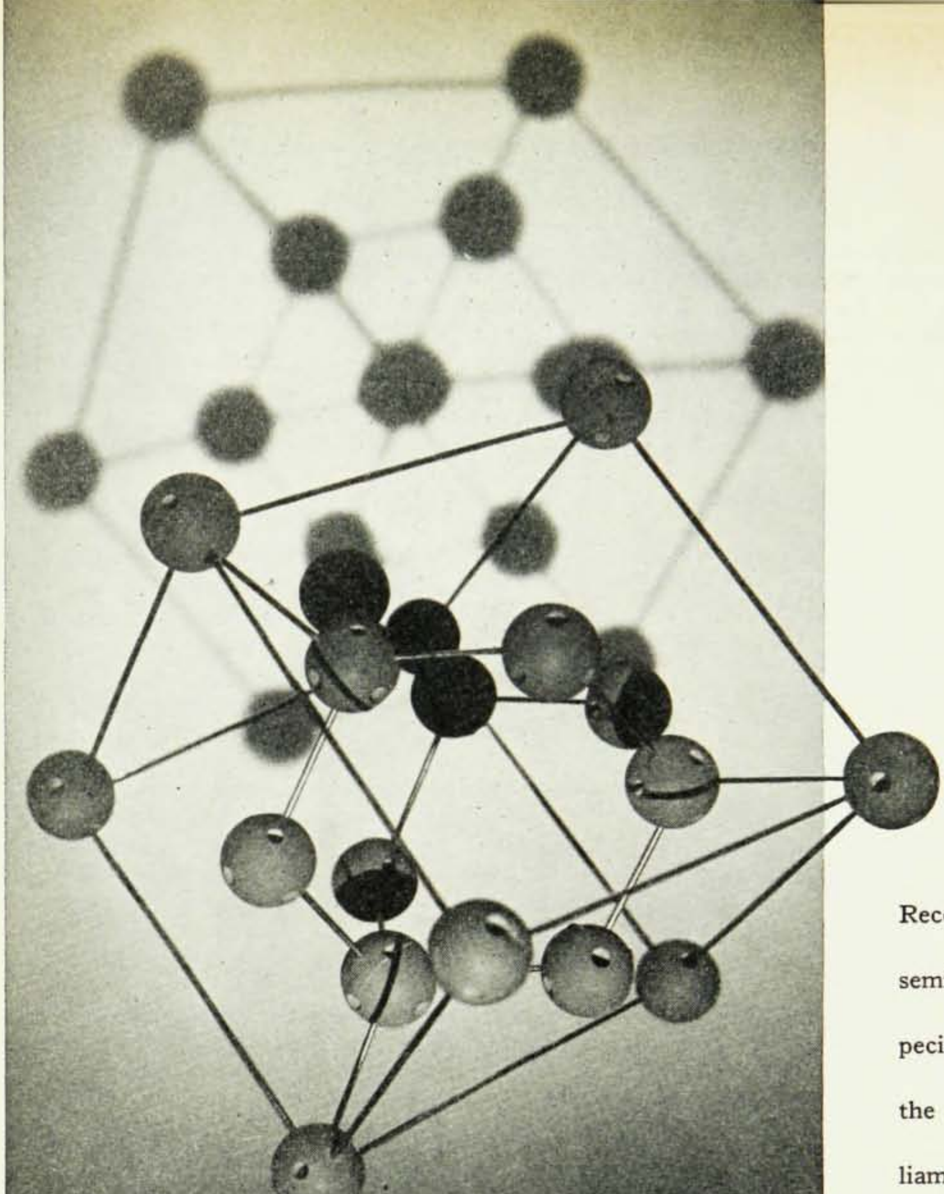

Silicon and germanium, characterized by the diamond lattice in which each atom is tetrahedally bonded to four nearest neighbors, have played a major role in solid state electronics. Study of the motion of electrons in structures of this type has led to a better understanding of the nature of semiconductors.

SOLID

Recent developments in semiconductor physics, especially the discovery of the transistor (See William Shockley's article, *Holes and Electrons*, in the October, 1950, issue of *Physics Today*), have greatly stimulated the entire field of solid state electronics. The present article reviews recent work in this subject at the National Bureau of Standards.

