

the halide ion involved. Williams's calculations tell nothing explicit about the simple cubic structure, but one can see from the initial blue shift that there is a marked effect of crystal symmetry. Potassium chloride has a transition at a pressure of 19 kilobars to the simple cubic structure. On the basis of the results at low pressures and of Williams's theory, one would expect a discontinuous shift to higher energy for the absorption peak at the transition. Figure 2 shows that just such a shift occurs—a finding which also confirms the basic features of the picture.

Finally, in Fig. 3 is shown the shift of the absorption peak at high pressure for a series of alkali halides having both the sodium chloride and the cesium chloride structure. One can see that there is a remarkable similarity in the slopes at high pressure, all showing a large shift to lower energy. While there is as yet no theory which predicts the behavior at very small interatomic distances, it is clear that any such theory must predict that the ground state and the first excited state get closer together in energy under these conditions, quite independent of the crystal lattice.

We see, then, that the results at high pressure allow us to choose between

available simple theories, although we must understand that these may be oversimplified. Secondly, the results present a test for any theory formulated to describe the potential energy surfaces at small interatomic distances.

### Approach to the Metallic State

A second type of problem where optical and electrical measurements at high pressure make a unique contribution involves the approach to the metallic state at high pressure. As discussed earlier, in an insulator or semiconductor there is a filled valence band, separated by an energy gap, which is large compared with the fluctuations in thermal energy of the electrons, from an empty band available for electrical conduction.

In the absence of impurities the process of supplying electrons capable of moving through the lattice involves excitation of electrons across this gap. The smaller the gap the more likely it is that this can occur by thermal excitation, and the higher the conductivity. This excitation is an activation process. Theory shows that the activation energy is half the energy of

the gap. Thus one can obtain a measure of the gap width from the temperature coefficient of the electrical resistance at constant pressure. In a solid of simple band structure one would expect the bands to broaden with increasing pressure, and the gap to narrow accordingly. Thus one would expect a rapid decrease in electrical resistance with increasing pressure, accompanied by a decrease in the temperature coefficient of resistance.

In addition to exciting electrons by thermal fluctuations it is possible to excite electrons across the energy gap by means of electromagnetic radiation of the appropriate energy. The conductivity obtained thus in the presence of light of the right wavelength is known as photoconductivity. The very intense absorption of light of the energy of the gap is called the absorption edge of the crystal. It provides an independent measure of the size of the gap.

In recent years my associates and I have made both optical and electrical measurements as a function of pressure on iodine crystals (7). Iodine forms a base-centered orthorhombic crystal with the  $I_2$  molecules lying in the  $ac$  plane. It is quite practical to grow single crystals of usable size from the vapor phase.

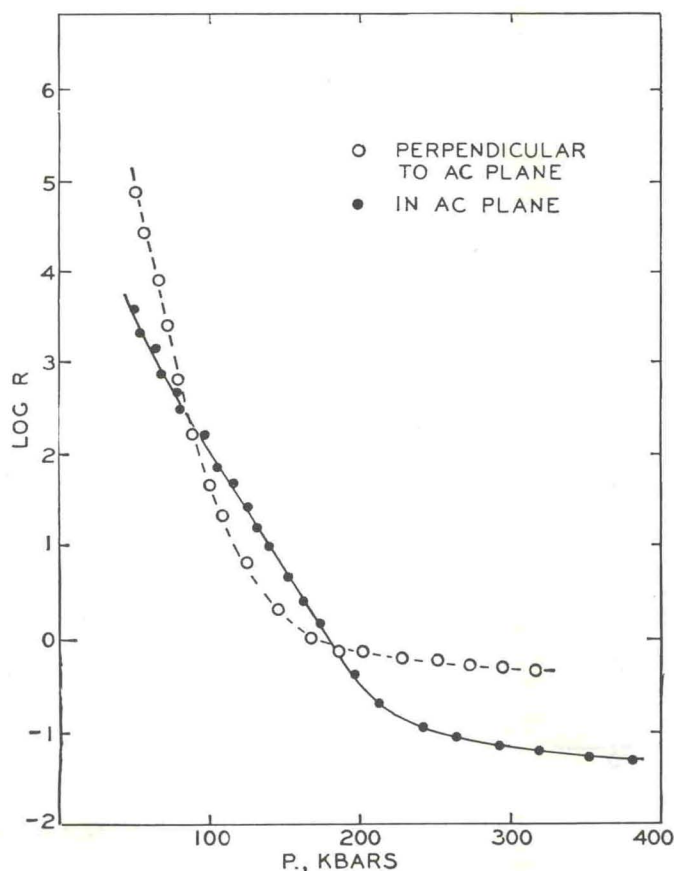
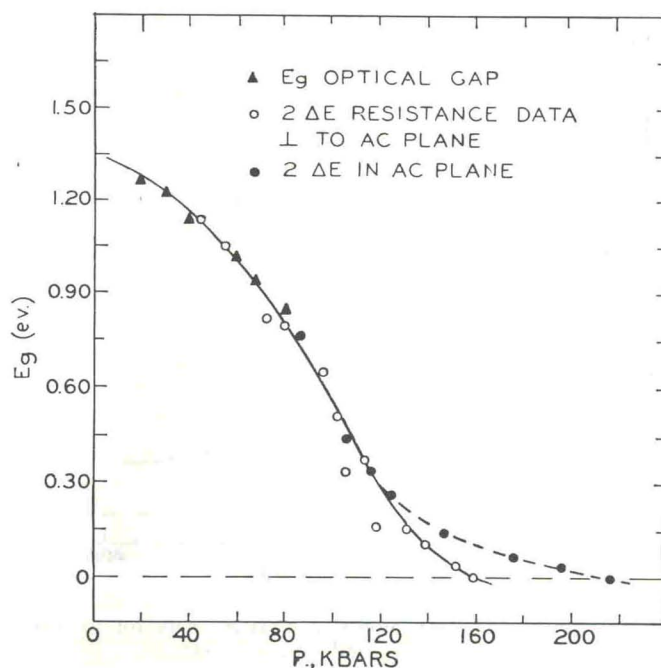


