

Electronic Structure and Electronic Transitions at High Pressure

The primary effect of pressure on electronic behavior is to increase the overlap between orbitals on adjacent atoms or molecules. There results a broadening of the energy bands arising from these orbitals and a delocalization of the electrons. This produces a narrowing of the gap between the conduction and valence band as evidenced by a "red" shift (shift to lower energy) of the absorption edge. Ultimately, an insulator becomes a metal, either by the continuous disappearance of the energy gap as in molecular crystals like iodine and pentacene,^{1,2} or discontinuously as in the ideal "Mott" transition. (The discontinuous transition from semiconductor to metal by rearrangement of the atoms into a more closely packed lattice, which occurs in silicon, germanium, and many III-V compounds is a complication outside the range of the present considerations.^{1,2}) The decrease of resistivity of many metals with increasing pressure is, in a way, a result of the increasing overlap, as this overlap inhibits the amplitude lattice vibrations and reduces scattering. The first general result of increasing overlap is, then, an increasing delocalization and mobility for electrons.

Relative shifts of energy levels with pressure

Superimposed on the primary effect of pressure is a secondary effect of very broad significance. In general there is a relative displacement in energy of one orbital, or set of orbitals, with respect to other types. Since atomic orbitals of different quantum number differ in radial extent, in shape, and in deformability, it is not surprising that they are perturbed to different degrees by increasing interaction. In fact, it would appear coincidental when such a relative displacement does not occur. The common way to observe these shifts is through optical absorption measurement. Typical examples would include:

(1) The change in the energy gap between the valence band and conduction band in materials like germanium and GaAs.² In the low-pressure region the gap increases with pressure, while in the high-pressure region it decreases. This is because different excited states shift differently with pressure, so that at low pressure one part of the conduction band is lowest in energy, and at high pressure a different part.

(2) In transition-metal-ion complexes there occur absorption peaks which measure the splitting of the 3d levels due to the symmetry of the ligand field. These absorptions also give the magnitude of the Racah (interelectronic repulsion) parameters. In general the splittings increase as the intensity of the field increases, while the Racah parameter decreases as the *d* orbitals are spread by increasing interactions with the nuclei of the ligands.^{1,2}

(3) The change in energy with pressure¹ of the ligand-to-metal and metal-to-ligand charge transfer peaks in transition-metal-ion complexes. The former transitions frequently shift strongly to lower energy with increasing pressure. This indicates a large relative increase in energy of the ligand non-bonding orbitals *vis à vis* the antibonding metal orbitals. In metallorganic crystals the metal-to-ligand transitions also decrease in energy with increasing pressure. This is caused by the strong pressure effect on the excited (π^*) orbitals of aromatic molecules as discussed in (4) below.

(4) The change in energy of the excited (π^*) orbitals *vis à vis* the nonbonding or π -bonding orbitals in molecular crystals of aromatic hydrocarbons and derivatives. These intense absorption peaks in the visible or UV often shift very strongly to lower energy with increasing pressure.²

(5) The change in energy of optical transitions which measure the difference in energy between the "no bond" ground state and "ionic bond" excited state in molecular charge transfer complexes. These transitions frequently decrease in energy rapidly with increasing pressure indicating an increasing probability of the formation of ions or free radicals.^{1,2}

These relative shifts in energy levels may or may not affect the degree of delocalization of the electron.

Electronic transitions

In many solid state systems there exist excited states not too high in energy above the ground state (relative to the ability of pressure to change the energy levels). Under these circumstances, at high pressure one may introduce a new electronic ground state for the system. This can have profound effects on both the chemical and physical behavior of the material. We designate this change of ground state an "electronic transition". This term has generally been restricted to a more narrowly defined phenomenon but it is important to show the significant common thread among a variety of events having rather different apparent characteristics. These electronic transitions can occur instantaneously at a given pressure and temperature or they can spread out over a range of pressures. They may or may not involve a volume discontinuity. Frequently there is no change in crystal structure, although one can occur. The process is usually reversible, with or without hysteresis, but it may be substantially irreversible.

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