STATE ELECTRONICS

By Robert G. Breckenridge

The detailed study of matter in the solid state has become one of the most active fields of modern physics. Solid state electronics, including the study of semiconductors, was greatly stimulated by the wartime development of crystal diodes, which were extensively used in radar and are now finding numerous applications in electronic components. The recent discovery of the transistor, a crystal triode which may be used as a replacement for vacuum tubes in amplifiers, has intensified interest in the subject. Although the semiconductor has been used in several practical applications, physical interpretation of the semiconducting phenomena is far from complete. For this reason, the major current objective of the solid state physics program at the National Bureau of Standards concerns the fundamental study of semiconducting systems. Some closely related problems of crystal properties are also being investigated in order to obtain the knowledge necessary for the maximum utilization of these and other new materials in electronic components.

Electrons in Solids

Studies of electrons in free space and of their interactions with electromagnetic fields and isolated particles such as photons, atoms, or ions, have led to a rather complete picture of their behavior in these comparatively simple situations. The theoretical information so obtained is contained in the laws of quantum mechanics and is reflected in such subjects as atomic or molecular structure and physical electronics. Parallel with these fundamental studies there has been an enormous growth of applied electronics based on vacuum tubes and other devices using electrons in dispersed systems.

Vital parts of any electronic system, however, include components where the electrons are not free but are confined to solids. These range from wiring and resistors to rectifiers and photocells. Although some progress had been made toward a theory of conductivity in metals before the development of quantum mechanics there was no well-established picture of the mechanism of conduction that could explain the large variation in conductivity encountered in passing from metals through semiconductors to insulators or the variety of other effects observed. One of the major triumphs of quantum theory has been the fact that such a picture can be suggested even though the behavior of electrons in a solid presents a difficult problem which cannot be considered completely solved.

The practical aspects of solid state electronics have provided a constant stimulus to further study. This has resulted in the development of a number of solid state electronic devices including such diverse accomplishments as the galena or lead sulphide crystal detector of the earliest days of radio and the phosphor in the screen of a television set. The first of these, the galena crystal detector, makes use of an extremely interesting phenomenon found at many semiconductor-metal contacts. It is frequently observed that current flows through such a junction much more readily in one direction than

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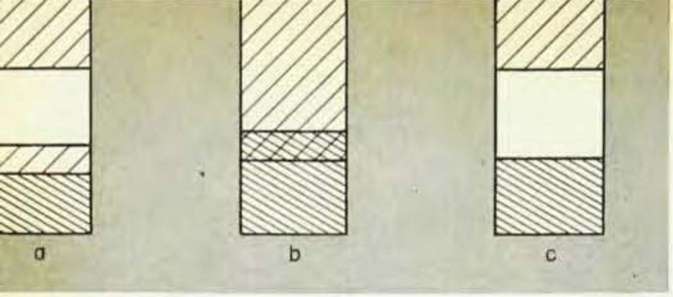

Figure 1. Typical Energy Bands in Solids

the other; that is, the junction rectifies. While the galena crystal was promptly replaced by vacuum-tube detectors because of its unreliability, it had inherent features that contained the germ of eventual success. For example, no filament or heated cathode is needed, with a consequent saving of power and elimination of undue heating; no warm-up time is needed; and finally, the device can operate at very high frequencies.

A much more successful solid state electronic device that has been known for some time is the copper oxide power rectifier. This rectifier—similar in principle to the galena crystal detector—is designed to rectify considerable amounts of low-frequency power rather than small amounts of radio-frequency power. This unit and the selenium and magnesium-copper sulphide types developed later showed the practical nature of dry rectifiers and served as a great stimulus to the study of electrons in solids. During World War II the crystal diode was perfected for use in microwave radar. This development, which used silicon or germanium instead of lead sulphide, contributed greatly to the understanding of semiconductors. A very important result of this work was the solid state triode, the transistor, which was discovered by Bardeen and Brattain of the Bell Telephone Laboratories.

The phenomenon of rectification is not the only interesting property of electrons in solids. According to present theory, a free electron can move in a perfectly regular periodic crystal without being deflected. At temperatures above absolute zero the thermal vibrations of the lattice disturb the regularity so that electrons are scattered as they move through the structure and thus the material has a finite resistivity. Disturbances of the structure by vacant lattice sites or foreign atoms also affect the motion of electrons, which may be scattered by the imperfection or may become trapped by its electrical field. Such trapped electrons have optical absorption bands in the visible region for alkali halide crystals and the study of these so-called "F centers" has provided some of our most detailed information about electrons in crystals. Such trapped electrons are important to the luminescence of materials. Similarly, optical absorption in semiconductors provides the basis for some types of photocells. Another closely related effect results in the use of crystals as counters for high energy nuclear particles.

