\pi)^3\det\mathbf{D}_{ij}\right]^{-1/2}\int d^3u\, v(\mathbf{R}_{ij}+\mathbf{u})\\&\qquad\times\exp(-\tfrac{1}{2}\mathbf{u}\cdot\mathbf{D}_{ij}{}^{-1}\cdot\mathbf{u})\,,\end{aligned} \tag{16}$$

the inverse of $\mathbf{D}$ being with respect to the 3×3 vector space.

This is the most practical form from which to develop a computational scheme. The frequencies $\omega_{\mathbf{k}\lambda}$ and polarization vectors $\hat{\epsilon}_{\mathbf{k}\lambda}$ satisfy the coupled set of Eqs. (13), (15), and (16), which together provide a definition of the self-consistent phonon approximation. Once these equations are satisfied, the minimum value of the free energy becomes

$$F_{\min}=\sum_{\mathbf{k}\lambda}\left[\beta^{-1}\ln(2\sinh\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda})-\tfrac{1}{4}\omega_{\mathbf{k}\lambda}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}\right] +\tfrac{1}{2}\sum_{i,j}\langle v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\rangle\,, \tag{17}$$

while the internal energy, from which we obtain the specific heat, is

$$U=\sum_{\mathbf{k}\lambda}\tfrac{1}{4}\omega_{\mathbf{k}\lambda}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}+\tfrac{1}{2}\sum_{i,j}\langle v(\mathbf{R}_{ij}+\mathbf{u}_i-\mathbf{u}_j)\rangle\,. \tag{18}$$

Having exhibited Eq. (8) shows immediately that our formulas for the self-consistent phonons are equivalent to those of Ranninger[8] and Choquard.[9] Our formulas are also identical to those obtained by Horner.[12]

III. NUMERICAL COMPUTATIONS

The numerical evaluation of the self-consistent phonon approximation Eqs. (13), (15), and (16) has been carried out using a computer program developed by one of us (T. R. K.). The program iterates the three equations in the order listed, beginning with an input for the tensors $\boldsymbol{\Phi}_{ij}$ in Eq. (13), and proceeding until elements of the $\boldsymbol{\Phi}_{ij}$ tensor between nearest neighbors are consistent from one iteration to the next to within one part in 10^4. This is achieved typically in four iterations. Phonon frequencies and polarization vectors were calculated at 259 points in $\frac{1}{48}$ of the first Brillouin zone. A mesh with this number of points proved to be of sufficient accuracy for evaluating the **k**-space sum in Eq. (15). The coordinate space sum in Eq. (13) was carried out over the 50 inequivalent shells of atoms nearest to the central atom. For the potential-energy contribution in Eqs. (17) and (18), on the other hand, sums of the nearest 96 inequivalent shells were used. The **u** integration of Eq. (16) was evaluated using a numerical procedure described elsewhere.[14]

A. Argon

The interatomic potential we have chosen for both argon and neon is the Lennard-Jones 6-12 potential,

$$v(\mathbf{R})=4\epsilon\left[(\sigma/R)^{12}-(\sigma/R)^6\right]. \tag{19}$$

The best method for determining the parameters ϵ and σ is still an open question, but in the case of argon we are fortunate that there is not serious disagreement among values obtained from fitting to a wide variety of gas, liquid, and crystal data. We have chosen the values determined by Whalley and Schneider[15] from gas data,

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[14] T. R. Koehler (to be published).

[15] E. Whalley and W. G. Schneider, J. Chem. Phys. 23, 1644 (1955).

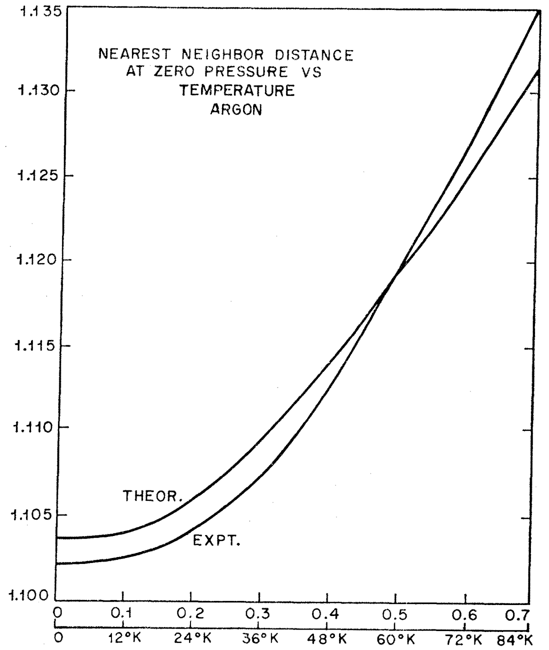

FIG. 1. Nearest-neighbor distance in units of σ for argon at zero pressure versus temperature. Experimental curve is from Ref. 16.

