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Elastic Constants and Phonon Dispersion Curves for Solid Argon near 0°K

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Elastic constants and phonon dispersion curves for crystalline argon at low temperatures are calculated using the accurate pair potential function developed by Bobetic and Barker together with the Axilrod-Teller three-body interaction. The phonon dispersion curves are in good agreement with experiment, but the elastic constants show substantial differences from current experimental estimates.

I. INTRODUCTION

Theoretical calculations of low-temperature elastic constants of argon using Lennard-Jones 6-12 potentials have shown discrepancies with experiment,[1] although the calculated phonon dispersion curves were in fair agreement with experiment.[2] To check whether these discrepancies are due to the somewhat unrealistic form of the 6–12 potential, or to neglect of the Axilrod-Teller three-body interaction, we have made calculations using an accurate pair potential derived by Bobetic and Barker,[3] which gives excellent agreement with experiment for a wide range of properties of gaseous and solid argon, including the low-temperature specific heat and thermal expansion of crystalline argon. These questions have been studied by Chell and Zucker,[4] by Goetze and Schmidt,[5] and by Huller *et al.*,[6] but the pair potential used here is much more realistic.

II. ELASTIC CONSTANTS

We calculated harmonic elastic constants by the method of long waves. Wave velocities v were calculated for the longitudinal and transverse waves in the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions, using the equation

$$v = d\nu / d|\vec{q}| \quad , \tag{1}$$

in which ν is the frequency and $\vec{q}$ the wave vector; the derivative is evaluated at $|\vec{q}| = 0$. The frequencies were calculated by the method described by Bobetic and Barker.[3]

The harmonic elastic constants c_{ij}^h were then calculated by solution of the equations

$$\rho v_1^2 = c_{11}^h \ , \tag{2}$$

$$\rho v_2^2 = c_{44}^h \ , \tag{3}$$

$$\rho v_3^2 = \tfrac{1}{2}(c_{11}^h - c_{12}^h) \quad , \tag{4}$$

where the wave velocities v_1, v_2, v_3 correspond to longitudinal $\langle 100\rangle$, transverse $\langle 100\rangle$, and slow transverse $\langle 110\rangle$ waves, respectively. To check the calculation we confirmed that the resulting elastic constants reproduced the remaining wave velocities in the three directions.

We computed anharmonic corrections using the method of Barron and Klein,[7] and neglecting the three-body interaction. Since the anharmonic correction amounts to only about 8% and the three-body interactions affect the frequencies by only a few percent, the error due to neglect of three-body interactions in computing anharmonic corrections should affect the elastic constants by only a few tenths of a percent.

In the method of Barron and Klein,[7] the anharmonic c_{ij} are given by

$$c_{11} = c_{11}^h + \beta_{11}(1) U_z / V \quad , \tag{5}$$

$$c_{12} = c_{12}^h + [\beta_{12}(1) + \gamma] U_z / V \quad , \tag{6}$$

$$c_{44} = c_{44}^h + [\beta_{44}(1) - \tfrac{1}{2}\gamma] U_z / V \ , \tag{7}$$

in which U_z is the zero-point energy and V the volume. The Grüneisen parameter γ and the quantities $\beta_{ij}(1)$ may be calculated from certain lattice sums which are set out in the paper of Barron and Klein; we evaluated these lattice sums by straightforward methods (omitting three-body contributions). Note that in evaluating these sums we summed over all neighbors, so that the present calculations are more accurate than those of Bobetic and Barker[3] (but confined to 0 °K).

In Table I we list harmonic and anharmonic values of the elastic constants, calculated both without and with the three-body interactions. For comparison we list also results of other theoretical calculations and the experimental results of Keeler and Batchelder,[8] derived from ultrasonic measurements and extrapolated to 0 °K. The bulk modulus B, the anisotropy A, and the parameter δ expressing the deviation from the Cauchy relation are given by

$$B = \tfrac{1}{3}(c_{11} + 2c_{12}) \quad , \tag{8}$$

$$A = 2c_{44} / (c_{11} - c_{12}) \quad , \tag{9}$$

TABLE I. Harmonic and anharmonic values of the elastic constants.

