SYMPOSIUM ON THE MINERALOGY OF THE SULFIDES
THE PHYSICAL PROPERTIES OF SEMICONDUCTING SULFIDES, SELENIDES AND TELLURIDES

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ABSTRACT

Research leading to an understanding of the fundamental properties of materials is becoming more and more an area of common interest which brings together the viewpoints of the traditional scientific disciplines, such as physics or chemistry. In the case of solid state materials, many of the physical properties are intricately interwoven with chemical properties, crystallographic properties and the metallurgy of materials. This paper will discuss some of the interrelations between physical and chemical properties of a group of heavy metal sulfide compounds. Among the materials discussed will be PbS, PbSe, PbTe, CdS, Bi_2Te_3 and SnTe. Some of the methods and techniques used by the solid state physicist for studying semiconductors will be described along with details on specific physical properties of the materials.

INTRODUCTION

Research leading to an understanding of the fundamental properties of materials is an area of interest which is pursued simultaneously by several of the traditional scientific disciplines, such as physics, chemistry, and metallurgy. In the case of solid state materials many of the physical properties are intricately interwoven with chemical properties, crystallographic properties and the metallurgy of the materials. A comprehensive research program in solid state materials must therefore bring in the viewpoints of many different scientific disciplines for effective understanding of the properties of solids.

In the case of semiconductors the greatest interest concerns the behavior of the relatively free electrons and holes within the crystal. These charges may originate from two types of sources. First the electrons in the valence energy levels of the atoms of the crystal are but weakly bound to a given atom. The binding energy, or intrinsic activation energy, for these electrons is of the order of an electron volt or less. Thus the addition of energy in the form of heat or radiation of the proper wavelength can dissociate some of these electrons from lattice atoms so that they may contribute to the conduction process until they recombine once more. At the same time the vacancy in the electronic structure of the atom caused by the removal of the electron is also free to conduct. This charge is effectively positive and is called a hole. A semiconductor can conduct electric current at the same time by both positive and negative carriers. The concentrations of these carriers is a strong function of temperature, increasing rapidly with increasing temperature according to an exponential law.

The second and important source of charge carriers in a semiconductor crystal is the presence of certain crystal imperfections such as vacant lattice sites, foreign atoms of valence different from the normal atoms occupying lattice sites or interstitial positions, or normal atoms in interstitial positions. Each of these imperfections may contribute a conduction electron or hole to the crystal so that the concentration and kind of imperfection in the crystal plays an important role in the electrical properties of a semiconductor. The binding energy for these charges is an order of magnitude smaller than for the intrinsic electrons so that even at room temperature most of these electrons or holes are dissociated from their respective imperfections.

The laws governing the concentration of lattice defects and impurities in a crystal lattice and the ways in which the concentrations change with temperature or other environmental conditions are known to the specialist in fields of physical chemistry or chemistry. Their help is therefore needed in order to interpret and guide some of the experiments on semiconducting materials.

The movement of charges through the crystal lattice and their lifetime in conducting states is influenced among other things by dislocations, grain boundaries or polycrystalline structure. To account for the effect of these defects upon the electrical properties of a semiconductor the solid state physicist must refer to the work of the specialist in crystallography or metallurgy.

Hence we find that the solid state physicist, who has primary responsibility for understanding the various properties of semiconductors, must consult specialists in other areas of science in order to account for some of the phenomena observed in semiconductors.

The studies made on the heavy metal sulfides illus-

trate in an effective way the interdisciplinary nature of solid state research and the importance of bringing together as many different viewpoints as possible to understand the fundamental properties of materials. The materials to be discussed will be principally the lead compounds though other sulfides such as Cd and Bi compounds will be referred to when appropriate.

We shall first consider the composition of the semiconductor crystal and the possible role of lattice vacancies, foreign impurity atoms, and interstitial atoms upon the electrical behavior. Factors governing changes in concentration of these defects in the crystal will be discussed. This will then be followed by a detailed description of various measurements which the physicist makes to understand the behavior of semiconductors. Finally a few of the applications of sulfide semiconductors will be given.

Defects in Compound Semiconductor Crystals

Crystalline defects such as foreign impurity atoms in normal lattice sites may contribute electrons or holes to the conduction bands in semiconductors. In the case of the sulfides of lead certain elements such as Sn, Ge, Fe, Co, Ni, Pt, Mg, Nb and Bi contribute electrons to the conduction band making the crystal electron conducting or n-type. Similarly other elements such as Au, Ag, Cu, In, Al, Zn and Cd produce holes in the valence band making the crystal p-type. The concentration and kind of foreign impurity atoms in the semiconductor is directly related to the number of mobile electric charge carriers in the crystal and determines its electrical conductivity. In the case of compound semiconductors additional concentrations of electrons or holes may arise from the presence of point defects in the crystals such as ions missing from normal sites or occupying interstitial sites. In crystals of the pure compound these latter point defects are the chief source of electrons or holes in the conduction bands. The concentration of these defects in a crystal is a complicated function of temperature and the composition of liquid or solid phases of the compound in equilibrium with the crystalline phase.