Band Theory of Solids

The theoretical model that may be used to provide a picture of all these phenomena is known as the band theory of solids. When isolated atoms or ions are brought close together to form a perfectly regular crystal lattice, their discrete allowed electron energy levels become broadened by interaction effects. The resulting allowed energy bands for a crystal may be widely separated by unallowed energy states or they may overlap; the bands may be filled with electrons, partially filled, or empty. These different band structures can be directly correlated with differences in electrical properties.

In Figure 1a, the lower allowed band of energies is only partially filled, and there are allowed states available to an electron, differing only slightly in energy from those already occupied. If an electric field is applied to a solid with this band structure, an electron at the top of the filled states may acquire enough energy from the electrical field to enter one of the empty, allowed states above it and become free to move in the field direction. This is the mechanism of electronic conduction in a crystal. This picture applies to the alkali metals, which have only one valence electron in an outer s state. Since two electrons may be in the same s state, the band is just half full.

In Figure 1b, the allowed bands overlap—a condition actually believed to be typical of all metals. For the alkaline earth metals, the s band is completely filled, since there are two s electrons, but the p band of next higher energy overlaps the s band so that an electron may be accelerated as before. The alkaline earth metals are thus electrically conductive. In Figure 1c, the lower band is completely filled and is widely separated from the next allowed band. A crystal with this band structure is an insulator.

The behavior of semiconductors may also be explained with the aid of the band picture as suggested by A. H. Wilson. Three possible cases are represented in Figure 2.

An intrinsic semiconductor, one that behaves as a semiconductor even when no impurities are present (Figure 2a), has an energy gap ΔE comparable to kT between the completely filled band and an empty allowed band, so that electrons may be thermally excited from the filled to the empty band. When this happens, not only are the excited electrons accelerated by the field, but, since there are now a few empty allowed states in the normally filled band, the remaining electrons may be accelerated as well. The situation is analogous to a filled checkerboard on which no moves are possible until a piece is removed. This mechanism, in which the electron vacancy behaves like an electron with an effective positive charge, is known as "hole" conduction. Such intrinsic semiconduction is usually only found at rather elevated temperatures.

Most semiconductors depend for their conductivity

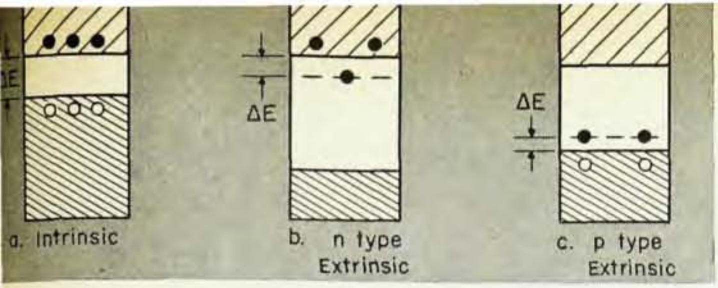

Figure 2. Energy Bands in Semiconductors

on impurities within the crystal lattice; that is, they are extrinsic semiconductors. Figure 2b indicates a possible effect of adding an impurity to a crystal that would normally be an insulator. The foreign atoms introduce new isolated energy levels into the band diagram. In Figure 2b, these levels are at a small distance ΔE_1 below the empty band. If ΔE_1 is comparable with kT, the foreign atoms may ionize and provide electrons in the conduction band. Impurities of this sort are called "donors". This material is thus an "*n*-type" semiconductor, which indicates that the sign of the charge carriers is negative.

The third type of semiconductor in Figure 2c is the converse of that just described. The impurity levels are close to the filled band, and may be ionized by accepting an electron from the filled band leaving a hole in that band. Conduction is then by holes, and the name "*p*-type" indicates the positive sign of the charge carriers. Impurities of this sort are known as "acceptors". New levels or irregularities may be introduced into the characteristic bands of the perfectly regular, infinite crystal, not only by foreign impurities or excess atoms of one constituent of the crystal, but also by the presence of free surfaces and lattice defects. Such disturbances may have a great influence on the electrical properties of the crystal.

