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:

$$G_{\mathrm{V}} = (c_{11} - c_{12} + 3c_{44})/5,$$
$$G_{\mathrm{V}} - G_{\mathrm{R}} = 3[2c_{44} - (c_{11} - c_{12})]^2/5[4c_{44} + 3(c_{11} - c_{12})].$$

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:

$$\rho V_l^2 = K + (\tfrac{4}{3})G, \quad \rho V_t^2 = G,$$

where ρ is the crystal density. At $0^\circ\mathrm{K}$, 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

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

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^{qj} and $c_{\mathrm{v}}{}^{qj}$ are the internal energy and specific heat contributions from the mode ω^{qj} 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.

Fig. 1
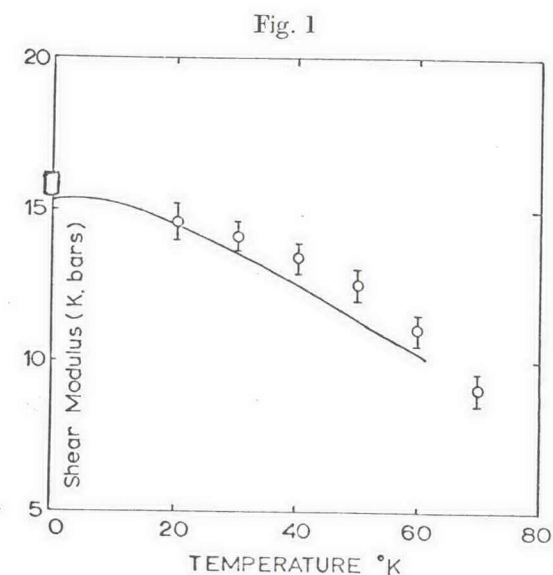
Temperature dependence of the polycrystalline shear modulus of solid argon. The circles are derived from the work of Jones and Sparkes (1964). The $0^\circ\mathrm{K}$ value is taken from Peterson *et al.* (1966). The smooth curve is calculated for a Mie–Lennard–Jones (12-6) nearest-neighbour model.