In principle any real crystal of a compound may incorporate in its structure vacant sites from which the atoms or ions are missing or atoms occupying interstitial positions. Statistical theories predict that all ionic or covalent crystals should have finite concentrations of these defects at any temperature above 0° K., although these concentrations may be very small in some crystals. When these defects are predominantly of one atom or ion species, which is the
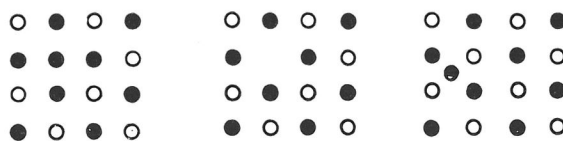
POINT DEFECTS IN A DIATOMIC CRYSTAL

Fig. 1. Types of defects in a diatomic crystal.

usual case, then the composition of the crystal will deviate from the ideal or stoichiometric chemical proportions of the compound. Generally the departures from the stoichiometric proportions are less than 1% since larger departures tend to distort and break up the crystal structure. A deviation of only 0.01% from the stoichiometric proportions in a binary compound semiconductor such as PbTe results in about 10^{18} conducting electrons or holes/cm³ in the crystal which is very high for a semiconductor. Thus we see that even very small departures from ideal stoichiometry are very important in determining the electrical properties of a compound semiconductor.

In a binary compound having the formula AB, stoichiometric deviations may be incorporated in the lattice in three ways. For the case where there is an excess of B atoms in the crystal, Anderson (1946) lists the following types of nonstoichiometric solids:

1. Substitutional: Extra B atoms replace A atoms on sites normally occupied by A atoms.
2. Subtractive: B atoms occupy normal B sites, but some A sites are vacant.
3. Interstitial: Extra B atoms occupy interstitial positions.

The three types of defects are illustrated in Fig. 1. In any real crystal all three types of defects could be present simultaneously, but generally one type dominates. It is possible to identify the important defect type on the basis of certain tests. In semiconductors with substitutional defects the crystal will be p-type with an excess of the cation, and n-type with an excess of the anion. On the other hand, with subtractive or interstitial defects the reverse is true; the excess cation crystal is n-type and the excess anion crystal is p-type.

A distinction between interstitial and subtractive defect solids can sometimes be made on the basis of careful x-ray and density measurements. Most nonstoichiometric crystals contain defects of the subtractive or interstitial types and only a few incorporate substitutional defects.

Substitutional crystals are likely to be intermetallic compounds in which ion repulsion is weak. Fur-

thermore, a difference in atom valency of unity is desirable. The compounds of the group Bi_2S_3, Bi_2Se_3 and Bi_2Te_3 show substitutional defects. For example, excess Te may occupy Bi sites in the crystal, resulting in n-type conductivity, while excess Bi may reside in Te sites making the crystal p-type.

The family of compounds PbS, PbSe and PbTe may incorporate subtractive defects in either cation or anion lattice positions, being n-type for excess cation and p-type for excess anion concentrations.

EQUILIBRIUM CONDITIONS FOR DEFECTS IN CRYSTALS

Departures from the stoichiometric composition are smallest in crystals having covalent bonding and are generally somewhat larger in crystals having appreciable ionic bonding. In the family of lead sulfides there is a fairly large ionic component to the bond between atoms in the solid state, and these materials can exist with significant departures from stoichiometry.

In a given crystal, addition or removal of excess atoms or ions generally takes place with the gas or liquid phases surrounding the solid. The equilibrium concentration of the excess atoms in the solid depends upon the temperature and composition of the vapor phase or liquid phase contacting the solid. The principle of this phase relationship was established over 30 years ago by Wagner and Schottky (1930) but only recently has been used effectively to control the composition of binary compound semiconductors.

Consider the system composed of a crystal of PbS in equilibrium with its vapor, which might be composed of atoms of Pb and S as well as of molecules of PbS and perhaps other molecular species of Pb and S. By Gibbs' phase rule, this system has only two degrees of freedom. By fixing the temperature and the pressure of one component of the vapor, one fixes all the related properties of the system, such as the crystal composition and its electrical properties.

While in principle the idea of controlling the crystal stoichiometry through control of the pressure of a component of the vapor is simple, in practice the process is complex.

Changes in crystal composition appropriate to the equilibrium values for the solid and vapor states at a given temperature start at the solid-vapor boundary and are propagated to the interior of the crystal by a diffusion process. Diffusion coefficients must be large enough to permit reaching equilibrium in a reasonable length of time. In the sulfides these times are of the order of a day for temperatures of about

400° to 500° C. and decrease to a few minutes for temperatures around 900° to 1000° C. Below about 300° C. diffusion becomes so slow that for all practical purposes the solid composition becomes fixed and independent of the surrounding vapor condition.