While the concept of bands in crystals may seem somewhat abstract, it is possible in some simple cases to give a more concrete physical picture of the situation. For example, silicon and germanium crystallize in the diamond lattice in which each atom is tetrahedrally bonded to four nearest neighbors. Each bond consists of a shared pair of electrons, and these electrons in their normal unexcited state constitute the filled band. If an atom with a normal valence of 5, say arsenic, is introduced into the lattice, four of its valence electrons may be used to form shared-pair bonds with its neighbors; the fifth, however, may be thermally released, ionizing the atom. The electron then becomes free to move in the lattice and conduct a current. This is the situation indicated in Figure 2b. Similarly, the addition of a trivalent atom such as aluminum causes a disturbance in the electronic structure because only three shared electron-pair bonds may be formed to neighbors. If an electron is drawn from some other bond in the lattice to complete the tetrahedral bonding around the aluminum, i.e. ionizing the aluminum, there results an electron deficiency in the structure or, in terms of the band picture, a hole in the filled band which of course can move from atom to atom. These same energy-level diagrams may be used to explain rectification at metal-semiconductor contacts and the various photo effects although the details are more complicated.

The work in solid state electronics at the National Bureau of Standards is centered on a basic study of the properties of a few interesting semiconducting materials. Related problems dealing with lattice defects in crystals are also being investigated since, as indicated above, the defects may have a marked effect on the crystal properties.

Experimental Investigations

The experimental study of the electrical properties of solids usually involves the investigation of conductivity and the Hall coefficient. From the variation of these quantities with temperature and other parameters, it is possible to obtain the information needed to understand the mechanism of conduction in the crystal and to evaluate the material for use in practical electronic devices. This information includes the number of charge carriers n, their sign, their mobility u, and the activation energy, E, for conduction.

In a typical experiment, the conductivity, σ, is found from a measure of the potential drop along a sample of regular shape while a current is flowing through it. A measure of conductivity alone, however, is not sufficient to determine n and u separately since the product of n and u is contained in σ. The necessary additional information is obtained from the Hall effect, discovered in 1897 by E. H. Hall. Hall observed that when a conductor in which a current is flowing is subjected to a magnetic field perpendicular to the current direction, charge carriers tend to migrate toward one side of the conductor producing an electric field. This effect is represented schematically in Figure 3.

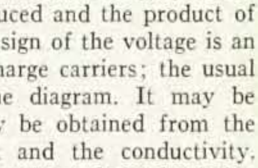

Figure 3. Hall effect. When a conductor carrying a current of density J_x is placed in a magnetic field (B_z) at right angles to the current, a voltage (E_y) is developed in a direction perpendicular to both J_x and B_z.

The Hall coefficient R is the constant of proportionality between the voltage produced and the product of current and field strength. The sign of the voltage is an indication of the sign of the charge carriers; the usual convention is indicated on the diagram. It may be shown that the mobilities may be obtained from the product of the Hall constant and the conductivity. Theoretical expressions have also been derived relating the mobility of electrons to their mean free path and giving the number of charge carriers as a function of temperature.

The activation energy for conduction, E, is obtained from the temperature variation of R and σ. This information also may be used to obtain the energy gaps shown in the band pictures. The measure of the Hall coefficient and conductivity as functions of temperature are ordinarily made simultaneously over as wide a temperature range as is convenient. An apparatus of conventional design for studies of this type using direct current has been assembled at the National Bureau of Standards. Typical results of such measurements on germanium are shown in Figure 5. While the properties of germanium at normal temperature have been studied in a number of laboratories, work is in progress at the Bureau to determine the suitability of germanium for use as a resistance thermometer at very low temperatures.

An important portion of the semiconductor work at the National Bureau of Standards has been concerned with the properties of titanium dioxide in the form of rutile single crystals and ceramics. When pure and of exact chemical composition, this material is an excellent insulator, the energy gap in Figure 1c being *ca.* 3.6 electron volts. It may be made into a semiconductor by the addition of foreign ions or by treatment with hydrogen at high temperatures to cause a loss of oxygen and consequently an excess of titanium in the lattice. When prepared in this latter way, it is an n-type semiconductor (Figure 2b), with properties that show promise for practical applications.

Another material under study at the Bureau is "grey" tin, which is a low-temperature form of ordinary or "white" tin, having the same crystal structure as silicon or germanium. Recent studies in other laboratories have shown that it is a semiconductor with a very low activation energy and a high mobility both of holes and electrons. Precise measurements of these quantities are not yet available because of the difficulty in preparing a sample in a form suitable for measurement. The work thus far indicates, however, that the substance will be of considerable theoretical and practical importance when the problems of its preparation are solved.

