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THE APPROACH TO THE METALLIC STATE AT HIGH PRESSURE*

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The theoretical considerations involved in the approach to the metallic state in insulators and semiconductors at high pressure are outlined briefly. Experimental results for three types of systems are discussed. In iodine both the shift of the optical absorption edge and the change of electrical resistance with pressure are consistent with the appearance of a metallic state by simple disappearance of the gap. Selenium may have a first-order phase transition. For compounds having the zinc-blende structure, an apparently metallic state appears discontinuously, accompanied by a first-order phase transition. For the thallous halides, with increasing pressure, one obtains first a region of increasing carrier concentration, then a region where mobility changes dominate, and finally there is a region of apparently metallic behaviour.

Introduction

The basic Bloch–Wilson description of solids can be illustrated concisely from the diagram shown in Fig. 1. The allowed levels of an electron on a free atom or ion are discrete and separated by relatively large energy intervals. The ground state and first excited state for a valence electron on a free atom are shown at the right. An array of such atoms with large interatomic distance preserves this energy configuration, as there is no interaction. As the atoms are brought together until they interact, the levels are depressed and spread out into a band of levels whose spacing depends on the size of crystal and equilibrium interatomic distance. This appearance of bands is a result of the Pauli principle, which states that no two electrons can have all four quantum numbers the same. Allowing for spin, there can then be two electrons in each level. The situation in an actual crystal depends on two factors, the number of electrons per atom, and the equilibrium interatomic distance. With one valence electron per atom, the situation is as shown in Fig. 1A, with the valence band half filled. As illustrated in Fig. 1B, with two valence electrons per atom, the band is filled. If it is presumed that the gap between bands is large compared with kT, case 1A represents a metal, and case 1B an insulator. It should be emphasised that this is not because the electrons are ' bound ' in case 1B and ' free ' in Fig. 1A. It is rather the Pauli principle which forbids a net movement of electrons in case 1B.

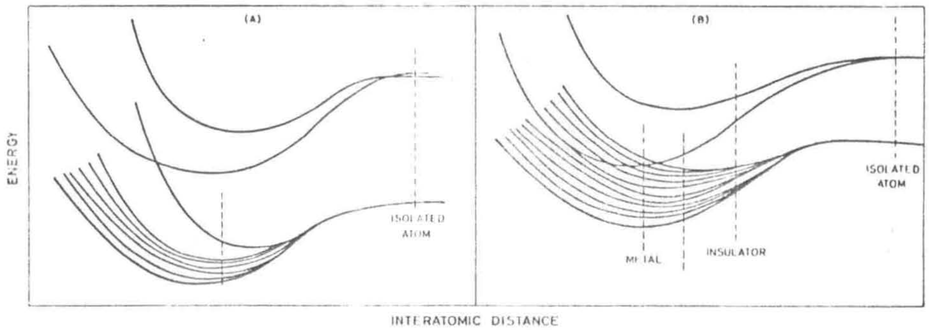

Fig. 1. *Energy vs. interatomic distance*
(A) metal (B) semi-conductor

As the interatomic distance is decreased (e.g., with increasing pressure), the gap between valence and conduction band decreases. Ultimately the bands overlap, and one obtains a metal, even though the valence band is filled. This is the situation in the alkaline earth metals.

At interatomic distances such that the energy gap is a few kT, a measurable number of electrons can be excited across the gap. One then has an intrinsic semiconductor.

For insulators and semiconductors the limiting factor is conductivity in carrier production, in this picture, and conductivity increases exponentially with increasing temperature. For metal, the limiting factor is mobility, i.e., mean free path. The mean free path decreases with increasing lattice vibrations, and for simple lattice scattering the conductivity of metals varies as $T^{-3/2}$.

This is probably a reasonable first-order description of many solids, but it can hardly be the complete story. There are crystals, such as many transition metal oxides, with partially filled

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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[1] 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[2] 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.[3] 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.[4]

Fig. 3 shows relative resistivities as a function of pressure for iodine and selenium.[5] 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.[6] 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_2) is 1·50, while the ratio of the slopes of the log resistance versus pressure curves (Se/I_2) 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,[7] the III–V compounds GaAs, GaSb, InAs and InP, and the II–VI compounds ZnS, ZnSe, and ZnTe.[8] 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 a large drop in resistance. The estimated resistivities of the high pressure phases vary from 10^{-2}—10^{-3} for ZnS to 10^{-5} for silicon, germanium and GaSb.

