

The author describes how, by providing precise and controllable means of varying the density of materials and by inducing crystal-structure changes, pressure can help to increase our understanding of the properties of solid materials.

High Pressure as a Research Tool for Solid-State Physics

by PAUL J. FREUD

SOLID-STATE PHYSICS encompasses the study of the diverse properties that characterize solids. Such properties as electrical conductivity, heat capacity, magnetism, electromagnetic interactions, thermal conductivity, and thermoelectricity are just a few. Three basic questions dealt with in solid-state physics can be stated as follows: (1) How do the atoms make up a lattice? (2) How do the electrons in the atoms interact with the lattice and each other? (3) How do the electrons and the atoms deviate from their equilibrium states in the lattice, including their behavior in the presence of electrical, magnetic, or thermal fields?

Many tools are available for studying solids in order to provide answers to these questions. X-ray diffraction studies can determine the crystal structure of solids and show how the different atoms are arranged to form a lattice. Increasing the temperature causes a greater deviation of the atoms from their equilibrium positions in the lattice, and the effect on the lattice and on the electrons in the lattice can be studied. The environment of the lattice can be changed by applying electrical, magnetic, and thermal fields, and the effect of this change on the lattice and the electrons can be investigated. The application of high pressure to solids is another tool that can be used in answering these questions.

HIGH-PRESSURE REGIONS AND THEIR USEFULNESS

To be able to determine the effect of pressure on solids, the changes produced obviously must be large

enough to measure. This criterion defines the term "high pressure" when applied to the study of solids. The compressibilities of solids are in the range of $1 \times 10^{-4}(\text{kb})^{-1}$ to $50 \times 10^{-4}(\text{kb})^{-1}$, where a kilobar = 14,500 psi. Applying 1 kb of pressure to a solid would result in a volume change in the range of 0.01 to 0.5 percent. Therefore, for solid-state research, high pressure implies a pressure in the kilobar-plus region.

Three regions of high-pressure generation are available.¹ The first, the hydrostatic region (0-30 kb), is employed for the most precise measurements. Pressure may be generated in this range by compressing a fluid; since a fluid cannot transmit shear forces, the effect on a solid immersed in the fluid is a simple reduction in volume with no distortion of crystal structure. The range of attainable fluid pressures is generally limited by the freezing pressure of the fluid.

The second region is usually called the ultrahigh-pressure region. In this case, the pressure-transmitting medium is a solid, and hence the pressure transmitted is only quasi-hydrostatic—i.e., there is some shearing of the solid immersed in the medium. The solid medium usually is compressed in a die by two opposed pistons. One such device is a cylindrical die into which two cylindrical pistons are inserted. The die is filled with a material of low shear strength, such as pyrophyllite—a soft machinable micaceous aluminum silicate—and the solid to be studied is immersed in this material. The pressure range available with solid-media devices is 0-300 kb.

The highest attainable pressures are produced by the use of shock waves. A shaped explosive is deto-

$E_g = f(V, T)$ Energy gap is a function of volume and temperature

$$\left. \frac{\partial E_g}{\partial T} \right)_p = \left. \frac{\partial E_g}{\partial T} \right)_v + \left. \frac{\partial E_g}{\partial V} \right)_T \frac{\partial V}{\partial T}$$

$$= \left. \frac{\partial E_g}{\partial T} \right)_v + \left. \frac{\partial E_g}{\partial p} \right)_T \frac{\partial p}{\partial V} \frac{\partial V}{\partial T}$$

$$= \left. \frac{\partial E_g}{\partial T} \right)_v + \left. \frac{\partial E_g}{\partial p} \right)_T \beta / K$$

(1) $\left. \frac{\partial E_g}{\partial T} \right)_p$ = the change of E_g with temperature at constant pressure

(2) $\left. \frac{\partial E_g}{\partial T} \right)_v$ = the change of E_g with temperature at constant volume

(3) $\left. \frac{\partial E_g}{\partial p} \right)_T$ = the change of E_g with pressure at constant temperature

K = compressibility

β = coefficient of thermal expansion

Fig. 1. Contributions to the Variation of Energy Gap (E_g). Term 1 on the left side of the equation and term 3 on the right are experimentally measured quantities. Terms 2 and 3 are the quantities of theoretical interest, for they determine the change of the band structure of a semiconductor as a function of volume and of temperature. Only through the use of high pressure can these values be determined.

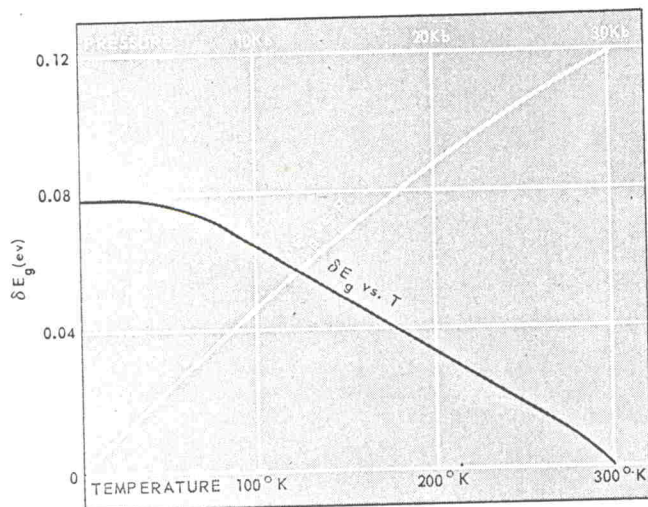


Fig. 2. Variation of Semiconductor E_g of Germanium as a Function of Pressure and Temperature. The curve δE_g vs P shows the increase in E_g as the hydrostatic pressure is increased. The curve δE_g vs T indicates the decrease in E_g as temperature is increased. The changes are relative to a value of $E_g = 0.66$ eV measured at room temperature and at one atmosphere of pressure.

nated near the material to be studied. This generates a wave of high compression that passes through the material in a matter of microseconds. By measuring the shock wave velocity and the particle velocity of the material as the wave passes through it, the pressure and density of the material can be calculated. Pressures in the megabar range can be produced using this technique, and the basic relationship of pressure, temperature, and density of solids can be determined.

The usefulness of high pressure is twofold. First, it provides a precise and controllable means of varying the interatomic spacing or density of the crystal lattice and thus of varying all properties of a solid that depend on density. When a property of a solid is explicitly dependent on density, the use of high pressure to vary the density is required to investigate this dependence. However, the properties of a solid often are not explicitly expressed in terms of density, and the dependence is only implicit through other parameters, as is illustrated in the second example below. In these cases, pressure provides a means for varying these parameters. By measuring parameter variations in independent experiments, the dependence of a property on these parameters can be examined. Thus, through the use of high pressure, a controlled and continuous variation of the properties of solids can be achieved.

Second, high pressure can be used to change the crystal structure of certain solids. Many solids are polymorphic—i.e., they may have more than one atomic array for a given composition. When subjected to high pressure, some of these solids transform to a new crystal structure. This polymorphic character of solids permits the study of the properties of a chemical substance under conditions of variable crystal structure.

These two uses of high pressure can be applied in many of the branches of solid-state research. The following section will discuss three specific examples of high-pressure research that utilize the ideas expressed above.

SEMICONDUCTOR ENERGY GAP

One of the important parameters that characterize a semiconductor is the energy gap (E_g). Its value determines, among other things, the temperature dependence of the resistance of the intrinsic material, the characteristics of diodes made of the material, and the optical absorption of the material. It is known that the value of E_g depends on temperature,² and this dependence can be measured readily. A partial explanation of this dependence is that the electrons of