

On the Elastic Constants of Polycrystalline Argon†

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ABSTRACT

A recent calculation of the explicit temperature dependence of the quasi-harmonic second-order elastic constants of the f.c.c. lattice with arbitrary nearest-neighbour central forces is used to calculate the bulk modulus, polycrystalline shear modulus and the polycrystalline longitudinal wave velocity for argon. The numerical calculations are based on a Mie-Lennard-Jones (12-6) potential and cover the range $0 < T \leq 60^\circ\text{K}$. There is reasonable agreement with available experimental data. At the highest temperatures comparison of the theoretical and experimental bulk modulus suggests that higher order anharmonic effects may be important for solid argon.

§ 1. INTRODUCTION

In the last few years a considerable number of experiments have been carried out on rare-gas solids and many of these experiments have been on polycrystalline samples. For example, Jones and Sparkes (1964) measured the resonant frequency of torsional vibration of a suspended polycrystalline rod of argon between 18 and 65°K. They were able to derive the temperature dependence of the shear modulus (or equivalently the transverse wave velocity) of the polycrystal by normalizing their data to the earlier measurements of Barker and Dobbs (1955). Lawrence and Neale (1965) obtained values for the polycrystalline longitudinal wave velocity at temperatures between 54 and 83°K using a diffraction of light technique. The isothermal bulk modulus has been measured at 4.25°K by Peterson *et al.* (1966) and at 77.7°K by Urvas *et al.* (1967), by studying the variation in the crystal lattice parameter with applied helium pressure. More recently, Moeller and Squire (1966) and Gsänger *et al.* (1967) have reported single crystal wave velocities.

In order to calculate the elastic properties of argon we need to know the interatomic forces in the solid. While there is no doubt that the dominant forces in the solid are of the central two-body type, there is increasing evidence (see, for example, the Faraday Society Discussion on Intermolecular

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Forces, 1965, 40) that three-body forces are also significant for solid argon. Unfortunately, at the present time the three-body forces are not sufficiently well known in the neighbourhood of the potential minimum to permit an accurate calculation of the elastic constants. We shall therefore adopt a phenomenological model, with central two-body forces acting between nearest neighbours only. The particular two-body potential that we shall subsequently use can best be regarded as an effective potential, including many-body effects in a crude fashion since the parameters of our two-body potential will always be fitted to experiment. The advantage of the nearest-neighbour model is that the explicit temperature dependence of the elastic constants can be calculated essentially exactly for this model. Some time ago, Barron and Domb (1954) used this model to calculate the static-lattice contribution to the polycrystalline elastic constants.

We have recently calculated the explicit temperature dependence of the f.c.c. lattice with an arbitrary nearest-neighbour central force, $\phi(r)$. For a particular choice of $\phi(r)$, say, a Mie-Lennard-Jones (m-6) potential, our calculations give the elastic constants which can then be compared directly with single-crystal measurements. However, in order to compare our calculations with the work of Jones and Sparkes (1964) and Lawrence and Neale (1965) we must first pass from results for the single crystal to the polycrystalline material. The method of averaging the single crystal elastic constants is discussed in the next section and a brief outline of our calculation is given in § 3. In § 4 our calculations are compared with the available experimental data. The calculations presented in this paper can be regarded as extending the work of Barron and Domb (1954) and Barron and Klein (1965) to finite temperatures. We shall see that the overall agreement of experiment with our Mie-Lennard-Jones nearest-neighbour model is quite reasonable.

§ 2. POLYCRYSTALLINE ELASTIC CONSTANTS

For a cubic crystal there are only three independent elastic constants c_{11} , c_{12} and c_{44} . The relationship of these to the elastic constants of an isotropic polycrystalline aggregate has been discussed by Hill (1952). For a cubic crystal the bulk modulus, K , is unaltered and the shear modulus, G , becomes an average of the two independent shear constants c_{44} and $\frac{1}{2}(c_{11} - c_{12})$. Upper and lower limits of the polycrystalline shear constant, G , are given by the approximations of Voigt and Reuss, defined by:

$$G_V = (c_{11} - c_{12} + 3c_{44})/5,$$

$$G_R = 3[2c_{44} - (c_{11} - c_{12})]^2/5[4c_{44} + 3(c_{11} - c_{12})].$$

In all that follows we shall work with the arithmetic mean of G_V and G_R . The velocities of longitudinal and transverse waves in the polycrystal are given by:

$$\rho V_L^2 = K + \frac{4}{3}G, \quad \rho V_T^2 = G,$$

where ρ is the crystal density. At 0°K, Horton and Leech (1963) have suggested an alternative method of averaging by using the zero-temperature

Debye theta and the zero-temperature bulk modulus. Barron and Klein (1965) showed that Horton and Leech's method agrees with the above mentioned procedure to better than 2%. Thus we can have some confidence in our averaging procedure. Horton and Leech's averaging procedure is not applicable to finite temperatures: so we shall not use it here.

