

The following examples serve to show the wide variety of systems for which a new ground state is established at high pressure.

(1) $s \rightarrow d$ transitions in alkali metals and $4f \rightarrow 5d$ transitions in rare-earth metals. The earliest examples of clearly defined electronic transitions were in cerium and cesium. In cerium there is a sharp resistance change and a volume discontinuity³⁻⁵ at low pressure which has been associated with the promotion of a $4f$ electron to the $5d$ shell, establishing a new ground state. It has been shown⁶ that the $4f \rightarrow 5d$ transition in cerium terminates with a critical point at sufficiently high temperature. Similarly, a cusp in the resistance of cesium⁷ at 40 kbar, associated with a volume discontinuity,^{8,9} was assigned by Sternheimer¹⁰ to the promotion of the $6s$ electron to the band arising from the atomic $5d$ orbitals. Rubidium exhibits² a sharp rise in resistance near 150 kbar and a maximum near 300 kbar, probably indicating the promotion of the $5s$ electron to the "4d" band. At room temperature the resistance of potassium rises with pressure continuously (by a factor of 30 in 500 kbar).² At liquid-nitrogen temperature there is a sharp discontinuity near 280 kbar which disappears near 250 °K. This may be a martensitic transformation, but it may also be the $4s \rightarrow 3d$ promotion disappearing at a critical point. A second cusp in the resistance of cesium near 125 kbar² may be associated with the promotion of an electron to the empty $4f$ band. Most of the rare-earth metals exhibit resistance discontinuities at high pressure² which have not been fully elucidated, but are very probably associated with promotion of $4f$ electrons to $5d$ orbitals. There appears to be a general tendency for rare-earth metals to assume increasing transition-metal character at high pressure.

Many rare-earth salts exhibit optical absorption peaks in the visible or near ultraviolet which are assigned as $4f \rightarrow 5d$ transitions.¹¹ It is clear that a moderate reduction in energy difference between these states could result in the establishment of a new ground state, so that electronic transitions should be a common feature for rare-earth ions in crystals at sufficiently high pressure, as well as for the corresponding metals.

(2) Changes of composition of complex conduction bands of metals at high pressure. Mössbauer resonance studies on iron as a dilute solute in a series of transition metals with close-packed structures indicates that there is a continuous increase in the d character of the combined $s-d$ conduction band with increasing pressure.^{12,13} Calcium, strontium, and ytterbium^{2,14-16} metals become semiconducting at high pressure, with no change of lattice arrangement. It has been shown that this is caused primarily by the effect of compression of the sp conduction band, but also in part to its increasing d character at high pressure.¹⁷ While these continuous changes are only distantly related to the discontinuities mentioned in (1) above, to the extent that there exists transfer of electrons to parts of the band with d character

from parts with s or p character, there is a change in the electronic character of the ground state.

(3) The reduction of ferric ion at high pressure. It has been shown that ferric ion reduces to ferrous ion with increasing pressure in a very wide variety of compounds.^{18,19} The process is reversible but sometimes with considerable hysteresis. The reduction occurs over a range of pressure which strongly depends on the coupling between sites. The process consists of the transfer of an electron from a predominantly ligand orbital to a predominantly metal orbital, so that at high pressure the ground state consists of a ferrous ion plus ligands with a hole associated with them. In chemical language, the ligands contain a free radical or radical ion. The process differs from that discussed under (1) above only in that there is a change of ground state between different molecular orbitals rather than between different atomic orbitals or metallic bands.

(4) The change of spin state of iron at high pressure. With increasing pressure it is possible to observe changes in the degree of spin pairing of iron ions. These may involve either a decrease or an increase in the spin of the ion.¹⁹ Spin pairing can be associated with an increased splitting of the $3d$ orbitals in the intensified ligand field, making it energetically advantageous to concentrate the electrons in the lower lying orbitals. This is then an electronic transition from one type of $3d$ orbital to another type, i.e. a transition with $\Delta n = 0$ and $\Delta l = 0$, but otherwise comparable to the transitions of (1).

In a number of compounds, iron has paired spins at one atmosphere. These generally involve strongly covalent bonding to ligands containing carbon or nitrogen with empty ligand orbitals (π^* orbitals). The iron $3d$ electrons of appropriate symmetry are partially delocalized into these orbitals. At high pressure the ligand orbitals tend to become occupied by ligand electrons and the metal electrons are relocalized on the iron, decreasing the bonding and giving rise to a higher spin configuration. This can be regarded as an electronic transition in which the new ground state is a molecular orbital of less covalent character than the low-pressure ground state.

(5) Reactions of aromatic hydrocarbon crystals and crystalline charge transfer complexes. As indicated in the early part of this paper, crystals of aromatic molecules have optical transitions from a nonpolar ground state to a polar excited state. With pressure these transitions shift strongly to lower energy with a large decrease in electrical resistance. For molecules such as pentacene and violanthrene, where the excited state is not over 2 eV above the ground state at one atmosphere, at room temperature, an irreversible reaction occurs for pressures above about 200–250 kilobars,^{2,20,21} forming a new type of polymer. For molecules such as pyrene, perylene, and anthracene, where the excited state is 3 eV or more above the ground state, no such reaction occurs. If the excited state is sufficiently low in energy it can be dis-