

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

$$\begin{aligned} \left(\frac{\partial E_g}{\partial T}\right)_p &= \left(\frac{\partial E_g}{\partial T}\right)_v + \left(\frac{\partial E_g}{\partial V}\right)_T \frac{\partial V}{\partial T} \\ &= \left(\frac{\partial E_g}{\partial T}\right)_v + \left(\frac{\partial E_g}{\partial p}\right)_T \frac{\partial p}{\partial V} \frac{\partial V}{\partial T} \\ &= \left(\frac{\partial E_g}{\partial T}\right)_v + \left(\frac{\partial E_g}{\partial p}\right)_T \frac{\beta}{K} \end{aligned}$$

(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.

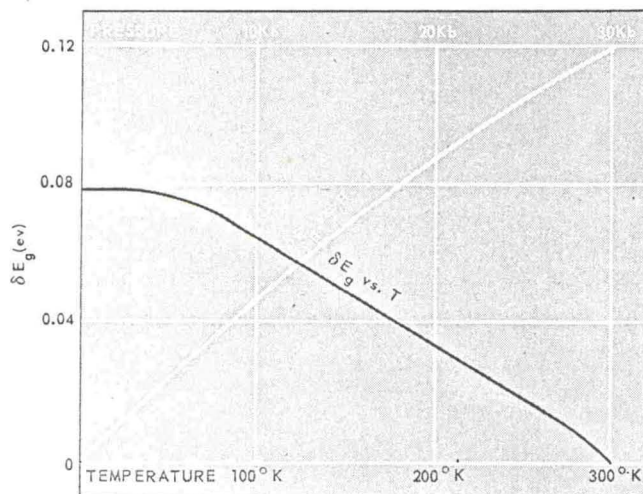


Fig. 2. Variation of Semiconductor E_g of Germanium as a Function of Pressure and Temperature. The curve δE_g vs P shows the increase in E_g as the hydrostatic pressure is increased. The curve δE_g vs T indicates the decrease in E_g as temperature is increased. The changes are relative to a value of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

the semiconductor interact with the lattice vibrations and cause a shift in the energy bands that determine E_g . As the temperature increases, the lattice vibrations become stronger, and E_g changes. The temperature increase also causes the lattice to expand and the energy gap to change.³ To separate the two possible causes of the temperature dependence, a high-pressure experiment is required to determine how the energy gap varies with volume. When this value is known, the total temperature dependence of the energy gap can be separated into the portion due to the temperature increase and that due to the volume increase associated with the thermal expansion, as expressed in mathematical terms in Figure 1. The pressure and temperature dependence of the energy gap for germanium is illustrated in Figure 2.

PRESSURE DEPENDENCE OF THE THERMOELECTRIC POWER OF GERMANIUM

The use of high pressure to vary the parameters that describe a particular phenomenon is illustrated by recent research findings on the thermoelectric power (T.E.P.) of germanium.⁴ The T.E.P. of germanium exhibits a marked increase below 150 K because of the "phonon drag" effect, a phenomenon caused by the interaction of the electron (or hole) electrical current with the lattice heat current. The theory of this phenomenon indicates a definite dependence on three parameters: μ , the carrier mobility; m^* , the effective mass of the current carriers; and c , the elastic constant.⁵ Values for the pressure dependence of these parameters have been measured and reported in the literature; the theory of the phonon drag effect and the experimental results of the pressure dependence can be compared directly, as shown in Figure 3.

In this study, measured values for *p*-type and *n*-type germanium were compared with the values calculated from the theoretical expression. The results show an agreement between the calculated and measured pressure dependence, indicating that the theoretical treatment is correct to within the accuracy of the experiment.

POLYMORPHISM

The third example of high-pressure research of interest in solid-state physics involves the creation of new forms of materials through polymorphic phase transitions. Under conditions of high pressure and sometimes elevated temperature also, many solids change crystal structure and exhibit new and interesting properties. The most spectacular demonstration of

$$Q_{ph} = f(m^*, \mu, c)$$

Phonon drag contribution to the thermoelectric power is a function of the variables m^* (the effective mass of the current carriers), μ (carrier mobility), and c (the elastic constant).

The change with pressure of Q_{ph} can be expressed in terms of the change with pressure of the variables m^* , μ and c .

$$\frac{dQ_{ph}}{dp} = \frac{\partial f}{\partial m^*} \frac{\partial m^*}{\partial p} + \frac{\partial f}{\partial \mu} \frac{\partial \mu}{\partial p} + \frac{\partial f}{\partial c} \frac{\partial c}{\partial p}$$

$\frac{dQ_{ph}}{dp}$ is the quantity measured in the experiment.