Fig. 4 (left). Log resistance plotted against pressure for iodine.

Fig. 5 (below). Energy gap plotted against pressure for iodine.





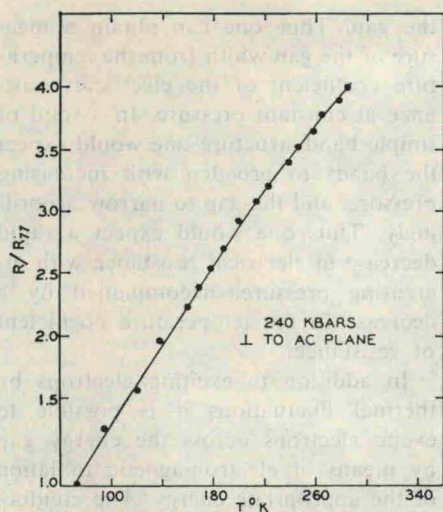


Fig. 6. Resistance plotted against temperature for iodine.

The measurements we have made include (i) optical absorption measurements (location of the absorption edge) as a function of pressure to about 90 kilobars, (ii) measurements of electrical resistance both parallel and perpendicular to the molecular plane as a function of pressures to over 400 kilobars, and

(iii) measurements of the temperature coefficient of resistance between 77° and 296°K at pressures from 60 to 400 kilobars.

Figure 4 is a plot of resistance versus pressure, measured both perpendicular and parallel to the molecular plane. In our apparatus it is not possible to correct for contact resistance, so the curves have been placed relative to each other by correcting for sample geometry only. Below 50 kilobars the resistances are too large to be measured in our apparatus, but they must be decreasing by many orders of magnitude. For measurements made in the *ac* plane, the rapid drop continues to pressures of about 230 to 240 kilobars, where there is a relatively sharp break. Beyond this pressure the resistance decreases at a rate which would be anticipated for a relatively compressible metal.

The broken curve of Fig. 4 represents measurements made perpendicular to the *ac* plane. The curve is qualitatively like the curves just discussed, but the break comes at 160 kilobars. In the high-pressure region the resistance perpendicular to the *ac* plane is appar-

ently 5 to 7 times greater than in the other direction; corrections for contact resistance could alter this number.

Figure 5 shows the measured optical absorption edge (triangles) as a function of pressure. Compared with this is shown the activation energy for electrical conductivity measured (open circles) perpendicular to the *ac* plane and (solid circles) perpendicular to the *ac* plane. In the pressure region where both optical and electrical measurements could be made, the agreement is excellent, confirming that the simple band picture is a reasonable description for iodine. The activation energy measured perpendicular to the *ac* plane vanishes at 160 kilobars, where the break in the resistance-pressure curve occurs. As one would expect, below 160 kilobars the activation energy is independent of direction. Above 160 kilobars the activation energy in the *ac* plane tails off to zero by about 220 kilobars.

