

shear strain, and involve considerations of the changes of neighbour distances by the applied strain. The unsophisticated 'power law' repulsion is considered for illustrative purposes only.

As in the case of the cohesive energy proper, the theory of the elastic constants and their pressure dependence is not completely straightforward.²³ A number of simplifying assumptions must be made for each material considered. We shall however consider some of the structural information which may be derived from the numbers in Table I. The conventional model³⁴ on which elastic constant calculations are based considers that the only important contributions arise from: (1) a long range coulomb energy (e.g. the Madelung term in ionic crystals), (2) the Fermi energy contributing principally to the bulk modulus in monovalent metals, but important to both shear and bulk moduli in polyvalent metals, and (3) a short-range repulsive interaction between neighbouring closed shell ion cores. The usual treatment considers the short-range repulsion to depend only on $|\bar{r}|$, i.e. the forces are assumed central. The first group of elements listed in Table I is arranged in order of increasing complexity of the interpretation.

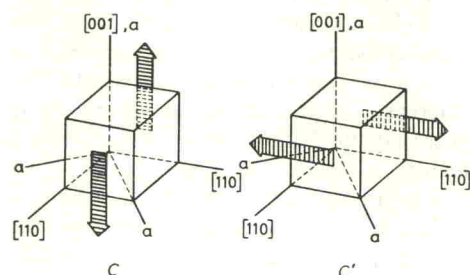


Fig. 5. Distortions appropriate to C and C' shears of a $[110]$ crystal

The C' shear is equivalent to compression along (100) extension (010) while maintaining constant volume

Sodium

The shear constants of sodium present the least difficult analysis.¹⁷ The salient features of the sodium data are (1) the elastic anisotropy ratio C/C' does not depend on pressure, (2) the value of the shear strain derivatives is -7.2 . The zero-pressure values of the elastic constants are accounted for quite well by consideration of the electrostatic contribution alone. The theoretical value of the electrostatic contribution calculated by Fuchs³⁵ on the basis of a model consisting of positive point charges imbedded in a uniform sea of negative charge is:

$$C = Ke^2/r^4, \quad C' = K'e^2/r^4$$

where K and K' are geometrical constants, r is the lattice parameter, e the electronic charge. These were modified³⁶ to take into account variations of charge density in the atomic polyhedron, yielding:

$$C = KZ^2e^2/r_4, \quad C' = K'Z^2e^2r^2$$

where Z is the ratio of the charge density at the boundaries of the atomic polyhedron to the value which would obtain if the valence electron charge were uniformly distributed over the cell. The direct ion core interactions in a bcc metal make a *positive* contribution to C , a *negative* contribution to C' and would be expected from arguments given before, to contribute relatively more strongly to the strain derivatives. The observation of independence of elastic anisotropy on volume indicates with certainty then that the ion core term may be neglected in this analysis.

Numerically, one would expect $\frac{d \ln C}{d \ln r} = -4 = \frac{d \ln C'}{d \ln r}$ if there were no re-distribution of charge within the atomic polyhedron when the crystal was compressed. The observation that the strain derivative is equal to -7.2 instead of -4 indicates that, as sodium is compressed, the charge density at the cell boundaries increases faster than $1/V$. Analytically this may be expressed as the volume dependence of Z , $\frac{d \ln Z}{d \ln V} = -0.54$, or in terms of the volume-dependence of the value of the normalised wave function of the lowest electronic state at the cell boundary, $u_0(\bar{r}_c)$, since $Z = |u_0(\bar{r}_c)|^2$, $\frac{d \ln u_0(\bar{r}_c)}{d \ln V} = -0.27$. Qualitatively this effect may be explained by the consideration that the space within the cell, into which the electron can be compressed as the volume is reduced, is only the space between the ion core and the cell walls (even though the cores in

adjacent cells do not overlap); so the charge density in that space increases more rapidly with compression than would be the case if the electron charge could condense in the entire cell. This effect is predicted theoretically by Brooks,^{37,38} but the experimentally observed effect is about twice that of Brooks' theoretical prediction.

Lithium

Jain¹⁸ has measured the pressure-dependence of the elastic constants of lithium. Since Cohen & Heine³⁹ discuss experimental evidence which indicates deviations from sphericity of the Fermi surface in lithium, it was of interest to examine the effects of the Fermi contribution to the pressure dependences of the elastic constants. Jain's measurements yield values $\frac{d \ln C}{d \ln r} = -4.1$, $\frac{d \ln C'}{d \ln r} = -2.8$. The observation $\frac{d \ln C'}{d \ln r} < \frac{d \ln C}{d \ln r}$ suggests at once the presence of a direct ion core interaction, but this can be ruled out by the fact that the ratio of nearest-neighbour separation to ionic diameter is even greater in lithium than in sodium where no ion core effect was found. Jain considers the Fermi contribution to the elastic constants using a modified form of the model applied by Jones⁴⁰ to the elastic constants of β -brass. The analysis indicates (1) the charge-density ratio Z at the atomic cell boundaries increases with decreasing volume as in sodium, but at about half the rate observed in sodium, (2) that the Fermi surface which at zero pressure bulges out about one-third of the distance between the free electron sphere and the [110] planes of the first Brillouin zone⁴¹ becomes more distorted as the pressure is increased. The sign and magnitude of the effect is in good agreement with the work of Blume⁴² on the theory of the shear constants in lithium and with Ham's theoretical predictions of the shape of the Fermi surface. The value of the energy gap across the (110) Brillouin zone planes inferred from these data using the model of Cohen & Heine, 0.128 Rydbergs (Ry), compares favourably with theoretical estimates ranging from 0.153 to 0.228 Ry.⁴¹ With Li, important information about the Fermi surface *and its change with volume* is obtained in a simple experiment, information extremely difficult (if not impossible due to the phase transformation in cooling), to obtain directly, e.g. by de Haas-van Alphen measurements carried out at high pressure.

Aluminium

As far as one is concerned with a study of the Fermi contribution to elastic constants, aluminium is the classical example, for which the theory has been worked out by Leigh.⁴³ Schmunk & Smith¹⁵ reworked the theory with better values of the elastic constants of aluminium, and in addition considered the effects of pressure. Two of the three valence electrons in aluminium can occupy the region contained by the first Brillouin zone (shown in Fig. 6), but the third must overlap into the second zone at points indicated by S and H on the Figure. The shear elastic constants are made up of (1) an electrostatic contribution of the form $C = K Z^2 e^2 / r^4$, $C' = K' Z^2 e^2 / r^4$ as for sodium and lithium, and (2) the contribution due to change of the Fermi energy by a shear strain. The ion core interaction is supposed to be an unimportant contributor because of the large ratio of nearest-neighbour distance to ionic diameter. The Fermi contribution is broken down into a contribution from the full zone, evaluated with use of a free-electron expression for the energy, plus a contribution due to the electrons in overlap positions S and H. In considering the contribution of the latter, one must take into account relaxation effects caused by redistribution of the electrons during shear by a transfer from higher to lower energy positions, an effect illustrated in Fig. 7b and 7c which shows a cross-section of the Brillouin zone and the shifts of electron populations with applied C and C' strains. Table III shows values of these contributions to the elastic constants.

Fig. 6. The Brillouin zone of aluminium, showing positions of electron overlap

