Fig. 7. *Schematic representation of the Brillouin zone and overlap electron populations of aluminium in various strains states*

Electron-overlap populations for the square and hexagonal faces are denoted by S and H respectively.

(a) Unstrained,   (b) *C'* shear strain,   (c) *C* shear strain, and (d) negative volume strain.

as shown in Fig. 7d. Numerically the values correspond to approximate fractional changes 0·002 and – 0·03 respectively in n_H and n_S for a pressure of 10 kb. (n_H and n_S are the number of electrons per atom overlapping each pair of hexagonal or square faces of the Brillouin zone). It is difficult quantitatively to assess the changes of interpretation brought about by use of a ' more modern ' Fermi surface, that described by Harrison.[44] Qualitatively however, the Harrison Fermi surface which implies nearly free electrons leaves the difficulty of accounting for the *observed elastic isotropy* $C \simeq C'$ in aluminium. A completely ' free electron ' model, i.e. a model giving a spherical Fermi surface, leads to zero Fermi contributions to the pure shear stiffnesses. If the Fermi contribution to C and C' is negligible, then the anisotropy ratio C/C' would have approximately the value obtained by consideration of the electrostatic contributions only, i.e. about 9 instead of the experimentally observed value 1·22.

Table III

Constitution of the present observed shear stiffnesses of aluminium as explained by Leigh's model

(units are 10^{12} dyne cm.$^{-2}$)

Contribution		C		C'
Coulomb (C_E)		1·106		0·1235
Fermi: Full zone	0·450		0·1500	
Hexagonal overlap	−1·320		0·5400	
Square-face overlap	0·047		−0·5817	
Net Fermi (C_F)		−0·823		0·1083
Total (observed) ($C_E + C_F$)		0·283		0·232

The notable feature of Leigh's theory is that it *accounts for the near equality of* C *and* C' which is remarkable when one considers that the electrostatic contribution taken alone has an anisotropy ratio C/C' of about 9. Table IV contains the contributions of these terms to the strain derivatives of C and C'. Qualitatively this interpretation indicates (1) as in the cases of sodium and lithium, the charge density at the boundaries of the atomic polyhedra increases as aluminium is compressed. In terms of the volume dependence of Z, $\dfrac{d \ln Z}{d \ln V} = -0.78$, a larger value than found in sodium; (2) as the pressure is applied to the specimen, part of the electrons in states overlapping the square faces of the Brillouin zone transfer to states overlapping the hexagonal faces

Table IV

Values for aluminium of the contributions $(-dC_i/d \ln r)/C$ *to the derivatives* $(-d \ln C/d \ln r)$ *of the shear stiffnesses* C *and* C'

The quantities $(-dC_i/d \ln r)/C$ arise from the contributions, C_i which are named.

Contribution	C	C'
Coulomb term	34·13	4·65
Net Fermi term assuming n constant	−14·52	2·32
Contributions from electron transfer with volume strain		
Hexagonal overlap	− 0·17	1·59
Square-face overlap	− 1·62	6·63
Total (and observed)	17·8	15·2

Copper, silver and gold

The monovalent noble metals copper, silver and gold represent a class of metals in which the elastic properties are dominated by the overlapping of nearest-neighbour ion cores. It is well known that these repulsive short-range interactions must be introduced to account for the low value of the observed compressibility. Almost all of our experimental knowledge of the ostensible form of the ion core interactions is derived from the elastic constants. The short-range interaction is an important one in the theory of diffusion in copper and several workers in this field have followed[45-47] the procedure of evaluating the repulsion parameters from the observed values of the elastic constants. This is reasonably satisfactory for the purpose, but attempting to account for the elastic constants of copper in detail in terms of a two-parameter exponential repulsion is less satisfactory. This failure is seldom pointed out explicitly, but it becomes more and more apparent when one examines the single-crystal elastic stiffness of the similar metals silver and gold. As pointed out earlier, the importance of a short-range interaction becomes more accentuated as one examines its contribution to each of the sequence: binding energy, the equilibrium condition, the elastic stiffnesses and finally the pressure derivatives of the elastic stiffnesses which will be determined almost entirely by the ion core repulsions in these metals. The original goals of the copper, silver, gold investigation which was our first high-pressure venture, were twofold. First we wished to obtain volume dependencies of the elastic constants for use in ' correcting ' to constant volume experimental data on effects of dilute alloying on elastic constants, i.e. to separate out the specific effects of alloying, from the effects due to change of lattice parameter on alloying. An example of the use of this correction is found in an article by Schmunk & Smith on elastic constants of copper–nickel alloys.[48] The second goal was to study the ion core interactions in detail under the favourable conditions that they made the largest contributions to the quantities measured. It was assumed that the stiffnesses were made up by (1) the electrostatic contribution and (2) the ion core interaction. At that time there was much less evidence than at present indicating the distortion of the Fermi surfaces from spherical. Accordingly it was assumed that E_F made no contribution to the shear constants or their strain derivatives, but that it did contribute to the bulk modulus. Inclusion of a Fermi term would not be very likely to affect the qualitative conclusions reached in our interpretation. Briefly, the study of the ion core interactions at close range, i.e. via the pressure derivatives of the elastic constants reveals serious failure of the assumption made in conventional elastic constant theory that the ion core interactions are central, i.e. that they act along the line between ion core centres. The failure becomes much more apparent as one considers in turn the behaviour of copper, silver and gold. The failure of the assumption of centrality of the interactions is so severe, that no reasonable extension may usefully be made of the usual consideration that the bulk modulus of the electron gas is responsible for failure of the Cauchy relations to hold in these metals.

Germanium and silicon

No thorough treatment of the elastic constants of the diamond-like semiconductors in terms of their cohesive energy has been advanced. Implications regarding their thermal properties are discussed later.

Rubidium iodide

This salt is in this list although measurements on it are not complete at this time. Buerger proposes a mechanism of finite C_{44} type strain to describe the CsCl–NaCl structure transitions.[49, 19] We thought it possible that the transformation in rubidium iodide (RbI) took place by loss of stability with respect to a C_{44} shear, i.e. that C_{44} would vanish at the transformation pressure as apparently happens in AuCd. Merely a 10% decrease in C_{44} is observed in compressing to the transformation pressure, ruling out that possibility. It is hypothesised that the structure becomes unstable by the vanishing of one of the *short wave-length* lattice frequencies in a mode of the C_{44} type (transverse acoustic [100] in more usual nomenclature). The thermal diffuse scattering of X-rays by RbI as a function of pressure is now being examined and, if the hypothesis holds, a large *change* is expected in thermal diffuse scattering from the modes whose frequency vanishes at the transformation pressure. Also, there should be a negative anomaly in the thermal expansion coefficient of RbI at low temperatures, due to negative dependence on applied pressure of those mode frequencies, as will be more generally discussed later.