§ 3. CALCULATION OF THE ELASTIC CONSTANTS

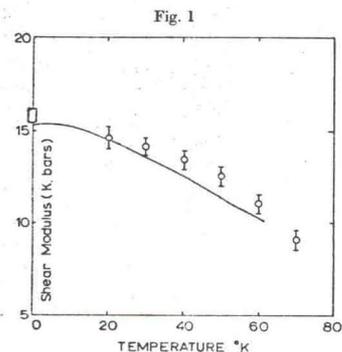
We have calculated the elastic constants from the equation

$$VS_{\alpha\beta\sigma\tau} = \left(\frac{\partial^2 \Phi}{\partial u_{\alpha\beta} \partial u_{\sigma\tau}} \right)_0 + \sum_{ij} \{ \beta_{\alpha\beta\sigma\tau}^{ij} e^{ij} - \gamma_{\alpha\beta}^{ij} \gamma_{\sigma\tau}^{ij} T c_{\nu}^{ij} \},$$

where

$$\gamma_{\alpha\beta} = - \frac{1}{\omega} \left(\frac{\partial \omega}{\partial u_{\alpha\beta}} \right)_0, \quad \beta_{\alpha\beta\sigma\tau} = \frac{1}{\omega} \left(\frac{\partial^2 \omega}{\partial u_{\alpha\beta} \partial u_{\sigma\tau}} \right)_0.$$

Here Φ is the static lattice energy, assumed to be the sum of pairwise additive contributions, e^{ij} and c_{ν}^{ij} are the internal energy and specific heat contributions from the mode ω^{ij} and $\gamma_{\alpha\beta}$ and $\beta_{\alpha\beta\sigma\tau}$ describe the dependence of the normal mode frequencies on the homogenous strain parameters $\{u_{\alpha\beta}\}$. In the actual calculation $\gamma_{\alpha\beta}$ and $\beta_{\alpha\beta\sigma\tau}$ have been evaluated to second order in perturbation theory.



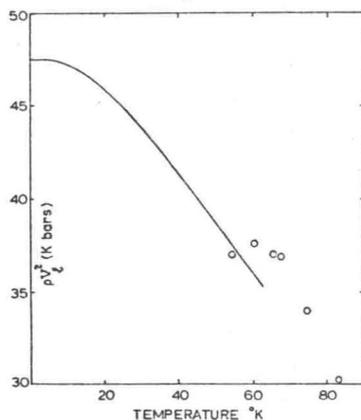
Temperature dependence of the polycrystalline shear modulus of solid argon. The circles are derived from the work of Jones and Sparkes (1964). The 0°K value is taken from Peterson *et al.* (1966). The smooth curve is calculated for a Mie-Lennard-Jones (12-6) nearest-neighbour model.

For an isotropic stress p , the constants S_{short} are related to the more usual elastic constants c_{short} by the equations (with the usual Voigt contractions):

$$c_{11} = S_{11}, \quad c_{12} = S_{12} + p, \quad c_{44} = S_{44}.$$

Full details of the calculation will be presented elsewhere (see also C. Feldman, Ph.D. Thesis, Rutgers University, 1967). From c_{11} , c_{12} and c_{44} the polycrystalline constants are then obtained by the method indicated in the previous section. Some results for argon are shown in figs. 1, 2 and 3 for the special case of a Mie-Lennard-Jones (12-6) nearest-neighbour model. The potential parameters of Horton and Leech (1963) which

Fig. 2



Temperature dependence of the polycrystalline longitudinal wave velocity plotted as ρV_L^2 versus temperature, where ρ is the crystal density. The circles are taken from Lawrence and Neale (1965). The smooth curve is calculated for a Mie-Lennard-Jones (12-6) nearest-neighbour model.

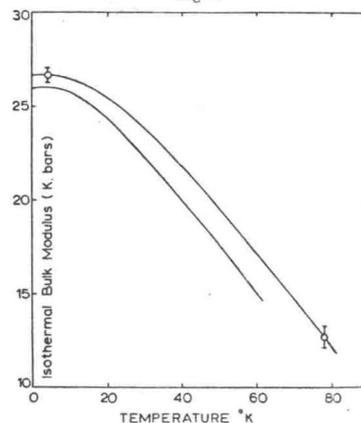
were fitted to the experimental latent heat and the 0°K molar volume were used. Our calculations were carried out at the observed experimental molar volumes, no attempt being made to solve the equation of state for the equilibrium molar volume of the model.

§ 4. COMPARISON WITH EXPERIMENT

Unfortunately our theoretical calculations are restricted to the range $0 < T \leq 60^\circ\text{K}$ but comparisons with experiment can still be made. Figure 1

shows a comparison of our model calculations with the data of Jones and Sparkes (1964). The theoretical curve, corresponding to $G = (G_V + G_R)/2$ is uncertain due to the averaging procedure (the difference between G_V and G_R is approximately 10%) but the temperature dependence is well defined (the difference between G_V and G_R is approximately temperature independent). Jones and Sparkes (1964) claimed a relative accuracy of 2%

Fig. 3



Temperature dependence of the isothermal bulk modulus for solid argon. The upper curve and the point at 4.25°K are taken from Peterson *et al.* (1966), the point at 77.7°K is taken from Urvas, *et al.* (1967). The lower curve is calculated for a Mie-Lennard-Jones (12-6) nearest-neighbour model.

