

the minimum number of critical points but give no upperbound. It is generally easy to find those which are at symmetry points of the Brillouin zone. In most cases investigated thus far,¹⁻³ these are the only critical points. This might be due to the assumption made in these cases that the forces are of short range. The number of critical points might be expected to increase with the range of the interaction, and their location is then more likely to be at nonsymmetry points of the zone. Rosenstock¹⁷ has devised a method for examining the presence of critical points inside the zone from the behavior of $\omega^2(\mathbf{k})$ on the boundary.

For three dimensions, with short-range forces, when the critical points are at the symmetry points the matrix $\mathbf{M}(\mathbf{k})$, is easy to diagonalize at these points to find the critical frequencies. To find the exact form of the distribution near the critical points x_c , degenerate perturbation theory has to be used to find the eigenvalues in the vicinity of \mathbf{k}_c . However, since in three dimensions $G(x)$ does not become infinite at x_c , it might be sufficient to use the right form of $G(x)$ near x_c ; the coefficients of the singular part would then be determined by the moment as mentioned above. This would agree with the results of Rosenstock.¹⁷

Electrical Properties and the Solid-Vapor Equilibrium of Lead Sulfide

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Natural PbS crystals were exposed to various pressures of sulfur-vapor near 500°C and then quenched. Calculations based on the penetration of *p-n* junctions gave an interdiffusion constant of 2×10^{-6} cm²/sec at 550°C. The temperature dependence of the Hall coefficient and resistivity for several treated crystals was determined. A forbidden energy gap of 0.37 ± 0.01 eV and an electron to hole mobility ratio of 1.4 was obtained.

I. INTRODUCTION

AT low temperatures the electrical properties of ionic or partially ionic binary compound semiconductors may be attributed to the presence of donor and acceptor levels produced either by foreign atoms or by deviations from stoichiometric proportions. In the absence of appreciable concentrations of foreign atoms the electrical properties are dependent to a large extent upon deviations from stoichiometry. Current statistical models predict that it is possible for all crystalline ionic compounds to show these deviations from stoichiometry.¹ The crystal can exist as a single phase over a range of composition through the inclusion of interstitial atoms and/or vacant lattice sites. While this range of composition is generally too small to be detected chemi-

cally it is revealed through variations in electrical properties which are composition sensitive.

The ability of the crystal to exist as one phase over a range of composition implies some thermodynamic consequences which are important in the preparation of these materials with desired electrical properties. In the case of lead sulfide the equilibrium system, crystal-vapor, has two phases and two components, lead and sulfur. According to the Gibbs phase rule this system possesses two degrees of freedom. Hence when the temperature and vapor pressure of either component are fixed, all of the intensive properties of the system, such as the composition of the crystal and vapor phases, are fixed also. The vapor phase will in general contain two components in a different proportion than the crystal.² Therefore, under equilibrium conditions, the crystal can be held at a fixed composition over a range of temperature only by appropriately adjusting the vapor pressure of one of the components or the total pressure. On the other hand, if one of these pressures is held constant and the temperature varied or *vice versa*, then the composition of the crystal will change in general.

In principle, therefore, the composition of a crystalline binary compound can be varied by heat treatments in a controlled atmosphere comprised of its components. In practice, it is necessary to work at those tempera-

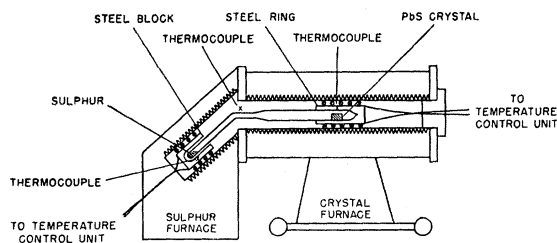


FIG. 1. Apparatus used for treating crystals.

¹ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1949), Chap. XII.

² C. Wagner, *Thermodynamics of Alloys* (Addison-Wesley Press, Inc., Cambridge, 1952), p. 67.

tures at which the crystal-vapor equilibrium is established in a reasonable length of time. The determination of this temperature range for lead sulfide and the corresponding vapor pressures of sulfur in equilibrium with the near stoichiometric solid, along with a study of some of the associated electrical properties, are the subject matter of this paper.

