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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.

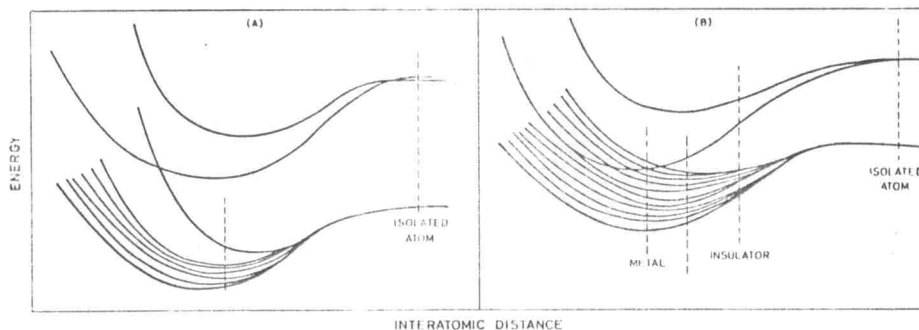


Fig. 1. Energy vs. interatomic distance
(A) metal (B) semi-conductor

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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