$\epsilon/k_B = 119.5°\text{K}$ and $\sigma = 3.407$ Å. The mass density of the Ar^{40} nucleus we take to be 1.65934×10^{-24} g/nucleon.

The thermal expansion at zero pressure was determined by minimizing the free energy as a function of lattice spacing for fixed temperature. The results for the nearest-neighbor distance are shown as a function of temperature in Fig. 1. The zero-temperature value is

$$(\text{nearest-neighbor distance})_{p,T=0} = 1.10373\sigma = 3.7604 \text{ Å}.$$

Also shown in Fig. 1 are the experimental data of Peterson, Batchelder, and Simmons[16] determined from x-ray diffraction measurements. They find

$$(\text{nearest-neighbor distance})_{p,T=0} = 3.7561 \text{ Å}.$$

We have ignored any correction due to the measurements being made at saturated vapor pressure rather than zero pressure; this correction has been estimated to be less than one part in 10^5. Theory and experiment differ in nearest-neighbor distance by only 0.14% at $T=0$ and by 0.32% at the triple point ($T=84°\text{K}$). However, this may be an unfair method of comparison, since the first one or two significant figures in the nearest-neighbor distance are a consequence merely of the static lattice energy and would be given correctly by any theory. More significant, then, is the fact that the theoretical expansion between $T=0°\text{K}$ and the triple point is 84% of the experimental expansion.

TABLE I. Sound velocities in argon at $T=0$.

	Longitudinal (m/sec)	Transverse (m/sec)
100	1528	1154
110	1779	709, 1154
111	1855	883
Polycrystal	1730	1000

Also from our calculations of free energy versus lattice spacing we have determined the compressibility. At zero temperature and pressure we find

$$(\text{compressibility})_{p,T=0} = (3.79\pm0.04)\times10^{-11} \text{ cm}^2/\text{dyn}.$$

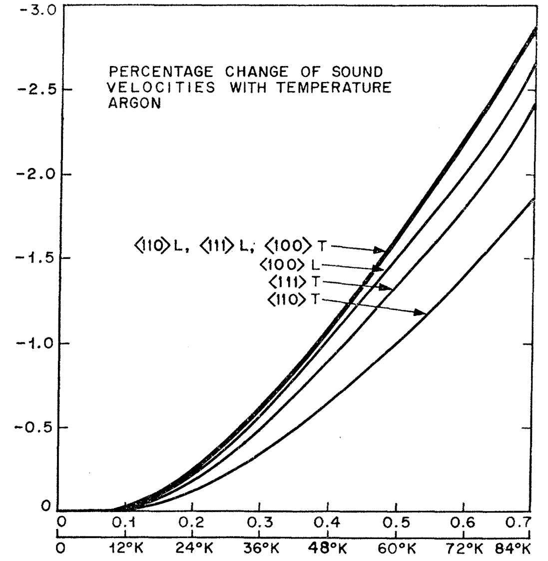

FIG. 2. Percentage change in sound velocities for argon along a few simple symmetry directions versus temperature. The symbols L and T refer to longitudinal and transverse branches, respectively.

This is to be compared with the experimental value[16] of

$$(\text{compressibility})_{T=4.25°\text{K}} = (3.75\pm0.05)\times10^{-11} \text{ cm}^2/\text{dyn}.$$

Although our calculations have produced phonon frequencies at 259 points in $\frac{1}{48}$ of the first Brillouin zone, we do not display the full results here. This is primarily because inelastic neutron-scattering measurements have never been carried out on argon and consequently no complete experimental data are available for comparison. We merely note that the dispersion curves are unexceptional in shape, looking much like those typical of fcc crystals. However, we do list in Table I values for acoustic sound velocities at $T=0$ in three primary symmetry directions and for a polycrystalline sample. Furthermore, Fig. 2 shows the percentage decreases in these velocities as a function of temperature, computed along the zero pressure line given by our theoretical thermal-expansion results.