Figure 6 is a plot of resistance versus temperature at 240 kilobars, measured perpendicular to the *ac* plane. It shows the linear increase of resistance with temperature which one would expect for a typical metal. Essentially identi-

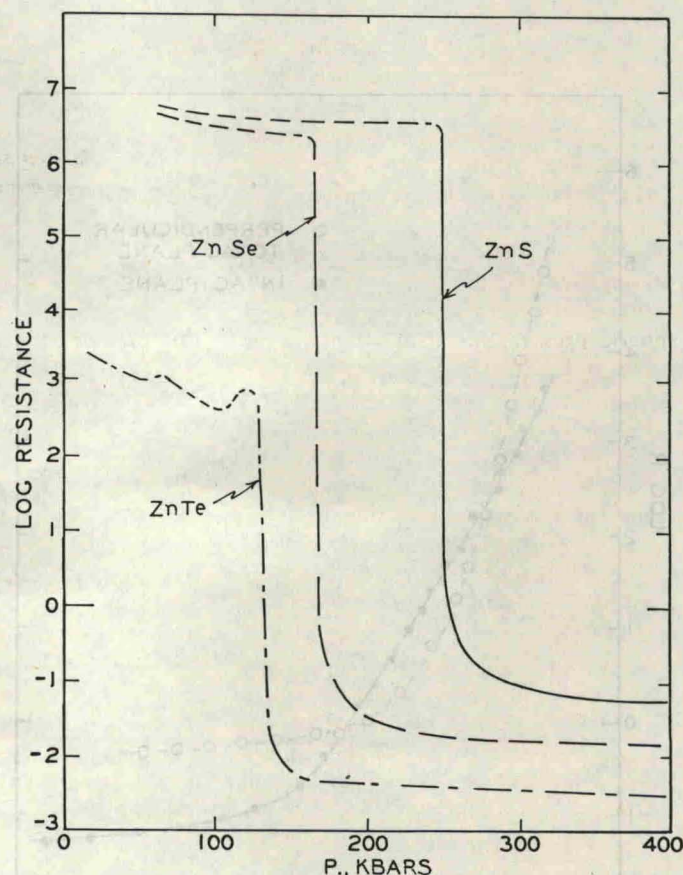
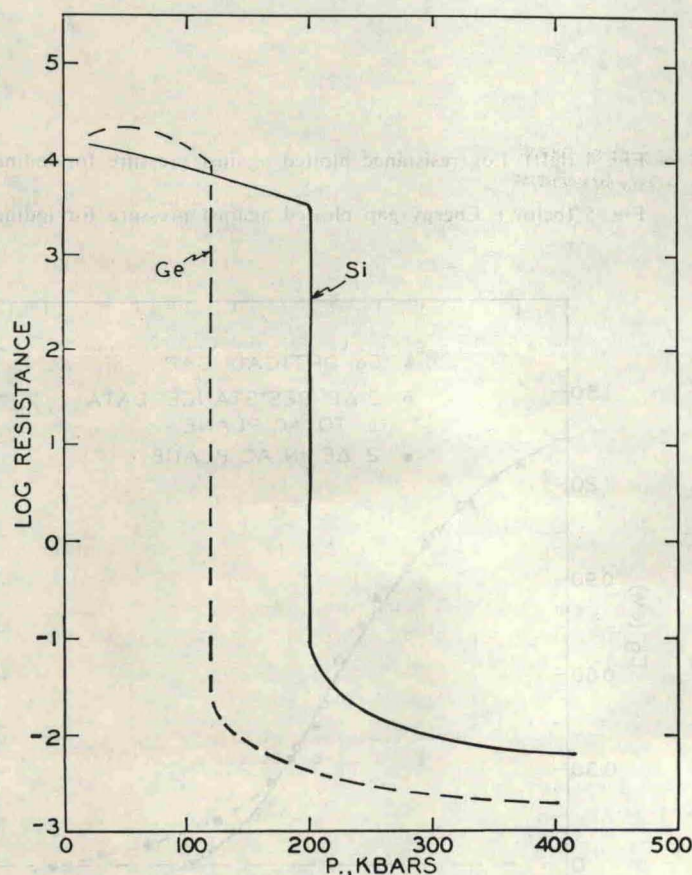


Fig. 7 (left). Resistance plotted against pressure for germanium and silicon. Fig. 8 (right). Resistance plotted against pressure for zinc sulfide, zinc selenide, and zinc telluride.