The maximum departure from stoichiometry in the solid at various temperatures has been established by Bloem (1956) for PbS, by Brebrick and Gubner (1962) for PbSe, and by Brebrick and Allgaier (1960) for PbTe. Figure 2 represents the limits of stability obtained by Brebrick and Allgaier for the PbTe system. It can be noted that the maximum solubility of excess Pb in the crystal is only about .005 atomic per cent and the maximum solubility of excess Te is only about .012 atomic per cent. Even such small deviations from the ideal composition result in about 10^{18} conducting electrons or holes per cm^3 in the crystal. Similar limits exist for lead sulfide and lead selenide.

The composition of PbTe at the maximum melting temperature is seen to be in the excess Te range and hence the first material to crystallize from a stoichiometric liquid will have excess Te atoms and will be hole-conducting or p-type. In the case of PbS, Bloem has shown that the maximum melting temper-
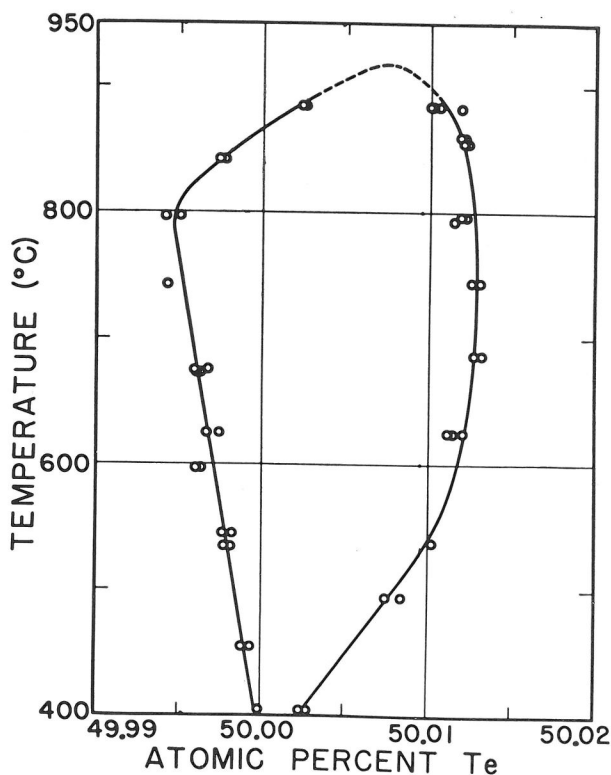

FIG. 2. Composition limits of stability for PbTe (courtesy of Dr. R. F. Brebrick and Dr. R. S. Allgaier).

ature composition results in the excess Pb or n-type conductivity.

The solid may exist with stoichiometric deviations less than the maximum values indicated by the curve in Fig. 2. The crystal composition is established through equilibrium with the gaseous phase at various temperatures. Some of this internal structure in the phase diagram has been obtained by Bloem and Kroger (1956) and by Brebrick and Scanlon (1954) for PbS. Figure 3 summarizes the data. The lines of constant composition as a function of temperature are determined by suitably adjusting the partial pressure of the sulfur component of the vapor.

Studies of the electrical properties of these crystals at high temperatures are complicated by the changing composition of the crystal unless special care is taken to suitably adjust the vapor composition at each temperature in order to maintain a fixed crystal composition. The phase diagrams show the equil-

ibrium conditions required to produce any desired crystal composition which define the electrical properties within the limits of solid stability of the compound.