The experimental situation in regard to sound velocities is somewhat confused. Several conflicting

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

measurements have been reported from various laboratories using different techniques and differing amounts of indirect inference. Jones and Sparkes,[17] using a torsion measurement on a suspended crystal, report $s_T=917$ m/sec at zero temperature. Lawrence and Neale[18] report $s_L=(1630\pm50)$ m/sec at zero temperature via measurement of the diffraction of light by an ultrasonic wave. With this datum, together with experimental specific-heat data, they infer $s_T=(940\pm20)$ m/sec. The reliability of this number can be judged by comparing their further inference, compressibility $=(3.84\pm0.2)\times10^{-11}$ cm^2/dyn, with the presumably more reliable value obtained by Peterson *et al.*[16] The latter authors use similar arguments to obtain from their lattice constant measurements the values $s_L=1640$ m/sec, $s_T=944$ m/sec. These measurements are presumably to be compared with polycrystal theoretical values which are higher by about 6%. Ultrasonic measurements by Moeller and Squire[19] along an unknown direction of a single crystal yield an extrapolation to $T=0$ of $s_L=1555$ m/sec, $s_{T1}=1000$ m/sec, and $s_{T2}=835$ m/sec. Moeller and Squire guess the direction of propagation to be 110. In contrast, ultrasonic measurements by Gsänger *et al.*[20] on a neutron-oriented single crystal give $s_{110L}=1446\pm7$ m/sec at $T=4$°K, differing from our computed value by about 20%.

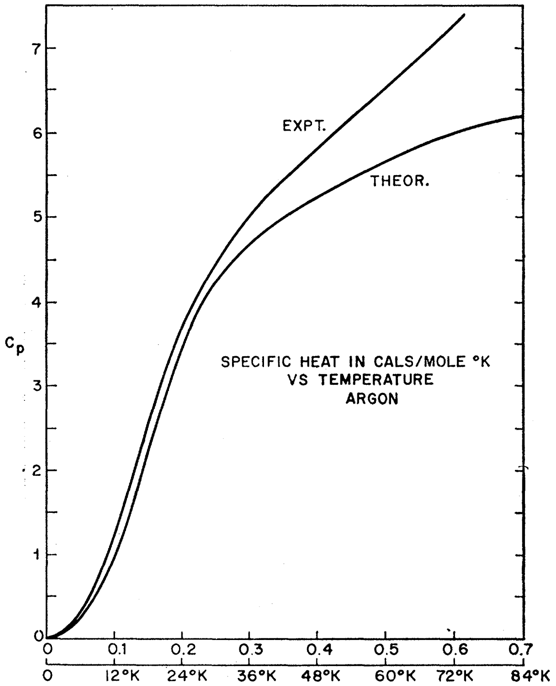

FIG. 3. Specific heat of argon at zero pressure in cal/mole °K versus temperature. Experimental curve is from Ref. 21.

The temperature dependence of the sound velocities is similarly unsettled. Moeller and Squire[19] extrapolate their high-temperature measurements down to $T=0$°K, and obtain a percentage change $1-[s(T=0°\mathrm{K})/s(T=84°\mathrm{K})]$ equal to 19%(L), 44%($T1$), and 48%($T2$). They follow the temperature dependence found by Jones and Sparkes[17] for transverse velocities. On the other hand, Gsänger *et al.*[20] report only an 11% drop in s_{110L} from $T=4.2$°K to $T=76.8$°K. Both of these conflicting results are in sharp contrast to our calculated percentage change with temperature of approximately 2–3%. Although this latter figure would increase if our calculated thermal expansion were closer to the observed value, the percentage change would still not be more than about 5%. Phonon frequencies at the zone boundary are somewhat more sensitive to temperature, but we do not find them to vary by more than 6%.

The specific heat was evaluated by plotting the internal energy versus temperature, and graphically differentiating the curve. This technique was necessitated because of the comparatively few temperature points (8) at which we performed the computation. Our mesh in temperature was too coarse to make more sophisticated numerical differentiation techniques worthwhile. Thus our C_p values are much less accurate (±5%) than any other quantity we report. For this reason, we do not convert our specific heats into an equivalent Debye temperature, which would magnify the uncertainty.