For all zinc blende compounds at atmospheric pressure the liquid is denser than the solid. Thus $\partial p/\partial_r$ is negative, and melting of the sample at high pressure could be observed. It is believed, however, that in all cases except possibly GaAs, a solid–solid transition is obtained.

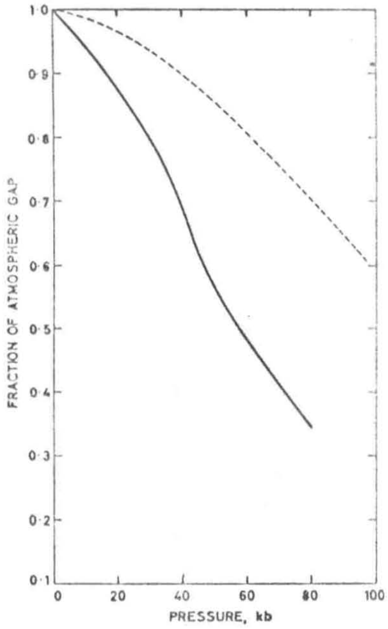


Fig. 2. *Optical gap vs. pressure*

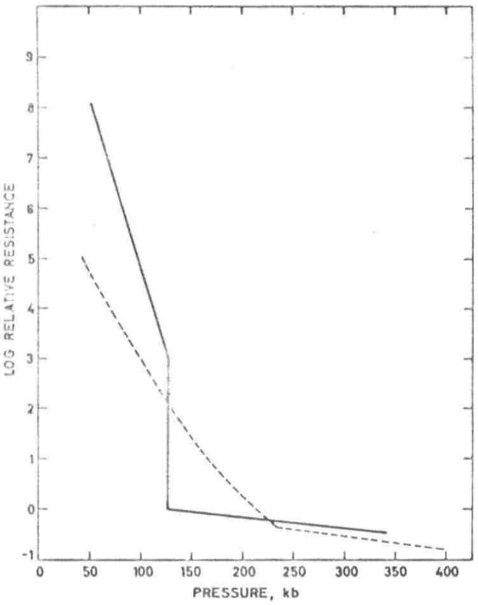
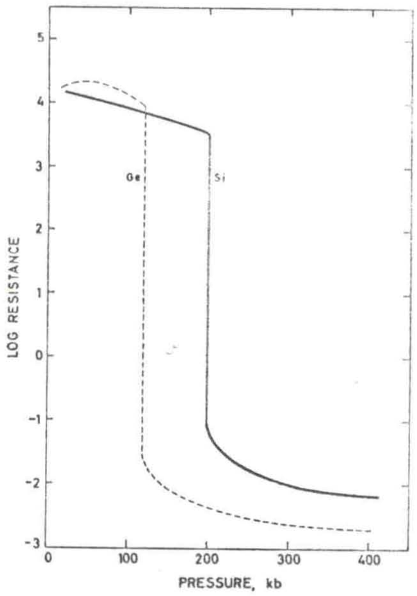
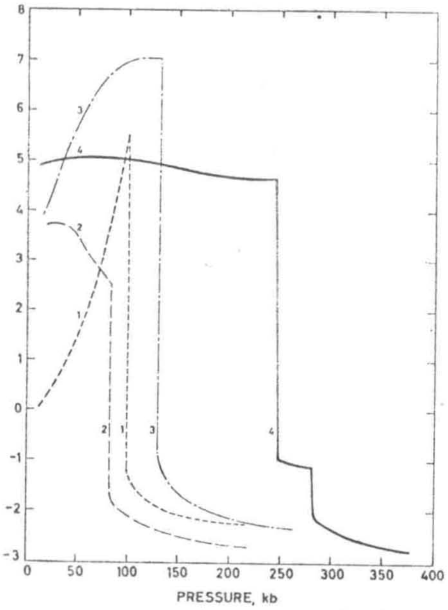