	c_{11} (10^{10}dyn cm^{-2})	$c_{11}-c_{12}$ (10^{10} dyn cm^{-2})	c_{44} (10^{10}dyn cm^{-2})	B (10^{10} dyn cm^{-2})	A	$\delta \times 100$	$\theta_c(0)$ (°K)
Experiment[a]	4.39	2.56	1.64	2.68	1.28	−10 ± 7	90.5
Present[b]	4.16	1.86	2.28	2.93	2.46	−1.0	92.5
Present[c]	3.79	1.73	2.12	2.64	2.46	(+2.9)	89.1
Present[d]	3.87	1.87	2.28	2.62	2.44	(+14.1)	92.3
Present[e]	3.50	1.74	2.12	2.34	2.45	(+20.7)	88.9
6-12[f]	3.71	1.64	2.15	2.62	2.62	+3.9	
6-12[g]	3.98	2.06	2.01	2.61	1.95	+4.7	

[a] From Ref. 8; the $\theta_c(0)$ is that calculated from the elastic constants.

[b] Anharmonic with three-body forces.

[c] Harmonic with three-body forces.

[d] Anharmonic, no three-body force.

[e] Harmonic, no three-body force.

[f] 6-12, all-neighbor interactions (Ref. 7).

[g] 6-12, nearest-neighbor interactions (Ref. 7).

$$\delta = (c_{44} - c_{12})/c_{12} \quad . \tag{10}$$

In addition, we list values of the Debye temperature $\Theta_c(0)$ calculated using the tables of de Launay.[9]

The third, fourth, and fifth lines of this table are included in order to show the magnitude of the three-body and anharmonic contributions. The most interesting qualitative feature is that the shear constants $\frac{1}{2}(c_{11} - c_{12})$ and c_{44} are essentially unaffected by the three-body force, although c_{11}, c_{12}, and the bulk modulus are increased substantially. As far as c_{44} is concerned, this disagrees with the results of Zucker and Chell.[4] The reason is that Zucker and Chell omitted a nonzero contribution which they believed to vanish by symmetry; this is discussed more fully elsewhere.[10] This is the explanation of the discrepancy between the results of Zucker and Chell[4] and those of Huller *et al.*[6]

It is of interest that our theoretical calculation (line 2 of Table I) predicts a very small deviation from the Cauchy relation, in spite of the substantial three-body effect. This deviation is not a very strong diagnostic for three-body forces since a comparable and partially cancelling contribution arises from the zero-point energy, and comparison of our results with those of Huller *et al.* indicates that this contribution depends on the form assumed for the pair potential. The large negative deviation calculated by Zucker and Chell[4] is incorrect for the reason cited above.

For the anisotropy A, our calculation agrees with the previous theoretical calculations in predicting a value much higher than is indicated by all published experiments. This appears to be a rather unequivocal theoretical result, since it is relatively insensitive to the form of the two-body potential and essentially independent of the presence of the three-body interaction.

Turning now to the individual elastic constants, we note that our calculated value of c_{11} is in moderate agreement with experiment, and this is a slight improvement over the 6-12 two-body calculations. However, the calculated values of c_{12} and c_{44} are much higher than the experimental values, even substantially higher than the values calculated with two-body 6-12 interactions. As a consequence of this, the calculated bulk modulus is higher than the experimental value by about 9%, whereas the 6-12 calculations were roughly in agreement with experiment. The bulk modulus obtained by Keeler and Batchelder agrees closely with the x-ray result of Peterson *et al.*[11]

In connection with these disagreements a number of remarks can be made. First, the agreement of the 6-12 bulk modulus with experiment is partly fortuitous since it results from a high value of c_{11} and a low value of c_{12}. Second, our potential model should be much more realistic than the 6-12 model, and it undoubtedly correlates accurately a much wider range of data. Third, the close agreement which we find with experimental phonon dispersion curves (see below), including those for transverse modes, makes it seem highly unlikely that our shear constants are in error by as much as 30%. Fourth, Keeler and Batchelder observed anomalies (maxima in sound velocities) below 15 °K, which they ascribed to thermal strain due to differential thermal contractions at the crystal-substrate and crystal-transducer interfaces. They speculated that plastic flow took up the differential contraction down to 15 °K, but that below this temperature the crystals became brittle; assuming that the results were unaffected above 15 °K they were able to make at lower temperatures a correction which proved to be "unambiguous and relatively small." In support of these arguments they cited an observation of Stewart,[12] which was that the crystals become brittle somewhere between 65 and 4 °K. Since the total thermal expansion between 0 and 15 °K is very small, it seems equally likely to us that this effect, if present below 15 °K, was also present at substantially higher temperatures. If this were so the low-temperature correction would become more ambiguous and less obviously small, and could possibly lead to results closer to our calculated values. Even if this is the correct explanation of the discrepancy between theory and experiment at low temperatures there remains a discrepancy at high temperatures where published theoretical calculations[1,13] give a much higher value for the anisotropy A than do the results of Keeler and Batchelder.

