

High pressure, electronic structure and chemistry in solids

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High pressure is a powerful and effective tool for studying electronic behaviour. Solid state physicists have been making extensive and effective use of it for more than two decades but only recently has it become apparent that pressure studies have relevance in a variety of electronic problems of importance to chemists.

The basic effect of pressure is to increase overlap between adjacent electronic orbitals. Some of the consequences can best be described in terms of band theory in which more or less delocalized electrons are assumed to be distributed in bands of narrowly-spaced levels separated by energy gaps with no allowed electronic states. However, for most high pressure phenomena of interest to chemists, one is concerned primarily with more localized states.

One consequence of increased overlap is a broadening of energy bands with a reduction in the size of the forbidden gap between bands, and an increase in electron mobility. A second general consequence is the relative shift in energy of one type of orbital with respect to another. Since orbitals of different quantum number may differ in radial extent, or orbital shape (angular momentum) or in compressibility, this relative shift in energy is a common phenomenon. Such shifts and their consequences are considered in this article.

High pressure experiments can be divided into two classes—those involving hydrostatic pressure media (liquids or gases), over a pressure range of about 12 kilobars (1 kilobar = 10^8 Pa = 987 atm); and those employing quasistatic media and extending to several hundred kilobars. The former will be mentioned only briefly.

In the 12 kilobar range, a significant number of solid-state physics experiments have been carried out. There has also been considerable chemical experimentation—although not primarily concerned with electronic structure. Many of Bridgman's early studies¹ *e.g.*, compressibility and viscosity measurements, are of interest to chemists. Probably the most extensive modern work of a physical chemical nature in fluids is that done by Franck and his coworkers at Karlsruhe, which included a variety of studies on physical properties;² his experiments in the supercritical region are of particular interest. There have also been several optical absorption studies,³ studies of chemical kinetics^{4,5} and, more recently, studies of molecular motion (translational, rotational *etc.*) by nuclear magnetic resonance relaxation.⁶ These results have

been helpful in testing and differentiating between theories of the liquid state, of reaction mechanisms, of solvent effects on spectra *etc.* Perhaps the most general point which has been established is the importance of experimentation *at constant density* for understanding processes in fluids.

Bridgman, working in the 1930s and 1940s, made pressure-volume and electrical resistance measurements on solids up to 70–100 kilobars pressure. In the past 15 years this range has been extended to several hundred kilobars. But more significant than the higher pressures, is the extension of types of measurements to those more directly applicable to studies of electronic behaviour. This article mainly refers to measurements of optical absorption and Mössbauer resonance. No details are given of high pressure techniques—for these the reader should consult references 7–9. Likewise, references to individual research papers are not given—for these the reader should consult references 9–11 which contain extensive citations to the original literature, both for pressure-induced shifts of energy levels and for electronic transitions.

Energy level shifts

The usual method of measuring differences of energy levels in insulators and solids is by optical absorption. As discussed below, it is important in interpreting and applying optical data to remember the restrictions on optical processes (Franck-Condon effect, selection rules *etc.*) relative to thermal processes. Shifts of electronic energy levels as observed optically are reviewed in some detail in references 9 and 11: five categories will be mentioned here.

Changes in the gap between the top of the valence band and the bottom of the conduction band (the absorption edge) with pressure are affected by two processes. Broadening of the bands tends to decrease the gap. The relative shifts in energy of the bands may augment or oppose this effect. In some cases decreases in gap of the order of an electron volt ($1 \text{ eV/atom} \approx 23 \text{ kcal/gram-atom} \approx 8000 \text{ cm}^{-1}$) are observed for a pressure increase of 100–150 kilobars. These shifts may ultimately lead to band overlap and metallic behaviour.

Impurity centres in alkali halides and related ionic crystals have also been extensively studied. The most thoroughly investigated is the F centre—an electron trapped in a halide ion vacancy. With increasing pressure the volume of the hole decreases and the energy of excitation increases. One finds, in fact, that the simple 'particle in a box' analysis gives a reasonable first approximation to the energy change.

An electronic process of more direct interest to chemists is

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