1 kb, and the shift is very small in that range, which probably explains the lack of agreement.

The lack of change of the shape of the absorption edge under pressure, coupled with the agreement between the optical and electrical measurements, led Paul and Warschauer to state that the shift in the range of absorption could be attributed primarily to the displacement of the (100) conduction band minima, relative to the valence band maximum at (000); see the band structure of silicon, shown in Fig. 7.

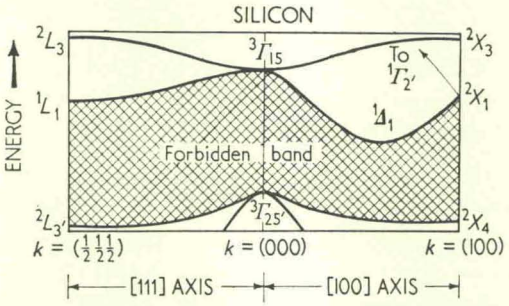

FIG. 7. The band structure of silicon. (Reproduced with permission from Herman, 1955.)

The behaviour of germanium is somewhat more complicated under pressure, and foreshadows several of the phenomena to be encountered in the intermetallics. Its shift changes direction under pressure, as the shift of the absorption edge is initially blue, and then in the neighbourhood of 50 kb the shift reverses direction, and becomes a red shift, which behaviour persists to well over 100 kb, as shown by Slykhouse and Drickamer (1958c). The edge of germanium has also been studied at lower pressures (to 7 kb) by Paul and Warschauer (1958a). Their data confirm the initial blue shift of the edge, or the increase of the energy gap. Though the numerical agreement is not as satisfactory as one might hope, the shift of the edge has also been determined by Fan *et al.* (1956), and Neuringer (1959). All of these experiments are well below the pressures necessary to reverse the direction of shift.

This reversal of the direction of shift with increasing pressure can be understood by reference to Fig. 8, which shows the band structure of germanium. At low pressures the edge is caused by a transition in the (111) direction, to the L_1 minimum. This minimum, shifts to higher energies relative to the (000) maxima with increasing pressure, while the (100) minima shift downward. Thus at high enough pressures, the minima responsible for the transition will change, or the transition will change directions. The (100) minima will continue to fall relative to the (000) minima, giving rise to an eventual red shift. Very similar

behaviour is shown by a large class of the compounds in the zincblende structure, as will be seen below. Thus these data may be taken to show

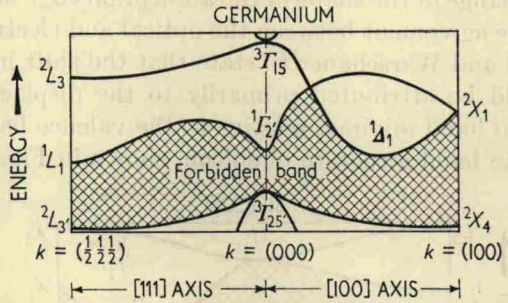

FIG. 8. The band structure of germanium. (Reproduced with permission from Herman, (1955.)

that states with L_1 and $\Gamma_{2'}$ symmetry shift to higher energies with increasing pressures, while those with Δ_1 symmetry shift to lower. The transition in silicon, discussed above, is probably an indirect transition to the (100) minimum, with Δ_1 symmetry. Then, since this minimum falls in energy relative to the (000) maximum, the edge should shift to the red, as indeed it does. Another way of putting this, due to Slykhouse and Drickamer (1958c), can be seen in Fig. 9. This is a plot of the

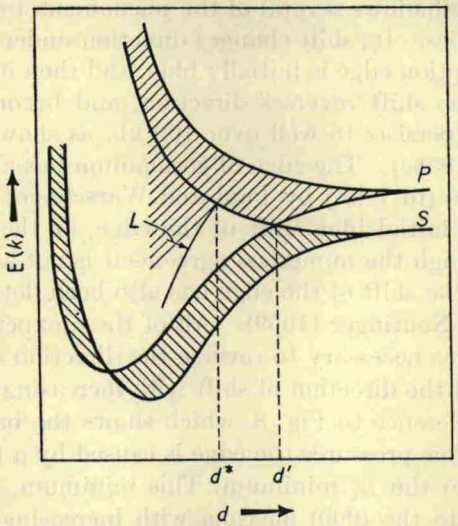

FIG. 9. A general $E(k)$ *versus* d diagram for the zincblende lattice. (Reproduced with permission from Slykhouse and Drickamer, 1958c.)

energy *versus* interatomic distance (d), and is based on calculations by Kimball (1935). Evidently, a shift will be obtained if d is greater than