Lattice Defects

As mentioned above, defects in crystal structure may serve as electron traps or scattering centers, and may thus have a great influence on the electrical properties of solids. Although some type of lattice defect seems to be present in all real crystals, the situation is most clearly understood in ionic crystals. The mechanism of the observed ionic conductivity in the alkali halide crystals is difficult to explain on the basis of the perfectly regular lattice indicated by x-ray studies, since the field strengths at which conduction is observed are much smaller than that needed to move an ion from a lattice site. It was suggested by Frenkel that when the crystal is in thermal equilibrium, a number of ions have actually left their sites and migrated to interstitial positions in the lattice, leaving behind a vacant site. The crystal is still electrically neutral because the charge of the interstitial ion is compensated for by the charge of opposite sign at the vacant site. An alternative suggestion by Schottky and Wagner assumes that the crystal contains equal numbers of positive and negative ion vacancies. These two explanations are indicated schematically in Figure 4.

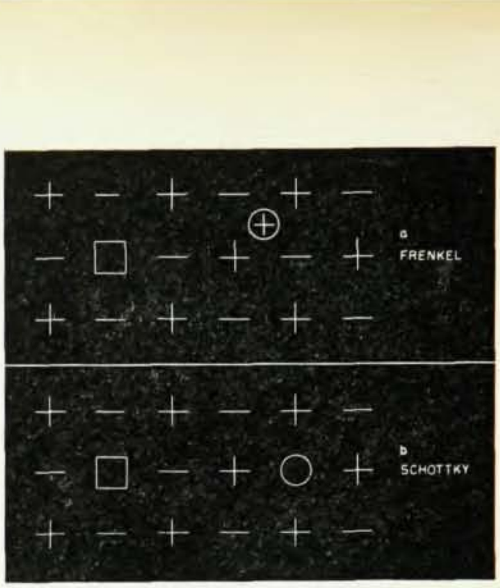

Figure 4. Lattice Defects in Ionic Crystals.

Either mechanism may be used to explain ionic conductivity, since the vacancies or interstitial ions can migrate under the influence of the field; but there are some differences between them. The Frenkel defect can carry charge either by the motion of the interstitial ion or of the vacant site, while in the Schottky case only vacancies are present. Frenkel defects may be formed anywhere in the crystal, but Schottky defects form only at free surfaces and then diffuse into the interior of the crystal.

The number of these defects in thermal equilibrium in a crystal can be calculated from the increase in entropy on distributing n defects on N lattice sites. The mobility of the defects may be calculated in terms of the activation energy required to move the vacancy to

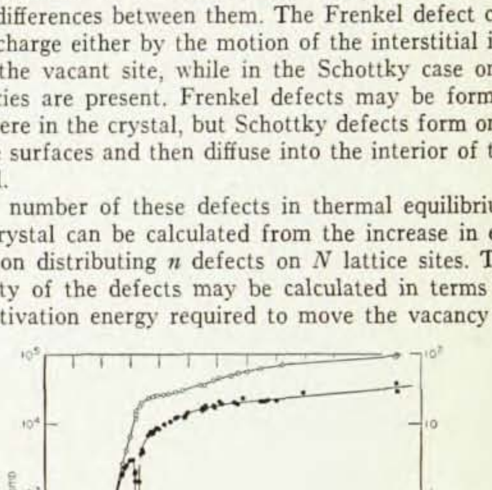

Figure 5. Typical results of measurements of Hall coefficient and resistivity, in this case for p-type germanium containing 0.001 percent of aluminum. These measurements were made at the Bureau to determine the suitability of germanium as a resistance thermometer at very low temperatures.

an adjoining site in the lattice. In finding the number and mobility of the defects, just as in the electronic case, the conductivity alone does not provide enough information. Unfortunately, reliable Hall effect measurements are not obtainable because of the very low mobility of the ions, so alternative methods must be used.

One method, suggested by Koch and Wagner, is to make the number of defects independent of temperature by the addition of a divalent ion impurity. To preserve electrical neutrality, a positive ion vacancy is formed for each divalent ion in the lattice. The variation of the conductivity with temperature then depends only on the mobility, so the activation energy may then be found. There is some question, however, whether the assumption that each divalent ion produces a positive ion vacancy is completely correct, since any clustering of the foreign ions would modify the neutrality requirements and the degree of aggregation would be expected to change with temperature. This is particularly true when relatively large amounts of the foreign ion are present.