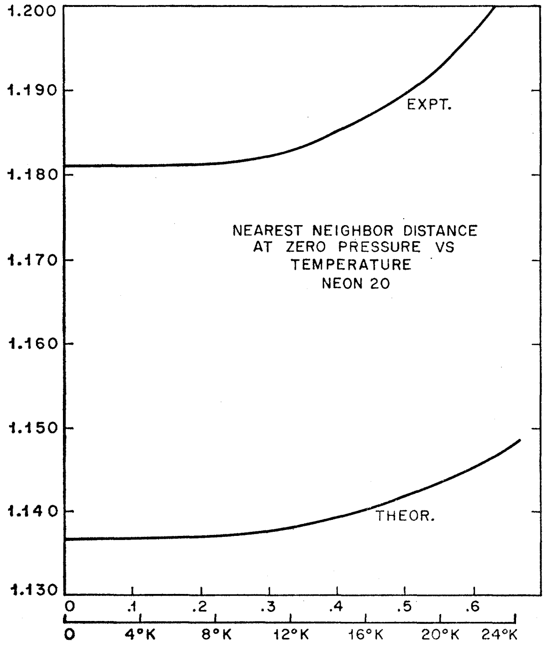

FIG. 4. Nearest-neighbor distance in units of σ for Ne^{20} at zero pressure versus temperature, using potential parameters of Ref. 22. Experimental curve is from Ref. 23.

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[17] G. O. Jones and A. R. Sparkes, Phil. Mag. **10**, 1053 (1964).

[18] D. J. Lawrence and F. E. Neale, Proc. Phys. Soc. (London) 85, 1250 (1965).

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

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

The results for $C_p(T)$ of argon are shown in Fig. 3, together with the observations of Flubacher *et al.*[21] There is reasonable agreement for temperatures below about 36°K, but the experimental curve rises rapidly in a mysterious way above about 48°K. While there is considerable doubt as to the exact causes for the rise, it is likely to be associated with crystal imperfection.

B. Neon 20

The calculations presented above for argon have been repeated for neon. In this case there is considerable ambiguity in the choice of potential parameters, and so our results must be regarded as less definite than for argon.

A priori, the most reasonable choice of parameters would seem to be those of Boato and Casanova.[22] These authors assume "the validity of a universal two-body law of interaction and therefore the applicability of the quantum theory of corresponding states," an assumption which certainly must be appropriate if the Lennard-Jones potential is to be at all sensible. They obtain potential parameters for all the rare gases by requiring that a variety of vapor data fall on universal corresponding states curves, and by further assuming that the Whalley-Schneider potential parameters for argon are correct. Considerable use is made of vapor data on isotopic shifts between Ne^{20} and Ne^{22}. For neon, they find the parameters $\epsilon/k_B=37.1$°K and $\sigma=2.67$ Å.

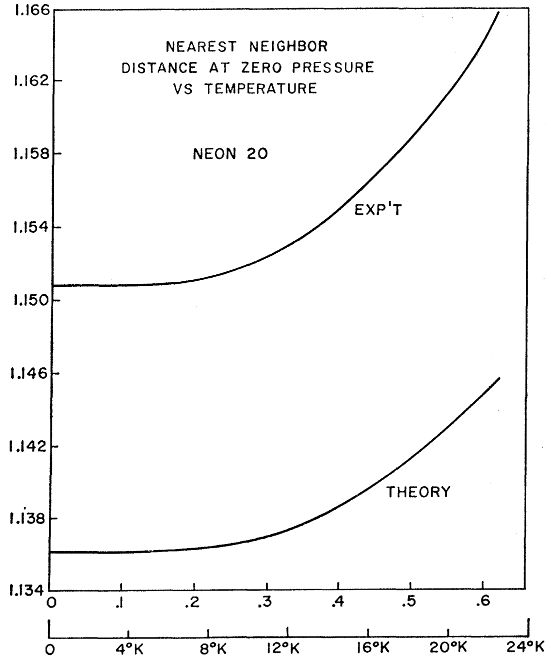

FIG. 5. Nearest-neighbor distance in units of σ for Ne^{20} at zero pressure versus temperature, but using potential parameters of Ref. 24.

We initially adopted these parameters. Taking the mass density of the Ne^{20} nucleus to be 1.66126×10^{-24} g/nucleon, we obtained the nearest-neighbor distance at zero pressure shown in Fig. 4. The experimental curve is the work of Bolz and Mauer[23] using x-ray diffraction. It seemed to us that the difference in nearest-neighbor distance between theory and experiment was unacceptably large, and that further computation should be carried out only for a set of potential parameters which gave promise of better agreement, even if with less fundamental justification.