PRECIPITATION IN CRYSTALS

It can be seen in Fig. 2 that the maximum solubility of excess Pb or Te in a PbTe crystal decreases at temperatures below about 700° C. This is called retrograde solubility. Within the retrograde solubility region a crystal containing the maximum concentration of one of the atom species at a given temperature will be come supersaturated upon being cooled to a lower temperature. The crystal may dispose of the excess atoms by precipitating them as neutral atoms on imperfections such as edge dislocations in the crystal. There is an accompanying reduction in free electron or hole concentration in the crystal. This process is reversible. The time required to come to
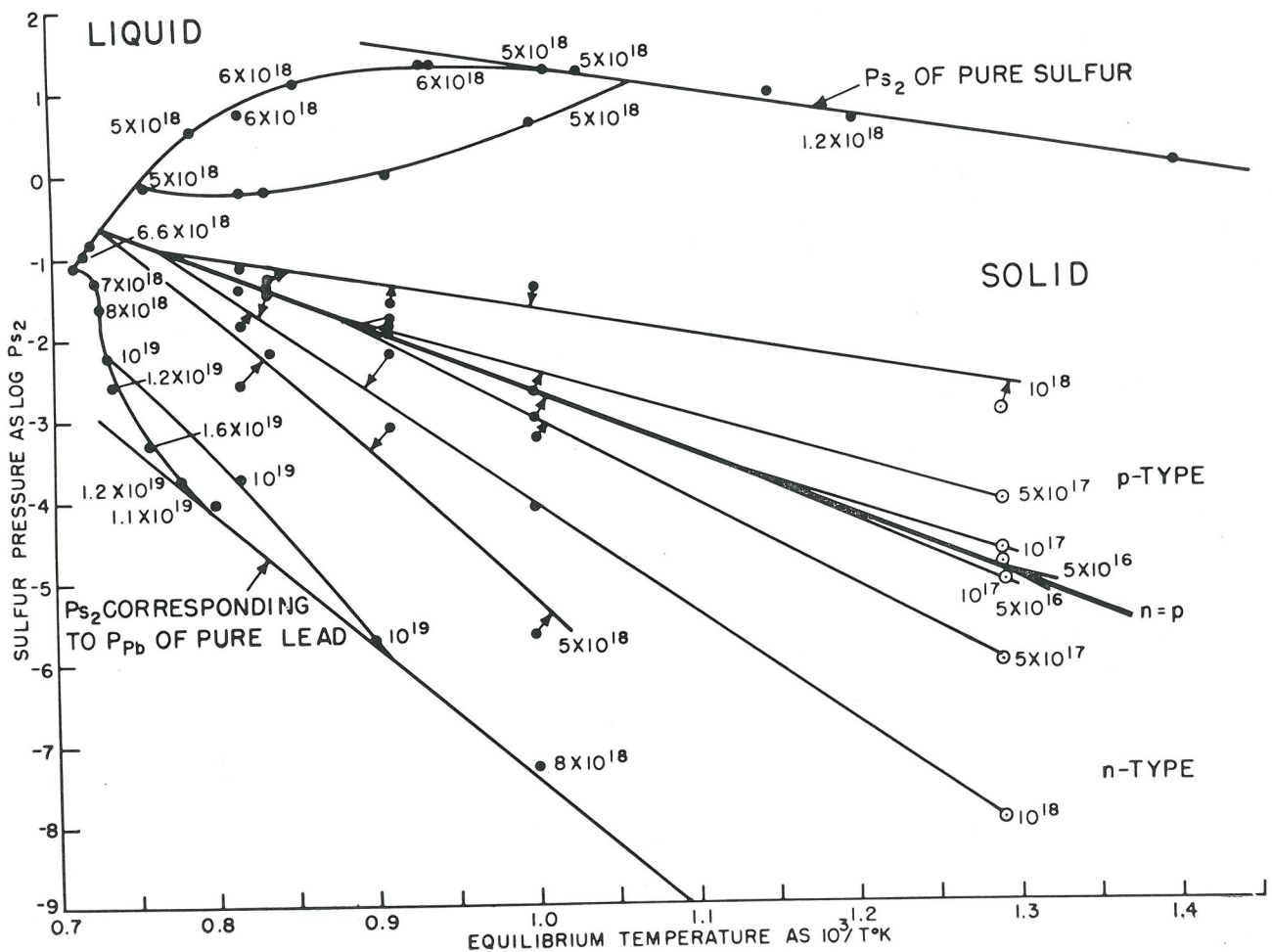

FIG. 3. Solid-vapor phase diagram for PbS.

equilibrium for this internal process is much less than for exchange of material with the external gaseous or liquid phase discussed previously, since the diffusion distance to precipitation sites is small relative to the diffusion distances to the surface of the crystal.

A study of precipitation phenomena in PbTe (Scanlon, 1962) shows it to be a useful technique for altering the carrier concentration in semiconducting crystals. It is particularly useful in preparing crystals having low carrier concentrations.

Figure 4 shows the maximum solubility of Te in PbTe crystals as a function of temperature. These data were obtained from precipitation experiments. The times required to reach approximate equilibrium ranged from a few hours at 400° C. to a month at 180° C. The slope of the curve indicates an activation energy of 0.58 ev for the process.

ELECTRICAL PROPERTIES

The behavior of the free carriers has an important bearing on the electrical properties of semiconductors. This behavior is determined to a large extent by the nature of the energy bands in the crystal and by the various charge scattering processes which are present in the crystal. Information on these properties may be deduced from a variety of interrelated electrical, magnetic, thermal and optical experiments.