Another method of investigation has been proposed by Breckenridge. In a study of the dielectric loss of crystals that had been heat-treated to introduce relatively large numbers of defects, and of crystals containing divalent foreign ions, dielectric loss maxima were found at certain frequencies and temperatures which were attributed to a relaxation process due to the reorienting of pairs of defects in the a-c field. These defect pairs are formed by the electrostatic attraction between vacancies of opposite sign or between divalent impurity ions and vacant sites. The height of the dielectric loss maxima can be related to the number of paired vacancies and the activation energy for pair reorientation can be found from the temperature and frequency at which the maximum loss is found. This method, of course, does not give the activation energy for moving single vacancies directly, the value for pairs being appreciably less than for single vacancies. The degree of association of the defects is not known precisely either, so that information about the number of single defects cannot be found directly in this manner.

In spite of the difficulties involved in the studies, it seems reasonably certain that the lattice defects present in the alkali halides are of the Schottky type while those in the silver and thallium halides are of the Frenkel type. In general, the available evidence suggests that in a typical alkali halide crystal there are about 10^{15} or 10^{16} vacancies per cubic centimeter, i.e., a mol fraction of 10^{-5} or 10^{-6}, and that the activation energy for the migration of a vacancy is of the order of 0.7 electron volt while the energy to form a Schottky defect is about 2.5 to 3.0 electron volts. For the silver halides, the fraction of defects is somewhat greater while the activation energies are somewhat smaller. These results are also in rough agreement with the experiments on the density of electron traps in these crystals. The methods previously used for the study of lattice defects apply only to ionic crystals with low conductivity, whereas much of the work of interest is being done on covalent crystals, such as diamond, or on conducting crystals such as germanium.

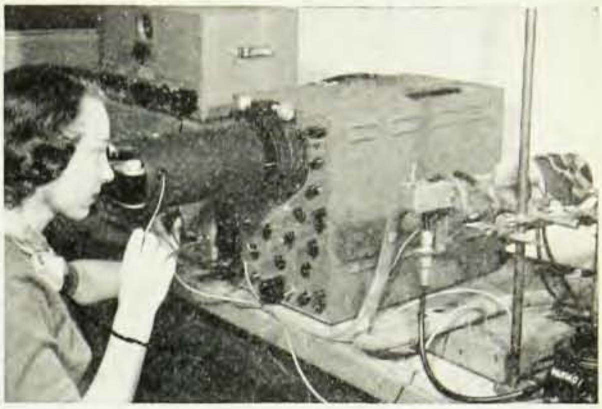

Figure 6. NBS scientists are using this specially designed apparatus for studying the internal friction of crystals. From measurements of the decay of free torsional oscillations of a composite piezoelectric resonator it is expected that the effects of crystal imperfections on semiconducting properties will be revealed.

A mechanical analogue of the measurement of dielectric loss is proving of considerable interest for the study of crystal imperfections and is under investigation at the National Bureau of Standards. In the Bureau's apparatus the internal friction in the crystal is studied by observing the decay of free torsional oscillations of a composite piezoelectric resonator which consists of a Y-cut quartz bar with the crystal to be studied cemented at one end. Plots of Q, the reciprocal of the elastic loss, as a function of temperature show maxima typical of a stress relaxation process in the crystal.

The interpretation of such processes in metallic crystals has been considered in detail by Zener, who showed that elastic stress relaxation with consequent absorption of energy can arise from a number of causes; thermal current flow, grain boundary diffusion, and atomic diffusion. Of these, the process of atomic diffusion should be the only one of interest in an ionic crystal.

Some preliminary values of activation energies for ion migration in ionic crystals have been obtained that are in excellent agreement with previous work by other methods. When the results are analyzed in greater detail, it may be possible to get considerable information about lattice defects. The method should be useful in the study of crystals not readily investigated by other techniques, e.g., the covalent and conducting crystals. In connection with this program, some studies are being made of the mechanical losses in quartz.

In addition to the fundamental investigations now underway, the Bureau plans to extend the work in solid state electronics to include optical, magnetic, and thermoelectric studies of crystals as well. Information obtained in these studies is expected to provide a clearer conception of the electronic character of solids. It is hoped that fundamental information on the properties of solids and the nature of the processes of conduction and rectification will be obtained from this program.