Finally, we remark that the bulk modulus obtained by Peterson *et al.*[11] at low temperatures is not entirely unambiguous because of the observed effect of the helium used as pressure fluid on the lattice spacing; Bobetic and Barker[3] pointed out that in the plot of lattice parameter against pressure the points corresponding to the *initial* increase of helium pressure appeared to have a slope close to that indicated by our theoretical bulk modulus. In view of these remarks, we feel that the source of the discrepancy between theory and experiment should be sought both in theoretical and in experimental areas.

We note that our calculated value of $\Theta_c(0)$, 92.5 °K, is about 0.4 °K higher than the value obtained by Bobetic and Barker, and that this confirms that their error estimates were realistic. Our value is a little high, because of our neglect of three-body forces in calculating anharmonicity, while theirs is a little low because of the oppositely directed and larger effect of neglecting also interactions between non-nearest neighbors in calculating anharmonic corrections.

III. PHONON DISPERSION CURVES

We have calculated phonon frequencies for waves in the three directions ⟨100⟩, ⟨110⟩, and ⟨111⟩. Quasiharmonic frequencies were calculated in the way described by Bobetic and Barker.[3] To calculate anharmonic corrections, we assumed as an approximation that all frequencies for a given mode and direction were multiplied by the same factor as the frequencies of very long waves for the same mode and direction. Since we had calculated anharmonic corrections to the elastic constants by the method of Barron and Klein,[7] these factors could be determined immediately. The effect of anharmonicity is to increase the frequencies of long waves by an amount which varies between 3 and 5% for different modes and directions. We have confirmed by detailed calculation that at these temperatures the error in frequency shifts calculated in this way is never more than 20%, leading to error in phonon frequencies of less than 1%.

Since most of the experiments were performed with ^{36}A, we performed our calculations for this isotope, with the nearest-neighbor distance equal to 3.7575 Å, based on the theoretical estimate that

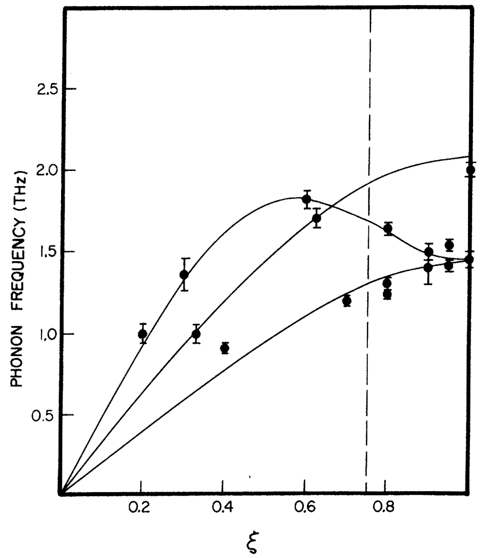

FIG. 2. Phonon frequencies for wave vector $\vec{q} = (\xi, \xi, 0)/a$, where a is the cubic lattice parameter; the dotted line is the zone boundary.