Fig. 3. *Relative resistance vs. pressure*

selenium — iodine — — —





Resistance vs. pressure (Fig. 4, left) *Germanium* (— — —) *and silicon* (——) (Fig. 5, right) III–V *compounds*

curve 1 In As curve 2 GeSb

curve 3 In P curve 4 GeAs

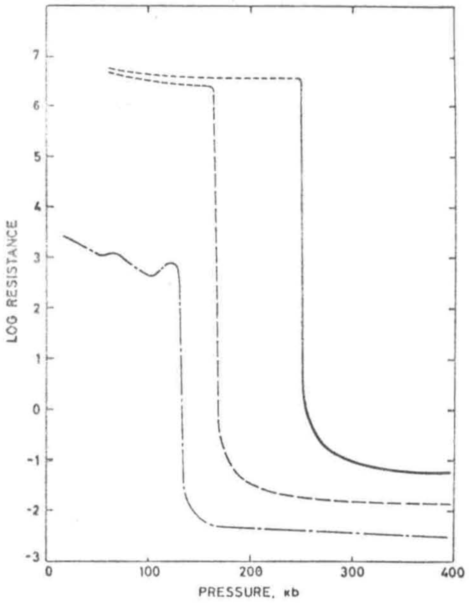


Fig. 6. *Resistance vs. pressure*
ZnS —— ZnSe — — — ZnTe - - - -

The data of Jayaraman *et al.*[9] for InSb indicate a triple point at 335° and about 20 kb with a solid—solid transition at room temperature and 23 kb. The data of Gebbie *et al.* [10] indicate that there is a large drop in resistance at this point. By analogy it is expected that a similar transition is occurring in these substances. Also, a microscopical examination of the samples after a run gave no indication of melting, although they were rather badly distorted on removal from the bomb so that the evidence is not clear-cut.

In the case of GaAs there is a sharp drop in resistance at 245 kb, a relatively small change to 280 kb, and a second drop of about an order of magnitude. It is speculated that here we are above the triple point at room temperature and that the region from 245—280 kb represents the liquid state. Both resistance measurements as a function of temperature and high-pressure *X*-ray measurements would be most desirable on this and the other zinc blende type compounds.

Fig. 7 shows the fractional change of optical absorption edge with pressure for TlCl, TlBr and TlI.[11] All of these have the simple cubic (CsCl) structure at high pressure. (TlI transforms to this structure at 5—6 kb.) All three exhibit a large red shift with pressure, the ratio of the slopes (TlI/TlBr/TlCl) being about 2·3/1·4/1·0.

Figs. 8—10[12] show the change of resistance with pressure at 25° and 120° (in the case of TlI, a 145° isotherm is also included). For the iodide there are three distinct regions: a very sharp drop with pressure up to about 90—100 kb, a second drop with about half the slope of the first part and, above 160 kb, a relatively small change of resistance with pressure. In the first region there is a decrease of resistance with increasing temperature. The activation energy is about 1·1 eV. In the second region there is a small but definite increase of resistance with temperature. In the third region there is a significant increase in resistance with temperature.

TlBr exhibits the same three regions, but the difference in slope between regions 1 and 2 is less distinct, and the transfer from region 2 to region 3 is less abrupt. In TlCl region 2 is no longer distinguishable, but the isotherms cross as for the other two compounds. The TlCl and TlBr have activation energies of 0·8—0·9 eV, in the low-pressure region.

Since these compounds were not intensively purified, the source of conduction electrons is almost certainly impurities. Nevertheless, in region 1, we are undoubtedly measuring an increase in carrier concentration with pressure, probably due to movement of the bottom of the conduction band with respect to impurity levels. The relative slopes of the log resistance versus pressure curves (TlI, TlBr, TlCl) are 2·7/1·2/1·0. This is quite comparable with the relative gap changes observed optically.

In region 2, one is undoubtedly observing primarily the increase in mobility with increasing pressure, probably due to broadening of the conduction band.

