Drickamer, H.G. Comments Solid State Phys., 3, 53-8 (1970

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 sdecrease as the *d* orbitals are spread by increasing interactions with the nuclei of the ligands.[1,2]

(3) The change in energy with pressure[1] 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 nonbonding 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.

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 discontinuity[3–5] 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 shown[6] that the $4f \rightarrow 5d$ transition in cerium terminates with a critical point at sufficiently high temperature. Similarly, a cusp in the resistance of cesium[7] at 40 kbar, associated with a volume discontinuity,[8,9] was assigned by Sternheimer[10] to the promotion of the $6s$ electron to the band arising from the atomic $5d$ orbitals. Rubidium exhibits[2] 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 kbar[2] 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 pressure[2] 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-

placed until it forms a new, reactive ground state in which polymerization can occur. As we have indicated, many electron donors such as pyrene, perylene, and anthracene form complexes with acceptors like iodine, tetracyanoethylene, or chloranil which have low lying excited states that shift to lower energy with increasing pressure. At high pressure all these systems are relative and form new products which may or may not include the acceptor. Clearly, however, the major function of the acceptor is to provide an excited state sufficiently low in energy that one can create a reactive ground state for the donor at high pressure. Perhaps one could design electron donor–acceptor complexes with appropriate geometry and electronic structure so that one could induce different desired reactions and thus create a chemistry of the organic solid state at high pressure.

Possibly, a special case of this phenomenon is the collapse of graphite[2,20,24–26] to hexagonal diamond at high pressure, where the molecular (van der Waals) forces between graphite layers are replaced by new covalent bonds.

While these events at high pressure have widely different characteristics they share the feature that a new ground state is created. Transitions involving metals tend to occur discontinuously and reversibly. Where the transition involves local strain which may perturb neighboring sites, the process may occur over a considerable range of pressure and involve significant hysteresis. These new ground states may have distinctly different chemical and physical properties.

In summary, the basic effect of pressure is increased orbital overlap. A general result of this overlap is the shift of one type of orbital with respect to another. Where different electronic states do not differ too greatly in energy, this shift in orbital energy may create a new ground state for the system. Electronic transitions, so defined, are not an uncommon phenomenon in metals and in ionic, covalent, and molecular crystals. In fact, perhaps the major interest in exploratory research at very high pressure is in investigating the nature of the new ground states created by orbital overlap.

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References

1.* H. G. Drickamer, in *Solids under Pressure*, edited by W. Paul and D. Warschauer (McGraw-Hill, New York, 1963), pp. 357–385.
2.* H. G. Drickamer, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1965), Vol. 17, pp. 1–135.
3. A. W. Lawson and T. Y. Tang, Phys. Rev. 76, 301 (1949).
4. I. Lihkter, N. Riabinin, and L. F. Vereschagin, Soviet Phys.—JETP 6, 469 (1958).
5. R. Herman and C. A. Swenson, J. Chem. Phys. 29, 398 (1958).
6. A. Jayaraman, Phys. Rev. 137, 179 (1965).
7. P. W. Bridgman, Proc. Nat. Acad. Sci. U.S. 81, 165 (1952).
8. P. W. Bridgman, Proc. Nat. Acad. Sci. U.S. 76, 55 (1948).
9. H. T. Hall, L. Merrill, and J. D. Barnett, Science 146, 1297 (1964).
10. R. Sternheimer, Phys. Rev. 78, 238 (1950),
11.* C. K. Jorgenson, *Oxidation Numbers and Oxidation States* (Springer–Verlag, New York, 1969).
12. H. G. Drickamer, R. L. Ingalls, and C. J. Coston, in *Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. M. Emrick (Academic Press, New York, 1965).
13. R. Ingalls, H. G. Drickamer, and G. De Pasquali, Phys. Rev. 155, 165 (1967).
14. P. C. Souers and G. Jura, Science 140, 481 (1963).
15. H. T. Hall and L. Merrill, Inorg. Chem. 2, 618 (1963).
16. D. B. McWhan and A. Jayaraman, Appl. Phys. Letters 3, 129 (1963).
17. B. Vasvari and V. Heine, Phil. Mag. 15, 731 (1967).
18.* H. G. Drickamer, G. K. Lewis, Jr., and S. C. Fung, Science 163, 855 (1969).
19.* H. G. Drickamer, V. C. Bastron, D. C. Fisher, and D. C. Grenoble, Solid State Chemistry 2 (1970).
Also D. C. Fisher, private communication.
20.* H. G. Drickamer, Science 156, 1185 (1967).
21. W. H. Bentley and H. G. Drickamer, J. Chem. Phys. 41, 1573 (1965).
22. G. A. Samara and H. G. Drickamer, J. Chem. Phys. 37, 471 (1962).
23. F. P. Bundy, J. Chem. Phys. 38, 631 (1963).
24. R. B. Aust and H. G. Drickamer, Science 40, 817 (1963).
25. R. W. Lynch and H. G. Drickamer, J. Chem. Phys. 44, 181 (1966).
26. F. P. Bundy and J. S. Kasper, J. Chem. Phys. 46, 3437 (1967).

* These reviews contain references to the original papers.