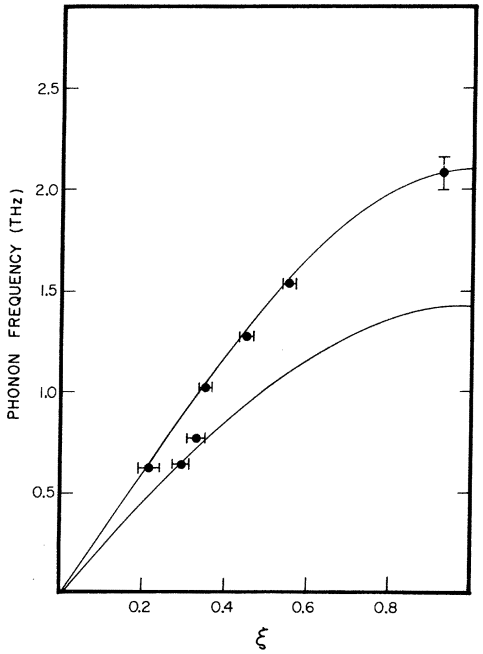

FIG. 1. Phonon frequencies for wave vector $\vec{q} = (\xi, 0, 0)/a$, where a is the cubic lattice parameter.

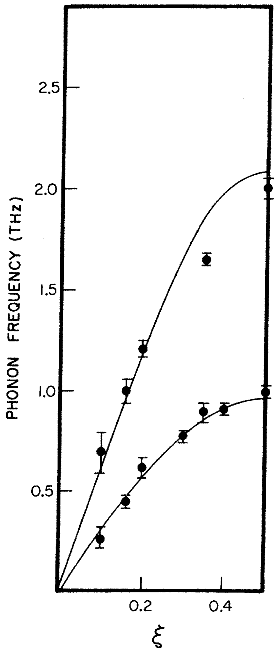

FIG. 3. Phonon frequencies for wave vector $\vec{q} = (\xi, \xi, \xi)/a$, where a is the cubic lattice parameter.

the volume of ^{36}A is 0.2% larger than that of ^{40}A. The results are shown in Figs. 1–3, with experimental data of Batchelder *et al.*,[14] and Egger *et al.*[15] The measurements of Egger *et al.* were made with natural argon and the frequencies have been increased by the factor $(\frac{40}{36})^{1/2}$.

The agreement with experiment is very good, considerably better than was found with nearest-neighbor 6-12 and 6-13 interactions by Goldman *et al.*,[2] and also considerably better than was found with five-parameter second-nearest-neighbor models by Batchelder *et al.*[14] This is particularly noticeable for the longitudinal $\langle 110 \rangle$ waves, for which none of the other models is satisfactory.

It is to be noticed that the unconstrained five-parameter fit of Batchelder *et al.* gave elastic constants (in units of 10^{10} dyn cm^{-2}) $c_{11} = 4.11$, $c_{12} = 1.90$, $c_{44} = 2.10$, and $A = 1.9$. These are appreciably closer to our theoretical values ($c_{11} = 4.16$, $c_{12} = 2.30$, $c_{44} = 2.28$; $A = 2.5$) than are the ultrasonic results of Keeler and Batchelder[8] ($c_{11} = 4.39$, $c_{12} = 1.83$, $c_{44} = 1.64$; $A = 1.28$), particularly in the value of c_{44}. The value of A is also much closer to all theoretical estimates.

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Vibronic Aspects of the CaO and MgO *F* Bands*†

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A useful extension is made to the existing theory of the optical absorption and emission bands of defects and impurities in low concentrations in crystalline host materials. This extension is able to account for the shape of the low-temperature absorption and emission bands in both the details of the sharp-line phonon-related peaks and the broad-band characteristics–as applications to defect centers in the alkaline-earth oxides (and alkali halides) demonstrate. A lifetime-broadening mechanism is introduced to explain the observed smearing and broadening of higher-energy multiple-phonon-assisted transitions, the manifold of such transitions giving rise to the broad band. We then specialize to the case of *F* centers in cubic (O_h group) materials; a short group-theoretical discussion shows for this case that only local modes belonging to the Γ_1^+, Γ_{12}^+, and Γ_{25}^+ representations may be active and that both transverse and longitudinal acoustic lattice modes near the L band point are expected to be most active in coupling the single trapped electron to the lattice. Comparison is made with recent experimental results for the *F* center in CaO and MgO.

INTRODUCTION

Many impurity and defect centers in solids show Gaussian absorption and emission bands.[1] Partly as a result of this and partly for the sake of mathematical convenience most optical theories of these centers assume *a priori* these bands to be Gaussian or very nearly so.[2] We present below in Sec. I a simple extension of these optical theories by carrying out explicitly the sum over inner products of