$\frac{\partial m^*}{\partial p}$, $\frac{\partial c}{\partial p}$, $\frac{\partial \mu}{\partial p}$ are measured in independent experiments.

$\frac{\partial f}{\partial m^*}$, $\frac{\partial f}{\partial c}$, $\frac{\partial f}{\partial \mu}$ are derived from theory.

Experimental and theoretical values of $\frac{dQ_{ph}}{dp}$ are then compared.

$$\left(\frac{dQ_{ph}}{dp}\right)_{\text{experiment}} \quad ? \quad \left(\frac{dQ_{ph}}{dp}\right)_{\text{theory}}$$

Fig. 3. Pressure Dependence of Thermoelectric Power. The analysis shows how the theoretical expression for the phonon drag contribution to thermoelectric power is used to derive the pressure coefficient of Q_{ph} using the pressure coefficients of parameters that are measured in independent experiments. This derived pressure coefficient is then compared with the experimentally determined pressure coefficients of Q_{ph} .

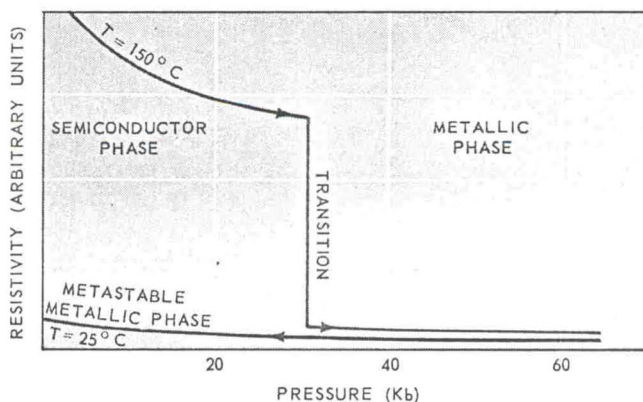


Fig. 4. A Plot of the Resistivity vs Pressure of Indium Telluride. The increasing pressure cycle at 150 C is shown by the upper curve, in which the transition from semiconductor phase to metallic phase is indicated by the sharp drop in resistivity at 30 kb. The lower curve shows the retention of the metallic phase in a metastable state when the pressure is released at 25 C.



Paul Freud's primary research interest has been the investigation of the effects of pressure on the charge transport characteristics of materials. Much of his effort has been directed to the study of charge transport in metal oxides, which have properties similar to those of typical semiconductors. Dr. Freud has been associated also with a series of studies on the effects of high pressure on the properties of a broad spectrum of materials. He received his Ph.D. degree in physics from Rutgers.

this phenomenon is provided by the high-pressure production of diamonds. Here carbon changes from one of the softest solids (graphite) into the hardest. Bismuth, a semimetal, undergoes four crystal structure changes as the pressure is increased from zero to 100 kb, while germanium, a semiconductor, becomes a metal at high pressure. Recent investigations of a number of intermetallic compounds have revealed transformations similar to that of germanium.

In the case of indium telluride, a compound investigated at Battelle-Columbus⁶ and elsewhere,^{7,8,9} it is found that the high-pressure and low-pressure forms of the compound have remarkably different properties. The low-pressure form shows typical semiconducting behavior, but the high-pressure form exhibits good metallic conductivity. The metallic form of InTe can be retained metastably if the pressure is released at room temperature or below, allowing one to study the new form at ambient pressure in this metastable condition. The pressure dependence of the resistivity is plotted in Figure 4, showing the transition from semiconductor to metal at 30 kb.

In addition to being a good metal, the high-pressure form of InTe has other interesting properties. At 3.3 K the high-pressure form becomes a superconductor. If the atomic ratio of indium to tellurium in the starting material departs from one, the superconducting transition temperature can be reduced to as low as 1 K.⁹

The nuclear magnetic resonances of the In and Te nuclei in the environment of the new crystal structure

have been studied,¹⁰ leading to the discovery that the nuclear resonances in the new environment showed anomalously large shifts and broad line widths that are of important theoretical interest.

Thus, through the use of high pressure to induce polymorphic phase transitions, a means is available for preparing a solid with a variety of crystal structures.

High pressure can be a useful tool in the investigation of solid-state phenomena. To determine a specific volume dependence, a high-pressure experiment is essential. The properties of a solid can be varied in a controlled way by means of high pressure, and the interdependence of various properties can be determined. Finally, by using high pressure to induce polymorphism, typical of many solids, studies can be made of the properties of a solid in various crystal structures.

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The physical sciences and engineering, though they may have started independently . . . have now been so intertwined and integrated, and the physical sciences themselves so advanced, that given an applied goal in engineering, there is often nothing but money that stands in the way of achieving the goal, provided basic science has shown this goal to be achievable.

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