The electron energy bands govern the excitation-recombination mechanism for charge carriers in the semiconductor as well as their effective masses. An important and useful characteristic of these bands is the minimum width of the forbidden energy gap between the valence and the conduction bands. Experimental information on the width of the forbidden energy band can be obtained from the temperature dependence of the free carrier concentration as determined from studies of the Hall effect or resistivity. This gives the minimum separation of the band edges for the case when quantum selection rules are relaxed due to the interaction of a lattice phonon in the excitation-recombination process. This energy gap is sometimes called the thermal activation energy. Its interpretation in small-energy-gap (less than about 0.5 volt) semiconductors, such as the lead sulfides, is questionable since the band edges in these semiconductors generally display multiple minima and maxima. Variations in the positions of the band edges due to thermal dilation or contraction of the lattice, thermal changes in the effective masses, and other thermal effects appear to play an appreciable role in these small-energy-gap semiconductors. These factors are not accounted for in the simple theory generally
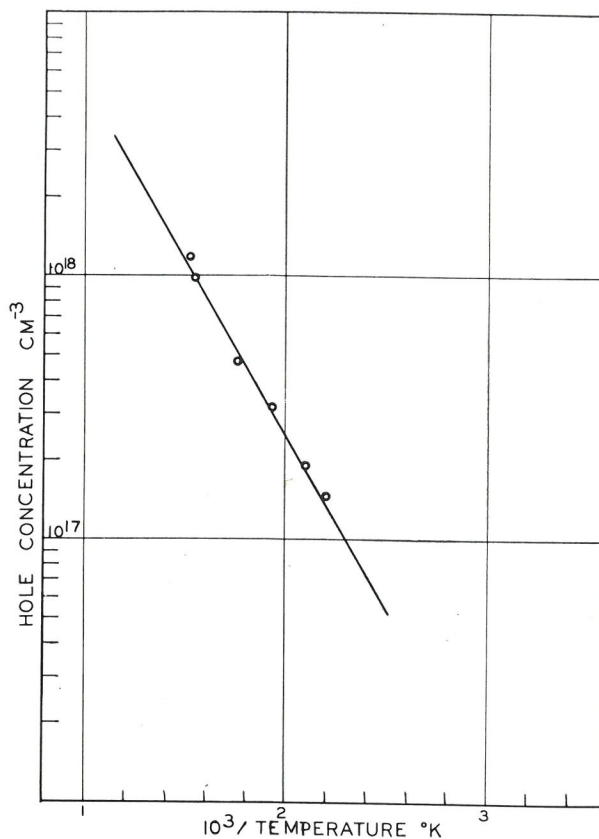

FIG. 4. Solubility of Te in a crystal of PbTe as a function of temperature.

used in interpreting resistivity or Hall effect data in terms of the forbidden energy gap, hence gap values so obtained should not be taken too seriously.

A much more satisfactory experiment for evaluating the minimum forbidden energy gap is to measure the transmission of the semiconductor to visible or infrared radiation. Photons having insufficient energy to excite electrons across the forbidden gap pass through with relatively little absorption. Photons with energies equal to or greater than the gap are strongly absorbed by the electrons in the valence band resulting in their excitation to the conduction band. Thus, there is a sharp drop in the transmission as the radiation energy corresponds to the band gap. Analysis of spectral transmission curves reveals not only the energy gaps for which quantum selection rules are obeyed, direct transitions, but also the energy gap for which lattice phonons assist in the transition, indirect transitions. Figure 5 shows optical transmission data for PbS, PbSe and PbTe crystals, and the analysis in terms of energy gaps is given in Table 1 (Scanlon 1959). It is interesting to point out
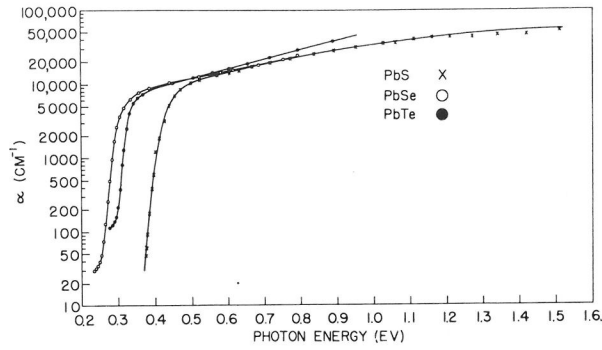
FIG. 5. Optical absorption in PbS, PbSe and PbTe crystals.

that the order of the energy gaps is not the same as the order of molecular weights as might be expected.

The lead sulfides are unusual in regard to the variation of the width of the forbidden energy gap with temperatures. In all three crystals the gap increases approximately 4×10^{-4}ev/°K. with increasing temperature. Most semiconductors have negative temperature dependence of the gap.

TRANSPORT PHENOMENA

The movement of free carriers in a perfect periodic crystal should, in theory, be unimpeded by scattering processes so that free path lengths should be infinite. In real crystals the free path length of an electron or hole is determined by the concentration of imperfections in the lattice which act as scattering centers. Free path lengths are generally very much greater than the atomic spacing, however. The mean time between collisions, τ, is called the relaxation time and is an important quantity in calculations of transport phenomena. Under the influence of various force fields the free electron gas in the crystal acquires a drift velocity in the direction of the applied force given by

$$dv_x = \frac{F_x}{m^*} \, dt \qquad (1)$$

where m^* is the effective mass of the charge carriers.

