

transition which may disappear in a critical point as discussed for cerium below.

It has been long known (30) that cerium exhibits a discontinuity in resistance (31) and in volume (32) with no change in structure at room temperature and a few kilobars pressure. Jayaraman (33) has shown that the magnitude of the discontinuity decreases with increasing temperature until it disappears. It has been frequently proposed (30, 32) that the transition involves transfer of a $4f$ electron to the $5d$ shell. Recent calculations by Ramirez & Falicov (34) indicate that a transfer of a $4f$ electron to the conduction band is probably involved. It has been shown (1, 35) that a variety of other rare earth metals show very distinct resistance anomalies at high pressure and that these transitions become sharper, rather than more sluggish, at 78°K . The transfer of an electron from the $4f$ shell to the $5d$ shell or to the conduction band must be a common phenomenon.

It has been pointed out that barium and europium exhibit a very similar resistance behavior (1), particularly in the region 100–150 kbar. There appear to be reasons to associate the transition in barium with $s \rightarrow p$ or $s \rightarrow d$ transitions. It is quite possible that europium, with a half-filled $4f$ shell, undergoes a similar transformation.

Interestingly, Jayaraman et al (36) have observed resistance anomalies in compounds of samarium (SmS, SmSe, SmTe) which they associate with the $4f \rightarrow 5d$ electronic transition, so that these transitions may occur in compounds as well as in the elements. In SmSe and SmTe these transitions occur over a considerable range of pressure, rather than discontinuously.

Another type of electronic transition takes place in certain crystals of atoms with filled shells such as calcium, strontium, and ytterbium. These materials are metallic because their conduction band is an s - p - d hybrid such that the Fermi surface intersects the Brillouin zone boundary in a complex manner. As pressure is increased these materials become semiconductors or semimetals (1, 37), i.e. the resistance decreases with increasing temperature. At sufficiently high pressure they again become metallic. There have been extensive theoretical analyses of calcium. Cracknell (38) reviews the theory up to 1969. Calcium, and probably also strontium, are semimetals rather than semiconductors. A recent study by McCaffrey, Papaconstantopoulos & Anderson (39) is also consistent with this viewpoint. Calcium becomes semimetallic near 200 kbar and transforms back to the metallic state near 300 kbar. The corresponding transitions occur at much lower pressures for strontium and ytterbium so that more extensive experimental evidence is available for them. McWhan, Rice & Schmidt (40) have made a particularly thorough study and analysis for ytterbium. Although its resistance behavior is very similar to calcium it becomes semiconducting rather than semimetallic. Very small variations in the relationship of the Fermi surface to the Brillouin zone boundary are sufficient to establish this difference. Important contributions to the study of these two compounds have also been made by Hall & Merrill (41), Souers & Jura (42), Jerome & Rieux (43), and McWhan & Jayaraman (44).

NONMETAL-METAL TRANSITIONS

As mentioned in the introduction, one of the primary effects of decreased interatomic distance is to broaden the bands of allowed energy states. It is easy to visualize that this broadening, possibly accompanied by a relative displacement of one band with respect to another, could transform an insulator into a metal. Such transformations with no apparent discontinuities in resistance or structure have been observed in iodine (1, 45); in crystals of certain aromatic hydrocarbons such as pentacene, hexacene, and violanthrene (46) at temperatures below 200°K; and apparently in the thallous halides (47).

One might expect that a relatively open structure could undergo a first order phase transition to a more closely packed structure, and that this structure could be metallic although the open structure was insulating or semiconducting. Such transitions, accompanied by very large discontinuities in resistance, have been observed in silicon, germanium, and numerous III-V and II-VI compounds with the zinc blende structure (1, 48, 49). X-ray analysis (50-53) indicates that in many cases the high pressure structure is that of white tin or the diatomic analog. Recently van Vechten (54) has been successful in calculating the transition pressure in silicon and germanium.

The foregoing discussion of insulator-metal transitions has been based on the elementary consideration of an empty conduction band and a filled valence band separated by a forbidden energy gap. This picture does not predict the insulating properties of transition metal oxides like NiO or V_2O_3 . Since the partially filled atomic 3*d* shell should give rise to a partially filled band, these materials ought to be metals. While a number of theories have been proposed to describe this phenomenon, the most widely discussed is that due to Mott (55). Basically he argues that the problem is one of electron-electron correlation. Above a certain electron density, the material is metallic; for lower densities it is an insulator. Adler (56) has reviewed a wide variety of related theories. While discontinuous transitions from insulator to metal are not uncommon as a function of temperature and pressure, they generally lack the precise characteristics of a true "Mott transition."

Probably the most interesting and informative experiments in this area have been those performed at Bell Laboratories by McWhan et al (57-60). They have studied the properties of crystals of the form $V_{1-x}Cr_xO_3$ and have shown that, in particular, the crystal $V_{0.96}Cr_{0.04}O_3$ exhibits essentially all of the characteristics of a Mott transition, with regions of temperature and pressure where it is a paramagnetic insulator, an antiferromagnetic insulator, or a metal. They have also demonstrated very clearly the equivalence of changing composition and pressure on the electronic properties as shown in Figure 4. Even for this material, the transition may not be a pure "electron-electron" interaction as demanded by the Mott theory, as it is probably phonon assisted. Mott, in fact, now believes (61) that the transition precisely as described by his theory may not be experimentally obtainable. Nevertheless, the proposal has given rise to much interesting work, both theoretical and experi-