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Pressure and Electronic Structure

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Experimentation at high pressures is essential to an understanding of the electronic structure of solids.

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Two of the basic properties which help determine the electronic structure of solids are the arrangement of the atoms (or ions) and the equilibrium interatomic distance. Pressure is a variable of prime importance for determining these two parameters. Experimentation at high pressures is, then, significant because it permits one to test theories where the variation of a property with interatomic distance is critical and because, on occasion, new polymorphic forms appear which permit one to study the relationship between atomic arrangement and electronic properties.

The range of pressure to be used depends on the type of measurement to be made, the degree of accuracy to which the data (and the pressure) must be known, and the degree of hydrostaticity required. The recent book *Solids Under Pressure* (1) gives a general review of experiments in this field. Techniques are discussed in a review article by Swenson (2) and in the book by Wentorf (3).

In this article I review some exploratory experiments on optical absorption and electrical resistance at relatively high pressures—in the optical work, to 160 kilobars (1 kilobar = 0.986 at-

mosphere); in the electrical measurements, to over 500 kilobars.

The pressures, especially in the electrical work, are rather imprecisely known. A complete understanding of the electronic structure would require a much wider variety of experiments. In particular, accurate knowledge of the interatomic distance as a function of pressure, and of the structure and lattice parameters of the new phases which appear at high pressure, would be desirable. Nevertheless these experiments have contributed to the understanding of a variety of problems and have unearthed a large number of new and interesting phenomena. I have selected a few illustrations which give some notion of the power and versatility of the techniques.

The energy states of an electron on a free atom or ion can be described in terms of its four quantum numbers. The lowest of these states is the ground state. These states are determined experimentally either by measuring the absorption of (usually electromagnetic) energy or by the emission of energy as an excited electron returns to the ground state. In this discussion we are concerned only with outer electrons, generally called valence electrons because they are involved when chemical reaction takes place. Only the ground state and the excited state nearest above

it are important in the phenomena considered here.

When an atom or ion appears in a crystal, the electronic energy states are affected to a degree which depends on the interaction between the wave functions which describe the state in question and the wave functions of the other electrons in the crystal.

Both the ground state and the excited state may remain closely associated with the original atom. In this case, the energy states may be perturbed by the potential of the surrounding atoms and affected, because this potential has less than spherical symmetry. The optical absorption which represents transitions from the ground state to the first excited state still shows discrete peaks, perhaps somewhat broadened by the interaction described. In some cases, a single peak in a free ion may be split into two or more peaks in the crystal. This sort of effect can be observed in transition-metal ions in crystals, or in the spectra of some crystals of fused-ring aromatic compounds. An impurity in an insulating crystal may have highly localized states. The phosphor made by dissolving the Tl^+ ion in alkali halides is an example. Since, in both the ground state and the excited state, the electron is highly localized, one obtains no electrical conductivity in such systems.

As the wave function becomes a little more delocalized it is no longer practical to think of slightly perturbed atomic levels. Solution of the Schrödinger equation to determine the periodic potential of the lattice gives what is known as a Bloch function. This is of the form

$$\psi = u(r) \exp(i\mathbf{k} \cdot \mathbf{r})$$

where $u(r)$ has the symmetry of the lattice and the exponential expression represents a wave motion. Vector \mathbf{k} is a reciprocal lattice vector which is called the crystal momentum since $\hbar\mathbf{k}$ represents the momentum of the wave. Solution of the wave equation indicates that there are bands of closely spaced allowed states separated by relatively

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