TABLE 1. ENERGY GAPS OBTAINED FROM THE OPTICAL ABSORPTION EDGE

	Energy Gap at 300° K (ev)	
Material	Direct	Indirect
PbS	0.41	0.37
PbSe	0.29	0.26
PbTe	0.32	0.29

In the case of an electric field the mean drift velocity becomes

$$\bar{v}_x = \frac{eE\tau}{m^*} \qquad (2)$$

We may write this expression in the form

$$\bar{v}_x = \mu E \qquad (3)$$

where μ is the mobility of the charge carrier and is

$$\mu = \frac{e\tau}{m^*} \qquad (4)$$

The temperature dependence of the relaxation time for various electron scattering processes can be calculated and the theoretical behavior of the mobility can be determined. Some of these calculations are summarized by Smith (1959).

Experimentally the mobility is readily obtained from measurements of the electrical resistivity and Hall effect. The electrical resistivity ρ for an electron conducting solid is

$$\rho = \frac{1}{ne\mu} \qquad (5)$$

while the Hall coefficient is

$$R = \frac{1}{ne}$$

Thus

$$\frac{R}{\rho} = \mu \qquad (6)$$

Typical experimental data on Hall effect and resistivity for the sulfides is shown in Fig. 6. At high temperatures the R and ρ behavior is seen to become independent of sample composition and is referred to as the intrinsic conductivity region. At lower temperatures carrier concentrations become constant as indicated by the constant value of the Hall coefficient. This is the extrinsic conductivity region where the carriers arise from low energy level imperfection centers which remain ionized even to the lowest temperatures studied, about 4° K.

By combining R and ρ data one obtains mobility curves such as are shown in Fig. 7 for typical crystals of PbS, PbSe and PbTe. There is a marked similarity in the general behavior for the three materials though the magnitudes differ. These semiconductors are unusual in that their mobility increases rapidly with decreasing temperature, even with carrier concentrations up to about 10^{19}/cm³. At the present time known electron and hole scattering models are unable satisfactorily to account for the observed behavior of the mobility. Recent studies by Allgaier (1962) are encouraging in that they qualitatively explain the ob-
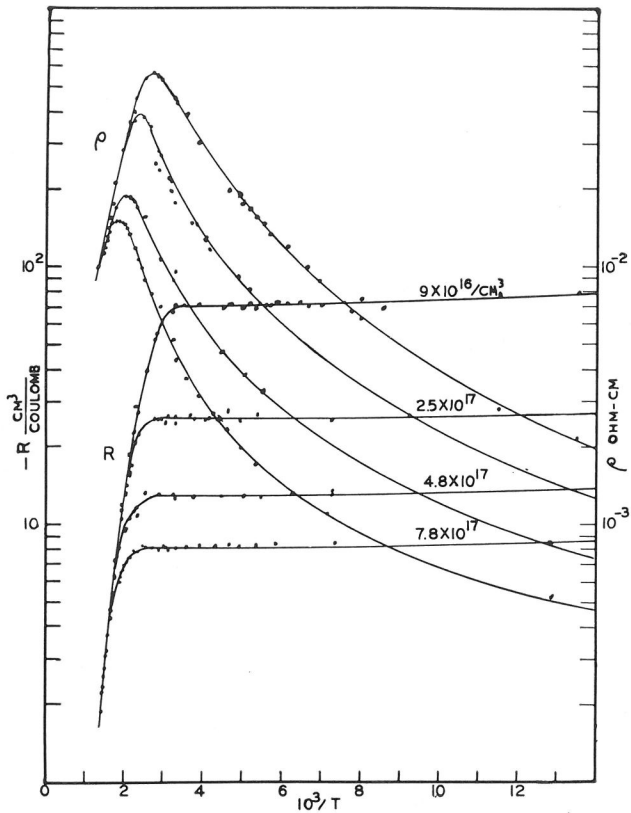
FIG. 6. Typical curves of Hall effect, R and electrical resistivity ρ for PbTe crystals of different compositions.
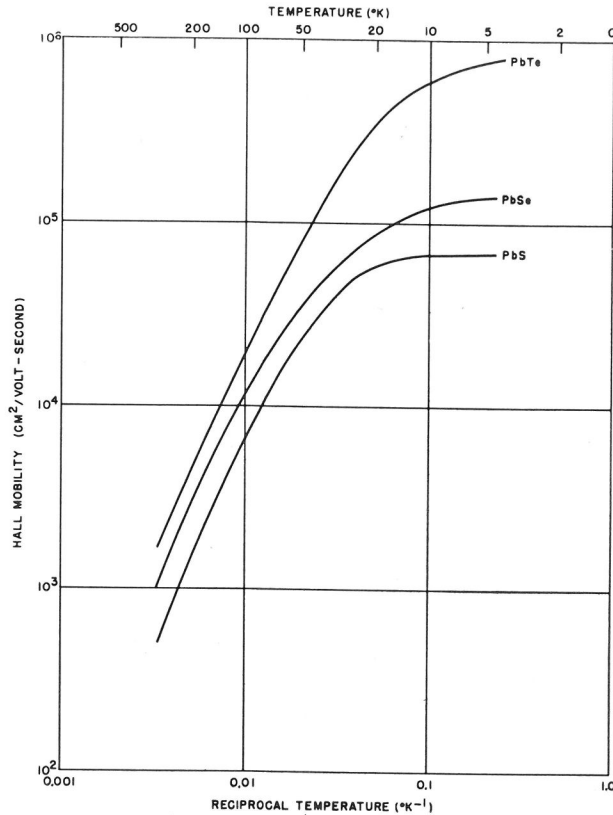