For this reason, we turned to the parameters $\epsilon/k_B=36.2$°K, $\sigma=2.74$ Å, which were originally chosen by Bernardes[24] and which have since been used by several others[11,25] in computations on neon. These parameters are also much closer to those obtained from second virial coefficient data by de Boer.[26] Since this value for σ is larger than the Boato-Casanova value, the experimental and theoretical nearest-neighbor distances should be moved closer to each other. This expectation is borne out in Fig. 5, which is similar to Fig. 4 but with the Bernardes potential parameters instead. The percentage difference between theory and experiment is reduced

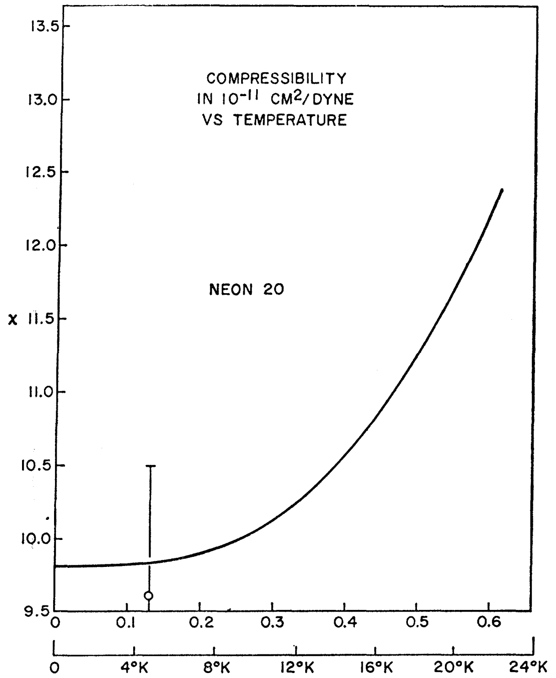

FIG. 6. Compressibility of Ne^{20} versus temperature. The single experimental point is from Ref. 27.

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[21] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Proc. Phys. Soc. (London) **78**, 1449 (1961).

[22] G. Boato and G. Casanova, Physica **27**, 571 (1961).

[23] L. H. Bolz and F. A. Mauer, in *Advances in X-Ray Analysis*, edited by W. M. Mueller and M. Fay (Plenum Press, Inc., New York, 1963).

[24] N. Bernardes, Phys. Rev. **112**, 1534 (1958).

[25] W. J. Mullin, Phys. Rev. **134**, A1249 (1964).

[26] J. de Boer and B. S. Blaisse, Physica **14**, 139 (1948).

by a factor of 3, and is everywhere less than 1.8%. However, this is still not nearly as good as our results for argon. Furthermore, the theoretical expansion from $T=0$°K up to the triple point is only 64% of the observed expansion, again inferior to the agreement for argon.

The remainder of this section is devoted to further results with the Bernardes parameters applied exclusively to Ne^{20}, which is also very close to natural neon.

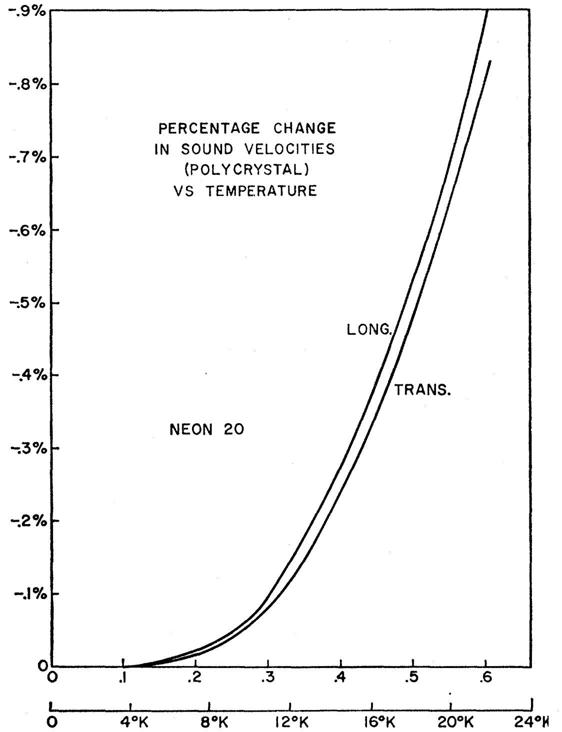

FIG. 7. Percentage change in the isotropic sound velocities of polycrystalline Ne^{20} versus temperature.