and an absolute accuracy of about 4%, consequently there is considerable latitude for adjustment to the figure. Even so, the agreement of the model with the experimental temperature dependence is quite reasonable. Figure 2 compares the results of Lawrence and Neale (1965), plotted as ρV_L^2 versus temperature, with our (12-6) nearest-neighbour model. The agreement here is again quite reasonable. Figure 3 compares the isothermal bulk modulus of Simmons and his co-workers with our model calculations. At the highest temperatures there is beginning to be a significant difference between the theoretical and experimental temperature dependence. This discrepancy is probably due to the neglect of the higher order anharmonic terms in our model. In fact, the work of Wallace (1965) already indicates that these higher-order terms would tend to increase the bulk modulus.

However, in this paper no attempt will be made to calculate these terms. Finally, we note in passing that for our (12-6) model Poisson's Ratio varies from 0.243 at 0°K to about 0.29 at 60°K. This is to be compared with the values 0.253 at 0°K and 0.27 at 70°K listed by Peterson *et al.* (1966).

§ 5. CONCLUSION

We have shown that the temperature dependence of the second-order polycrystalline elastic constants of argon are in fairly good agreement with the nearest-neighbour Mie-Lennard-Jones (12-6) potential. However, the very precise isothermal compressibility data of Simmons and his co-workers suggests inadequacies in the model at the highest temperatures. If this inadequacy is confirmed by good single-crystal elastic constant data it will probably mean that a more sophisticated treatment of the higher-order anharmonicity is required for argon.

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REFERENCES

- BARKER, J. R., and DOBBS, E. R., 1955, *Phil. Mag.*, **46**, 1069.
 BARRON, T. H. K., and DORN, C., 1954, *Phil. Mag.*, **45**, 654.
 BARRON, T. H. K., and KLEIN, M. L., 1965, *Proc. phys. Soc.*, **85**, 533.
 GSÄNGER, M., EGGER, H., and LÜSCHER, E., 1967, *Physics Lett. A*, **24**, 135.
 HILL, R., 1952, *Proc. phys. Soc.*, **65**, 349.
 HORTON, G. K., and LEECH, J. W., 1963, *Proc. phys. Soc.*, **82**, 816.
 JONES, G. O., and SPARKES, A. R., 1964, *Phil. Mag.*, **10**, 1053.
 LAWRENCE, D. J., and NEALE, F. E., 1965, *Proc. phys. Soc.*, **85**, 1251.
 MOELLER, H. R., and SQUIRE, C. F., 1966, *Phys. Rev.*, **151**, 689.
 PETERSON, O. G., BATCHELDER, D. N., and SIMMONS, R. O., 1966, *Phys. Rev.*, **150**, 703.
 URVAS, A. O., LOSEE, D. L., and SIMMONS, R. O., 1967, *J. Phys. Chem. Solids* (to be published)—(see also *Solid St. Commun.*, **5**, iv, 1967).
 WALLACE, D. C., 1965, *Phys. Rev. A*, **139**, 877.

Microanalysis of Al + 4 wt. % Cu by Combined Electron Microscopy and Energy Analysis

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ABSTRACT

Direct observations of the energy loss spectra from θ phase precipitates in Al-4 wt. % Cu alloy have been made by means of combined electron microscopy and energy analysis in order to examine the difficulties involved in using this technique for qualitative microanalysis of precipitated phases. It is concluded that a microanalysis will be completely reliable if the peaks in the characteristic energy loss spectra (0 to 50 eV) from matrix and precipitate are reasonably well defined and well separated. If this is not so, then the precipitate must extend from the top to the bottom surface of the electron microscope specimen before any reliable information can be obtained. As far as the extension of the technique to the study of segregation effects is concerned, it is concluded that the boundaries at which such effects are expected must be aligned parallel to the incident electron beam.

§ 1. INTRODUCTION

SEVERAL techniques have been developed for the microanalysis of metals and alloys. One such method depends on the measurement of the characteristic energy loss spectrum of fast electrons transmitted through thin foils of the metal or alloy. The principle of this method was originally outlined by Hillier and Baker (1944); they envisaged the use of the energy losses produced by the excitation of x-ray levels to identify, qualitatively, the constituent atoms of a specimen. The possibility of applying this technique in conjunction with conventional transmission electron microscopy has recently been realized by the construction of energy selecting electron microscopes (Watanabe and Uyeda 1962, Castaing and Henry 1962, 1964) and energy analysing electron microscopes (Metherell *et al.* 1965, Cundy *et al.* 1966). At present both types of instrument have energy resolutions ~ 1 to 2 eV, with operating voltages ~ 80 kv to 100 kv, and utilize the predominant energy losses of the transmitted electrons which lie between 0 and about 50 eV. These low energy losses are characteristic of the electronic band structure of the material of the specimen and do not necessarily indicate the composition of the specimen.

The purpose of this paper is to investigate the difficulties involved in using this technique to perform a microanalysis of an alloy containing a

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