

ventional theory taken at face value, reserving comment on the detailed assumptions which will be made for the next section.

In the alkali metals, the elastic constants consist almost entirely of the long-range contributions because the ion cores are quite far apart compared to their radii. In the case of the metals copper, silver, and gold, however, the short-range contribution predominates because of the overlap of ion-core wave functions of nearest-neighbor atoms. The long-range Coulomb contributions to both shear constants as calculated by Fuchs,<sup>22</sup> using as a model a lattice of point charges imbedded in a uniform sea of electrons, will be called the long-range shear stiffnesses  $C_{lr}$  and  $C_{lr}'$ . The results of Fuchs are

$$\Omega C_{lr} = 0.9479e^2/2a, \quad \Omega C_{lr}' = 0.1058e^2/2a, \quad (10)$$

where  $a$  is the lattice parameter,  $e$  the electronic charge, and  $\Omega$  the atomic volume. The long-range contributions to the hydrostatic strain derivatives are given quite simply by

$$\Omega dC_{lr}/d \ln r = -4\Omega C_{lr}, \quad \Omega dC_{lr}'/d \ln r = -4\Omega C_{lr}'. \quad (11)$$

The long-range contribution to the bulk modulus, which we shall call  $B_F$ , arises from the second derivative of the Fermi energy with respect to volume. For the monovalent metals,  $B_F$  is given simply by

$$\Omega B_F = \frac{2}{3} \bar{E}_F, \quad (12)$$

where  $\bar{E}_F$  is the average Fermi energy of the valence electrons. We shall use free electron theory with an

effective mass of unity throughout this analysis. The hydrostatic strain derivative of the bulk modulus is given by

$$\Omega dB_F/d \ln r = -7\Omega B_F. \quad (13)$$

A term arising from the first derivative of  $\bar{E}_F$  with respect to  $r$  has been omitted from Eq. (12), and will be omitted consistently from expressions for bulk modulus contributions because the condition for equilibrium applies and the sum of such terms is zero. This term must be included when deriving Eq. (13), but then first derivative terms are also omitted consistently in this and subsequent expressions for contributions to the hydrostatic strain derivative of the bulk modulus. This convention accounts for the somewhat unexpected factor of 7 in Eq. (13).

These long-range contributions to the elastic stiffnesses and to their hydrostatic strain derivatives have been subtracted from the experimental values of the respective quantities in order to obtain numerical values which represent the contribution of the short-range interactions. The process is shown in detail in Table VII where it may be observed that the long-range terms are not large. In Table VII experimental stiffness values at 0°K<sup>18,23</sup> have been used as described in the footnote; the hydrostatic strain derivatives are for room temperature, however.

The numerical values of the short-range contributions to the stiffnesses and hydrostatic strain derivatives, obtained in this way, may now be examined in the light of the conventional model. Analytical expressions for these terms are

$$\begin{aligned} \Omega B_{sr} &= \frac{2}{3} r^2 W'', & \frac{\Omega dB_{sr}}{d \ln r} &= \frac{2}{3} (r^3 W''' - 3r^2 W''), \\ \Omega C_{sr} &= \frac{1}{2} (r^2 W''' + 3r W'), & \frac{\Omega dC_{sr}}{d \ln r} &= \frac{1}{2} (r^3 W'''' + 2r^2 W''' - 6r W'), \\ \Omega C_{sr}' &= \frac{1}{4} (r^2 W'''' + 7r W'), & \frac{\Omega dC_{sr}'}{d \ln r} &= \frac{1}{4} (r^3 W'''' + 6r^2 W''' - 14r W'). \end{aligned} \quad (14)$$

In these equations,  $W$  is the repulsive energy per "bond" (such that the repulsive energy per atom is  $6W$  in these fcc materials with 12 nearest neighbors), and  $r$  is the nearest-neighbor spacing of the atoms. Differentiation of  $W$  with respect to  $r$  is indicated by primes, and the expressions are to be evaluated at the equilibrium value of  $r$ . The equations are written under the assumptions that the interaction  $W$  is (a) of such short range that only nearest-neighbor contributions need be considered; (b) two-body, that is, a function of  $|r|$  only.<sup>21</sup> The entries of Table VII which are labeled short-range are presumed to be given by Eqs. (14) in the conventional theory.

<sup>22</sup> K. Fuchs, Proc. Roy. Soc. (London) A153, 622 (1936); A157, 444 (1936).

At this point, there are six equations for the short-range terms, in three unknowns,  $rW'$ ,  $r^2W''$ , and  $r^3W'''$ . Examination of the numbers of Table VII reveals that no solutions can exist which are compatible with all equations within the variation arising from experimental error combined with uncertainties in the theoretically calculated long-range corrections. It is to be noted particularly that the long-range contributions to the hydrostatic strain derivatives are so small that the statement holds even if these contributions are neglected completely. The incompatible features of Eqs. (14) may be described in the following way: (1) the anisotropy of the short-range contributions to the shear constants, given by  $\Omega C_{sr}/\Omega C_{sr}'$ , is not equal

<sup>23</sup> W. C. Overton and J. Gaffney, Phys. Rev. 98, 969 (1955).