

valence bands, which are still insulators. It is implicit in the Bloch theory that the electron can be represented by a wave which keeps its form over many interatomic distances. If one has 'slow' electrons which reside on an atom or ion for periods long compared with a lattice vibration, the surroundings will then become polarised and the 'polaron' is transported through the lattice.

In a series of papers Mott<sup>1</sup> has suggested that, at least at absolute zero, the number of carriers will not increase continuously with interatomic distance, but that excited electrons will be bound as excitons until there are sufficient of them to shield the electron from the hole.

Holstein<sup>2</sup> has treated the polaron mobility problem and has indicated that there is a low-temperature regime where the conductivity is of a band type, and a high-temperature regime where the motion of electrons is an activated process.

There are other complicating effects which may be present in a real solid. At any given temperature and interatomic distance, a solid has a crystal structure established by a complex balance of forces. If this is a relatively open structure at one atmosphere, at higher pressures it may undergo a first-order phase transition to a more closely packed structure. This high-pressure phase may or may not be conducting. Examples where this occurs will be discussed below.

For any insulator where the gap between valence and conduction band is substantially larger than 1 eV, it is highly probable that any measurable conductivity is the result of electrons furnished by impurities or by the electrodes, rather than from the valence band of the crystal. In measuring the change of resistance with pressure, one may still be measuring the increase in number of carriers with pressure due to the decrease in gap between conduction band and impurities levels, which may well parallel the change in optical energy gap. At sufficiently high pressures, however, the impurities may all become ionised. Further decrease in resistance then is due to increased mobility due to conduction band broadening. In the mobility-controlled region, the temperature coefficient of resistance is controlled by scattering, and the conductivity is metallic in the sense that the temperature coefficient of resistance is positive, but not, perhaps, in the sense illustrated in Fig. 1.

#### Experimental and results

In the following sections is illustrated the approach to the metallic state for three types of systems: (1) the elements selenium and iodine, (2) a series of substances having the zinc blende lattice, and (3) the thallous halides.

Fig. 2 shows the fractional change in optical absorption edge with pressure for iodine and selenium.<sup>3</sup> This should be a relatively direct measure of the gap between conduction and valence band. The gap extrapolates to zero for selenium at 125–130 kb, and for iodine at 240–245 kb. The irregularity in the shift for selenium at about 40 kbars is reproducible and corresponds to a change in compressibility observed by Bridgman.<sup>4</sup>

Fig. 3 shows relative resistivities as a function of pressure for iodine and selenium.<sup>5</sup> There is a very large drop in resistivity with pressure for both elements. At 128 kbars selenium has a discontinuous drop of about three orders of magnitude, beyond which there is a small but continuous change in resistivity with pressure. The discontinuous drop in resistance may be due to a first-order phase change, or may be caused by an electronic rearrangement as suggested by Hyman.<sup>6</sup> For iodine there is a marked discontinuity in the slope of the resistance–pressure curve at about 235 kb. The resistivities in the high-pressure region are of the order of  $10^{-4}$  ohm cm. for both elements. One is strongly tempted to identify the discontinuities with the disappearance of the gap and the onset of metallic conductivity. These may well be examples of this expected behaviour. It would be most desirable to have measurements of resistivity as a function of temperature at high pressure, and X-ray measurements of the structure. Unfortunately, neither of these are yet available.

It might be mentioned that the ratio of slopes of the optical gap versus pressure curves (Se/I<sub>2</sub>) is 1.50, while the ratio of the slopes of the log resistance versus pressure curves (Se/I<sub>2</sub>) is 1.67. This would indicate that the change in conductivity is indeed dependent on the gap and is not primarily a mobility phenomenon.

Figs. 4–6 show plots of relative resistivities versus pressure for the elements silicon and germanium,<sup>7</sup> the III–V compounds GaAs, GaSb, InAs and InP, and the II–VI compounds ZnS, ZnSe, and ZnTe.<sup>8</sup> The elements have the diamond lattice, while the compounds have the related zinc blende structure. These structures are relatively open, and it is not surprising that in all cases a first-order phase change is observed. In each case the transition is accompanied by