The next section discusses isotopic differences between Ne^{20} and Ne^{22}. We first present, in Fig. 6, the compressibility as a function of temperature. The single experimental point with the large error bar is the measurement of Stewart.[27] Although the compressibility of neon has not yet been measured over a wide temperature interval, it has been estimated[16] for argon and is qualitatively similar to our neon calculations. [*Note added in proof.* The compressibility for neon has now been estimated from lattice constant measurements, in the same way as for argon, by D. N. Batchelder, D. L. Losee, and R. O. Simmons, Phys. Rev. **162**, 767 (1967). The compressibility is observed to double upon increasing the temperature from zero to melting, in contrast to our calculation of an increase of roughly 25%.]

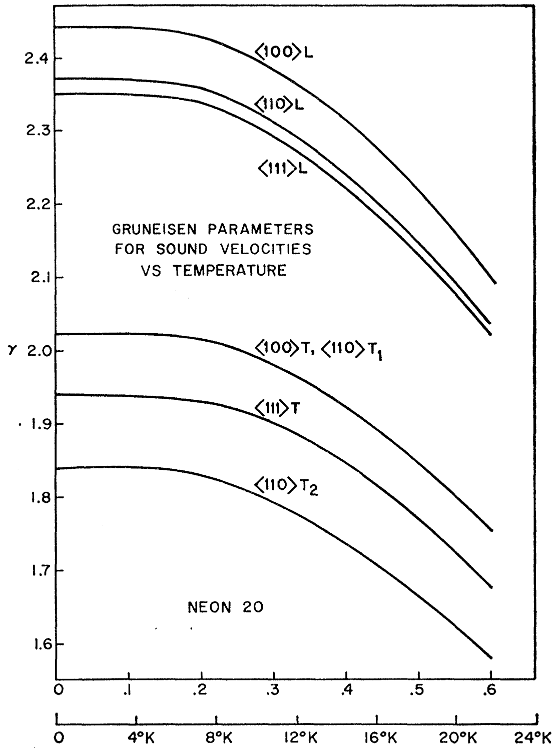

FIG. 8. Gruneisen parameters for sound velocities in Ne^{20} versus temperature. The symbols L and T refer to longitudinal and transverse branches, respectively; T_1 and T_2 refer to the two nondegenerate transverse branches.

Sound velocities in a few simple symmetry directions at $T=0$°K are listed in Table II, along with the isotropic velocities appropriate to a polycrystalline sample. We are not aware of any direct measurement of these quantities in neon. [*Note added in proof.* Inelastic neutron-scattering determinations of phonon frequencies in single-crystal neon are now becoming available, and preliminary measurements have been reported by W. B. Daniels *et al.*, Bull. Am. Phys. Soc. **12**, 1063 (1967). Their results are consistent with our calculations, if allowance is made for the fact that our calculated pressure-volume phase diagram is not in close agreement with observation.] The percentage change in the polycrystalline sound velocities with temperature is plotted in Fig. 7. It is interesting that this change is much less than in argon, even over the same reduced temperature interval. The probable cause is that the thermal expansion over the same reduced temperature interval is 2.5 times larger for argon than for neon. Furthermore, the dominant mechanism for the tempera-

TABLE II. Sound velocities in neon at $T=0$.

	Longitudinal (m/sec)	Transverse (m/sec)
100	1152	867
110	1338	538, 867
111	1394	666
Polycrystal	1303	753

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[27] J. W. Stewart, Phys. Rev. **97**, 578 (1955).