In region 3, the resistance is distinctly ' metallic ' in its temperature behaviour. If one

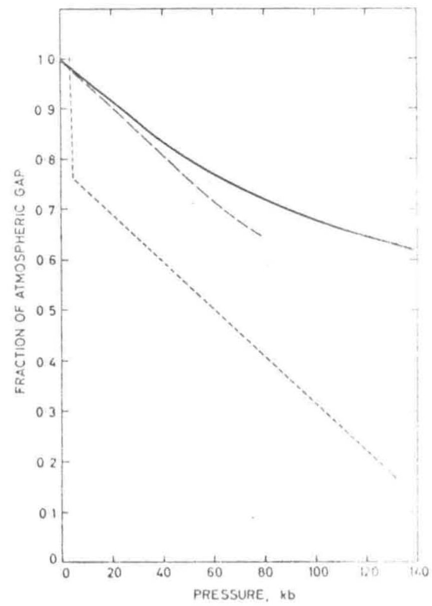


Fig. 7 (left) *Optical gap vs pressure*
— Th Cl — — — Th Br - - - Th I

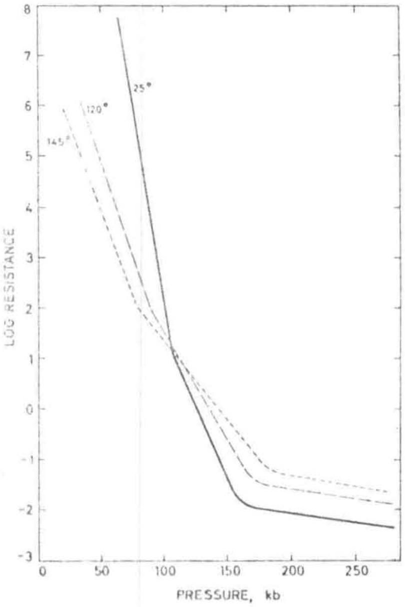
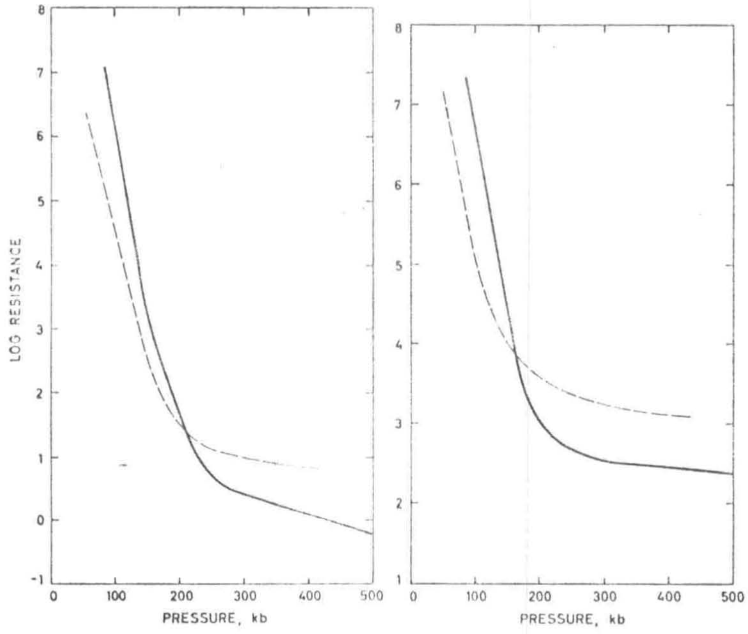


Fig. 8 (right) *Resistance vs pressure* for thallium iodide
— 25° — — — 120° - - - 145°



Resistance vs pressure for Fig. 9 (left) *thallium bromide*, (Fig. 10, right) ***thallium chloride***
—— 25° — — — 120°

considers a T^{-n} relationship, $n = 1$—2 about as expected for lattice scattering. Also the difference in resistivity among the three halides at high pressure is considerably larger than one would anticipate intuitively from differences in band structure. This may well be an impurity effect, which could be modified by zone refining of the material.

It should also be pointed out that the results can be 'explained qualitatively' in terms of Holstein's polaron model mentioned earlier. The low-pressure region of 'activated resistance' would correspond to Holstein's high-temperature regime of 'hopping motion' of polarons. The high-pressure region would correspond to his region of 'band-type mobility' at low temperature. Since the Debye temperature would increase by an estimated factor of 2—2·5 in 150 kbars over the pressure ranges used in this work, it would correspond to a significant decrease in reduced temperature.

Conclusion

These studies of the approach to the metallic state at high pressure are in their initial stages, but the results presented here serve to illustrate the kind of information obtainable from high pressure measurements.

Acknowledgments

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