FIG. 7. Typical curves of mobility in n-type PbS, PbSe and PbTe crystals (courtesy of Dr. R. S. Allgaier).

served curves by considering the combined influence of lattice scattering and defect scattering along with the variation of the effective mass and energy gap with temperature.

Thermal gradients in crystals also result in a drift of charge carriers giving rise to thermal-electric effects. One of these is the Seebeck effect, also known as the thermoelectric power. In the lead sulfides the thermo-electric power is relatively large for a material of low electrical resistance and low thermal conductivity. Curves of the thermoelectric power in PbTe as a function of temperature and carrier concentration are shown in Fig. 8. This group of crystals were p-type. An interesting feature is the reversal of the sign of the thermoelectric power at high temperatures. This is due to the increased number of electrons arising from excitations across the forbidden energy gap at high temperatures. When the number of these electrons approaches the number of holes the sign changes because the mobility of the electron is greater than the hole mobility. At absolute zero the thermoelectric power should, in theory, approach zero as $1/T$ and the

low-temperature experimental data appear to verify this prediction.

PHOTOCONDUCTIVITY

The lead sulfides are of particular interest because of their infrared photoconductivity. Their energy gaps
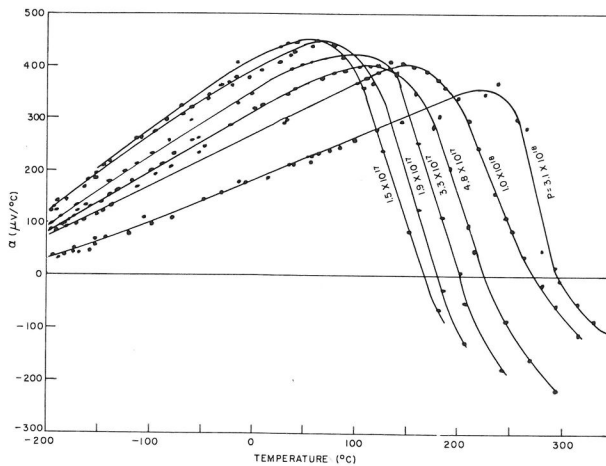

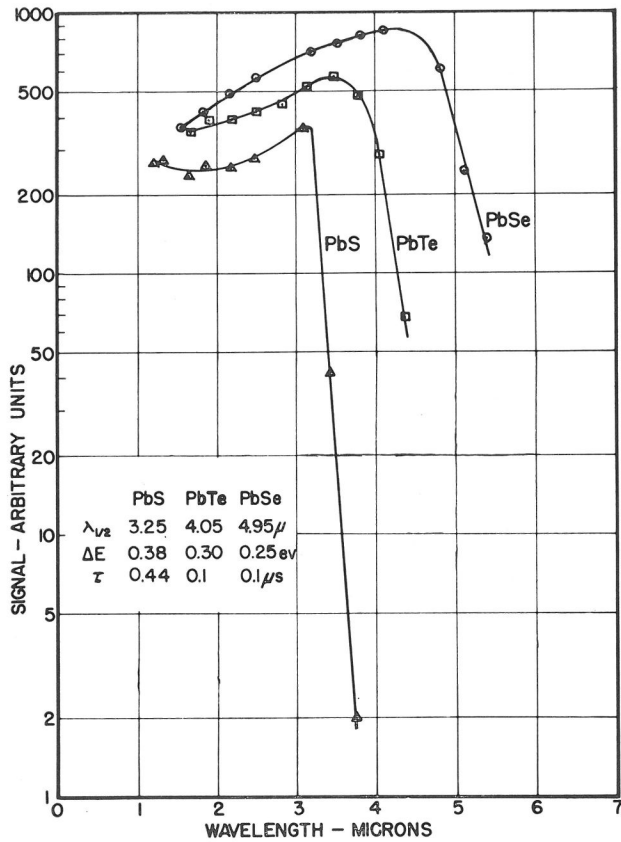FIG. 8. Thermoelectric power in ρ-type PbTe crystals.