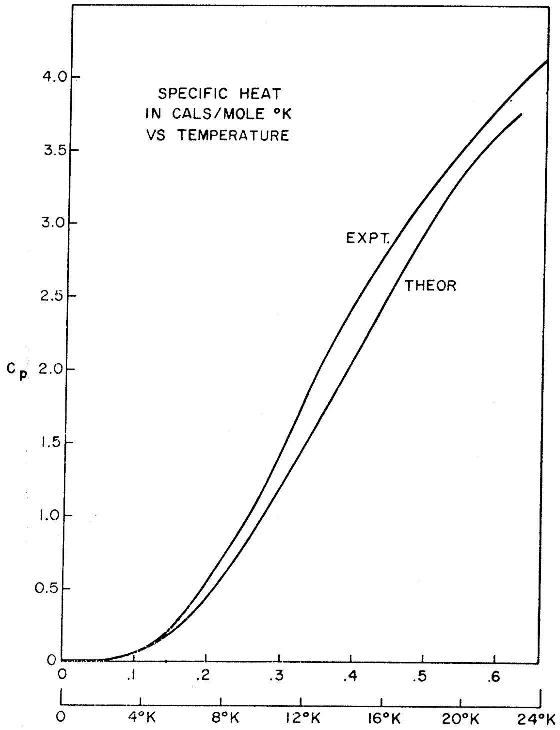

FIG. 9. Specific heat of Ne^{20} at zero pressure in cal/mole °K, versus temperature. Experimental curve is from Ref. 30.

ture dependence of the phonon frequencies is the change in lattice constant due to thermal expansion, rather than the explicit temperature factor entering into Eq. (15).

The change in sound velocities with volume at fixed temperature have been converted into Gruneisen parameters,

$$\gamma(\hat{k})\equiv -d\ln s(\hat{k})/d\ln V,$$

and illustrated as a function of temperature in Fig. 8. The $\gamma(\hat{k})$ are by no means independent of $\hat{k}$ as is assumed in deriving the Gruneisen equation of state. Furthermore, they do depend somewhat on temperature. While again no direct measurements exist for neon, the situation is indicative[28] of a behavior qualitatively similar to that illustrated here.

Finally, the specific heat C_p is shown in Fig. 9, together with the observations of Fenichel and Serin.[29] Agreement between the two curves is not satisfactory, with discrepancies exceeding 15% in the temperature region around 15°K. We improved the accuracy of our computation of C_p over that for argon by halving the mesh of temperature points and cross checking several different numerical differentiation techniques. We believe the accuracy of the theoretical C_p to be better than $\pm 2\%$ in this case. The measurements of Fenichel and Serin do contain a ripple in $C_p(T)$ which they conceed is an artifact probably ascribable to crystal defects (and which we have smoothed out in drawing Fig. 8), but this is not sufficiently large to account for the disagreement.

C. Neon 22

Computation has also been carried out for the isotope Ne^{22} using the Bernardes parameters. The results are not presented in detail here since little experimental information is yet available on crystals of this isotope. We note merely that the percentage change in lattice parameter from Ne^{20} to Ne^{22} at zero pressure and temperature is computed to be -0.21%. This is to be compared with the experimental determination of $-(0.19\pm0.01)\%$ by Batchelder *et al.*[30] via x-ray diffraction.

IV. DISCUSSION

The results presented above of the self-consistent phonon calculations and the comparison with experimental observations on argon and neon have certain limited implications for our understanding of lattice dynamics in these crystals. In the first place, we must emphasize that we by no means regard the self-consistent phonon equations implemented here as the ultimate in the theory of lattice dynamics. While a significant portion of the total anharmonicity of the crystal is indeed included, with an attendant improvement[31] over the quasiharmonic approximation in predictions of crystal properties, we have ignored in our programming other contributions which have already been formally written down,[8,9,12] in particular the contribution of the odd derivatives of the potential. These will certainly not be negligible. We rather regard the present work as a preliminary step toward programming the more complete theory, and as an exploration of the detailed numerical content of the self-consistent phonon equations as they stand.

Nonetheless, in spite of the incompleteness of our theoretical treatment of anharmonicity, it is tempting to use the present comparison between theory and experiment as a reflection on the adequacy of the input Lennard-Jones potential. We certainly share with many other workers the prevailing dissatisfaction with the R^{-12} form of the repulsive part of the potential, but we are unable to make any constructive criticism at this time. Of more significance, we feel, is the close agreement in the case of argon of the potential parameters determined from a variety of gas, liquid, and crystal data and the rather good agreement of our calculations with measured thermodynamic properties, in contrast to the case of neon. As we have noted, there are substantial variations in the parameters for neon depending on the method of determination, and the most

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[28] G. L. Pollack, Rev. Mod. Phys. **36**, 748 (1964).

[29] H. Fenichel and B. Serin, Phys. Rev. **142**, 490 (1966).

[30] D. N. Batchelder, D. L. Losee, and R. O. Simmons, in *Proceedings of the International Conference on Crystal Growth, Boston, 1966* (Pergamon Press, Inc., New York, 1967), p. 843.