II. DIFFUSION RATE IN PbS CRYSTALS

An indication of the time required for the crystal-vapor system to establish equilibrium can be obtained from the times required for an originally *n*-type (excess lead) crystal to become *p*-type (excess sulfur) when exposed to sufficiently high temperatures and sulfur pressures. The necessary composition change will occur first at the crystal surface, and will be subsequently propagated into the crystal interior by a diffusion process. If the crystal is quenched in the early stages of this composition change, it will contain a *p-n* junction which divides its *n*-type interior from its *p*-type exterior. The *p-n* junction can be located electrically by cleaving the crystal and determining the sign of rectification or thermal emf at different points on these cleavage faces. Under certain assumptions the penetration-time data can be used to calculate a diffusion constant and to estimate the time required for the crystal to come to equilibrium with its vapor phase.

The experimental setup is shown in Fig. 1. Two natural PbS crystals with known Hall coefficients and a quantity of sulfur are placed at the opposite ends of a sealed, evacuated quartz tube. The temperatures at the ends of the tube are controlled independently. The crystal temperature is fixed to within $\pm 2^\circ\text{C}$, the sulfur temperature to within $\pm 0.5^\circ\text{C}$. If the sulfur temperature is lower than that along any other part of the tube, the pressure of sulfur vapor in the tube is the vapor pressure of sulfur at this temperature. The crystals can be quenched at the end of a run by moving away the crystal furnace. In quenching, the crystals cooled to 300°C in about 1 minute and to 200°C in another minute.

In Fig. 2, mid-sections of two crystals run simultaneously are shown to indicate the penetration of a *p-n* junction after sixty minutes. The crystal temperature was 550°C ; the sulfur temperature was 123°C . The position of the *p-n* junction was located by a rectification test. An electrolytically sharpened tungsten probe was mounted in a fixed position in the field of view of a comparator microscope, while the PbS crystal was mounted on the micrometer stage. The rectification curve corresponding to a given point on the crystal surface was observed on an oscilloscope screen. Because of the sharp change in the rectification characteristics in crossing the *p-n* junction, its position could be located to a few ten-thousandths of an inch.

If the composition at the crystal-vapor interface is assumed to be constant and the diffusion constant *D* to

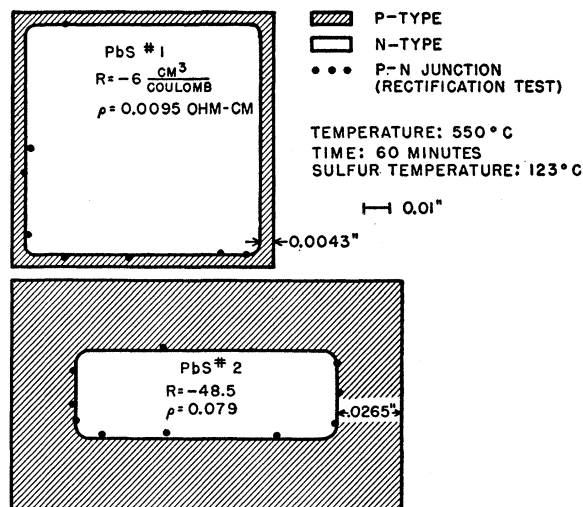


FIG. 2. Cross sections showing the penetration of the *p-n* junction in two crystals of different initial compositions.

be independent of composition, then the appropriate boundary value problem for a crystal of thickness *h* is

$$\begin{aligned} \partial C / \partial t &= D \partial^2 C / \partial x^2, \\ C(0, t) &= C(h, t) = C_s, \\ C(x, 0) &= C_i \quad (0 < x < h). \end{aligned} \quad (1)$$

The simplified analysis used here can be carried through with the concentration referring either to that of the lead or sulfide ions. In the following the concentration will be that of the sulfide ions. Then C_s is the constant concentration of sulfide ion at the crystal surface, while C_i is the initial concentration in the crystal. The solution of the boundary value problem is³

$$\begin{aligned} \frac{C(x, t) - C_i}{C_s - C_i} &= 1 - \sum_{\nu=0}^{\infty} \frac{4}{\pi} \frac{\sin \left[\frac{(2\nu+1)x}{h} \right]}{2\nu+1} \\ &\quad \times \exp \left[-\frac{(2\nu+1)^2 \pi^2 D t}{h^2} \right] \\ &= S(x, Dt). \end{aligned} \quad (2)$$

Since the initial compositions of the crystals used are such that they are in the exhaustion region at room temperature, the assumption is made that the initial concentration of sulfide ions C_i at a *p-n* junction, and the concentration *n* of conduction electrons are related by the equation

$$a(C_j - C_i) = n. \quad (3)$$

The constant *a* is the number of conduction electrons per donor center. By combining Eqs. (2) and (3) the following condition is obtained at the *p-n* junction:

$$n = [a(C_s - C_j) + n] S(x_j, Dt), \quad (4)$$

³ W. Jost, *Diffusion in Solids, Liquids, Gases* (Academic Press, Inc., New York, 1952), p. 37.