FIG. 9. Infrared photoeffect in PbS, PbSe and PbTe.

fall in the range from about 0.4 ev to 0.2 ev. Photons having wavelengths as long as 3 to 5 microns are energetic enough to excite electrons and holes into conduction bands. This results in a temporary increase in the electrical conductivity of the semiconductor, which returns to the dark value of conductivity upon the removal of the radiation. The relative spectral dependence of the photo effect is shown in Figure 9 for PbS, PbSe and PbTe crystals. The sensitivity for each material was arbitrarily adjusted so that the curves would not cross one another. The sharp fall-off in sensitivity at long wavelengths was used to estimate the energy gaps. The values so obtained are in reasonably good agreement with the more precise values obtained from absorption edge studies. The time τ for the signal to decay to $1/e$ of the maximum value is also given on the curve. Oxygen atoms in thin films of these materials act as traps for electrons and have the effect of increasing the decay time by orders of magnitude. The equilibrium concentration of charge carriers under illumination is correspondingly increased and the sensitivity is higher

for these oxygen treated films. Thin evaporated or chemically deposited films of the lead sulfides on glass or similar substrate are among the most sensitive infrared detectors known.

APPLICATIONS

One of the principal uses of the lead sulfide semiconductors is based upon their highly sensitive infrared photoconductivity. Numerous types of infrared cells are being manufactured today for use in military devices, such as target seekers or for mapping out ground areas. These detectors are also widely used by spectroscopists in studying molecular structure or for chemical analysis. The high sensitivity of the photoconductive detectors permits analysis of fine structure in molecular spectra far beyond the capacities of conventional bolometer or thermocouple infrared detectors.

Another application of these materials is somewhat related to photoconductivity in that it is also based upon the energy gap. This application is infrared filters. The sharp absorption edge in these semiconductors falls in a useful region of the infrared spectrum at about 3, 4 and 5 microns. Radiation of wavelengths shorter than the edge value are essentially cut off while longer wavelengths are transmitted. The transmission loss that occurs is principally reflection losses due to the high dielectric constant of the materials.

A more recent application for these materials is in thermoelectric devices for converting heat into electrical energy or for refrigeration. Lead telluride is one of the most useful semiconductors in these applications. Power supplies for isolated equipment such as weather reporting stations in the arctic regions or in satellites have been made using PbTe as the convertor and nuclear waste material such as Sr[90] or other nuclear fuel elements of the uranium series as the heat source. Such power supplies will last for many years.

Thermoelectric refrigeration devices for small scale cooling applications are now commercially available. Recently household size thermoelectric refrigerators and ice makers have been placed on the market. In these applications n and p-type PbTe are used for the two members of the thermocouple.

CONCLUSIONS

The lead sulfide semiconductors, owing to their large ionic bonding component, may incorporate significant departures from the stoichiometric proportions in the crystalline state. These imperfections

control the electrical properties in pure crystals. Studies of the maximum deviations in stoichiometry as a function of temperature have been made as well as studies of the internal composition of the solid in equilibrium with the vapor phase. The transport properties of electrons and holes and the detailed structure of the energy band edges in these semiconductors are beginning to be clarified. Applications for the lead sulfides are increasing and include a number of infrared as well as thermoelectric devices.

REFERENCES

ALLGAIER, R. S. AND B. B. HOUSTON (1962) Mobility studies in semiconductors with very high carrier densities. International Conference on Semiconductors, Exeter, England (in press.)

ANDERSON, J. S. (1946) Non-stoichiometric compounds. *Ann. Rept. Prog. Chem. Soc. London*, 104.

BLOEM, J. (1956) Controlled conductivity in lead sulfide single crystals. *Philips Res. Rept.* 11, 273.

———— AND F. A. KROGER (1956) The p-T-x phase diagram of the lead-sulfur system. *Zeit. Phys. Chem.* 7, 1.

BREBRICK, R. F. AND R. S. ALLGAIER (1960) Composition limits of stability of PbTe. *Jour. Chem. Phys.* 32, 1826.

———— AND E. GUBNER (1962) PbSe composition stability limits. *Jour. Chem. Phys.* 36, 170.

———— AND W. W. SCANLON (1954) Electrical properties and the solid-vapor equilibrium of lead sulfide. *Phys. Rev.* 96, 598.

SCANLON, W. W. (1959) Recent advances in the optical and electronic properties of PbS, PbSe, PbTe and their alloys. *Jour. Phys. Chem. Solids*, 8, 423.

———— (1962) Precipitation of Te and Pb in PbTe crystals. *Phys. Rev.* 126, 509.

SMITH, R. A. (1959) *Semiconductors*. Cambridge.

WAGNER, C. AND W. SCHOTTKY (1960) Theory of regular mixed phases. *Zeit. Physik. Chem.* 11, 467.