[31] F. W. de Wette (private communication).

justifiable set of parameters from vapor data gives the worst account of the crystal. Furthermore, agreement of our calculations with observation is not nearly as good for neon as for argon. Of course, the odd-derivative anharmonic effects that we have omitted may be much more significant for the lighter element, but this is not likely to account fully for the apparent relative inadequacy of the Lennard-Jones form in the case of neon. We also feel that a good case can be made, both by inference from the work presented here and from first-principles considerations, that the potential parameters change on going from the gas phase to the crystal. This point of view is an alternative in that it would then have to regard the fairly satisfactory consistency in the case of argon as partially accidental. The possibility of shifts in the Lennard-Jones potential between phases is not entirely the same thing as the possibility of "three-body forces,"[32] although there certainly are aspects of similarity, because three-body forces in the usual sense imply a noncentral effective interaction between atom pairs. Strictly speaking, of course, a local, instantaneous, central potential can only be an approximation to the true forces between atomic nuclei, which are given at the most fundamental level by the Coulomb potential shielded by the full nonlocal retarded electronic dielectric function.

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[32] L. Jansen, Phys. Rev. 135, A1292 (1964).

PHYSICAL REVIEW VOLUME 165, NUMBER 3 15 JANUARY 1968

Temperature and Pressure Dependence of the Dielectric Constants of the Thallous Halides*

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(Received 17 July 1967)

The effects of temperature (76–400°K) and hydrostatic pressure (up to 20 kbar) on the static dielectric constants of single crystal TlCl and TlBr and polycrystalline TlI were investigated. TlCl and TlBr have the CsCl structure, whereas TlI transforms from an orthorhombic structure to the CsCl structure at 4.8 kbar and 300°K. In all cases, the dielectric constant ϵ decreases with both increasing temperature (at low temperatures) and increasing pressure. At 1 bar and 293°K, $(\partial \ln \epsilon/\partial T)_P$ and $(\partial \ln \epsilon/\partial P)_T$ (in units of 10^{-4}°K^{-1} and 10^{-2} kbar^{-1}) are -3.94 and -1.81, -3.70 and -1.77, -0.68 and -0.65 for TlCl, TlBr, and TlI (orthorhombic), respectively. For TlI (cubic) the corresponding values at 3 kbar and 293°K are -4.04 and -1.47. At the orthorhombic → cubic transition, ϵ of TlI increases by 35%, but this change is found to be entirely due to the change in volume, the total polarizability per molecule being independent of crystal structure. The temperature dependence of ϵ is separated into volume-dependent and volume-independent contributions. For the thallous halides the latter contribution, which is determined by anharmonic lattice effects, is large and determines the sign of $(\partial \ln \epsilon/\partial T)_P$. On the basis of Szigeti's theory and the assumption that the optical dielectric constant ϵ_{op} is a unique function of volume, it is found that anharmonicities in the potential energy and nonlinearities in the dipole moment account for 30–40% of the lattice contribution to ϵ of the thallous halides. The effective charge ratio e^*/e at room temperature is 0.96 for TlCl and 0.95 for TlBr. At low temperatures, ϵ of TlCl and TlBr obeys a Curie-Weiss law $\epsilon = c/(T-T_0)$ with T_0 negative. At high temperatures (>300°K) the dielectric constant and dielectric loss are predominantly determined by the formation and transport of lattice defects. The activation energies calculated from the results agree well with values obtained from ionic-conductivity measurements.

I. INTRODUCTION

THIS paper deals with the effects of temperature (76 to 400°K) and hydrostatic pressure (up to 20 kbar) on the static dielectric constants of the three thallous halides TlCl, TlBr, and TlI. A knowledge of the dielectric constants of ionic crystals and their temperature and volume (or pressure) dependences is of considerable interest because the dielectric constant enters into the theoretical treatment of various physical properties, e.g., the theories of electron-phonon interactions and infrared dispersion and effective field considerations. In addition, the temperature and pressure dependences of the dielectric constant combined with a knowledge of the thermal expansion coefficient and compressibility make it possible to separate the temperature dependence of the dielectric constant at constant pressure into its volume-dependent and volume-independent contributions. As will be discussed later, the latter contributions are determined completely by anharmonic lattice effects.

The thallous halides are a particularly interesting group of compounds to study. Unlike most ionic crystals which exhibit an increase of dielectric constant with increasing temperature at low temperatures, the dielectric constants of the thallous halides decrease with in-

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* This work was supported by the U. S. Atomic Energy Commission.