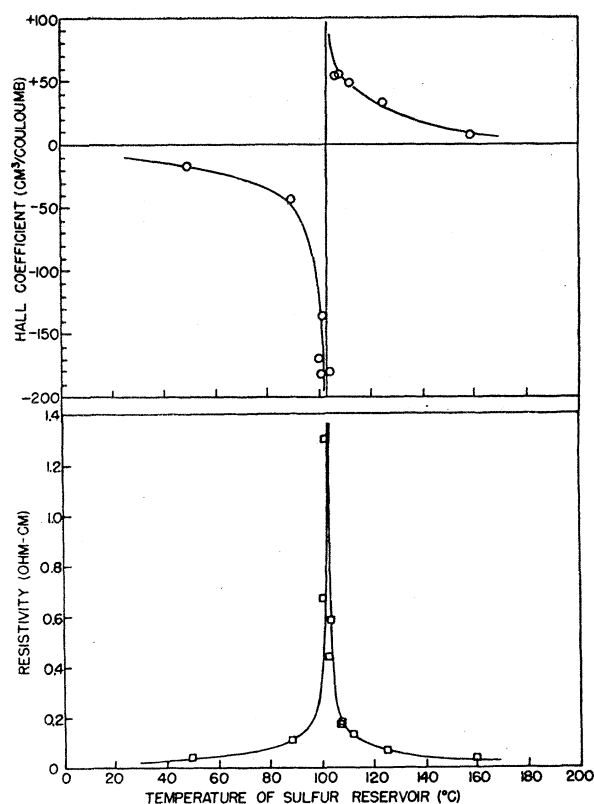


Fig. 3. Room-temperature values of Hall coefficient and resistivity of PbS crystals as a function of sulfur reservoir temperature.

where x_j is the distance of the p - n junction from the crystal surface. This equation contains two unknowns, $a(C_s - C_j)$ and D , which may be evaluated from measurements on two crystals of initially different compositions treated under identical conditions. From the values obtained on the two crystals given in Fig. 2, the diffusion constant obtained is 2×10^{-6} cm²/sec at 550°C. The value of $a(C_s - C_j)$ for the conditions of Fig. 2 is 6×10^{16} .

In subsequent experiments PbS crystals were treated at the somewhat lower temperature of 500°C. It is of interest to estimate the value of the diffusion constant and the time required for a crystal to come essentially to equilibrium with its vapor at this temperature. The results obtained using the value of the diffusion constant at 550°C and the usual equation for the tempera-

ture dependence of the diffusion constant,

$$D = D_0 \exp[-E/RT], \quad (5)$$

are given in Table I. The lowest value assumed for D_0 is of the order of magnitude expected from elementary derivations.⁴ The middle value is of the order of magnitude of the values recently observed in metal alloys. The times given are those required for the concentration change to be 99.8 percent complete in the middle of a 2-mm thick crystal. They are overestimated by the use of the one-dimensional solution of the diffusion equation. In the equilibrium experiments described subsequently diffusion is allowed to proceed for twenty hours.

The effect of oxidation on the diffusion rate in PbS was also studied. Natural crystals 1.5 to 2.0 mm thick with room-temperature Hall coefficients of $R = -48.5$ cm³/coulomb were used. When such crystals were exposed to sulfur vapor at 500°C for twenty hours with a sulfur reservoir temperature of 124°C, the room temperature values of the Hall coefficient changed to $R = +30$ cm³/coulomb. If, however, the crystal was heated in air for fifteen minutes at 500°C and then exposed to sulfur vapor under the same conditions as above, it was unchanged beneath a surface layer about 0.15 mm thick. The heating in air itself resulted in a surface layer about 0.10 mm thick, beneath which the crystal was unchanged. The surfaces of the oxidized crystals were bluish in color but were less so after exposure to sulfur vapor.

III. EQUILIBRIUM EXPERIMENTS

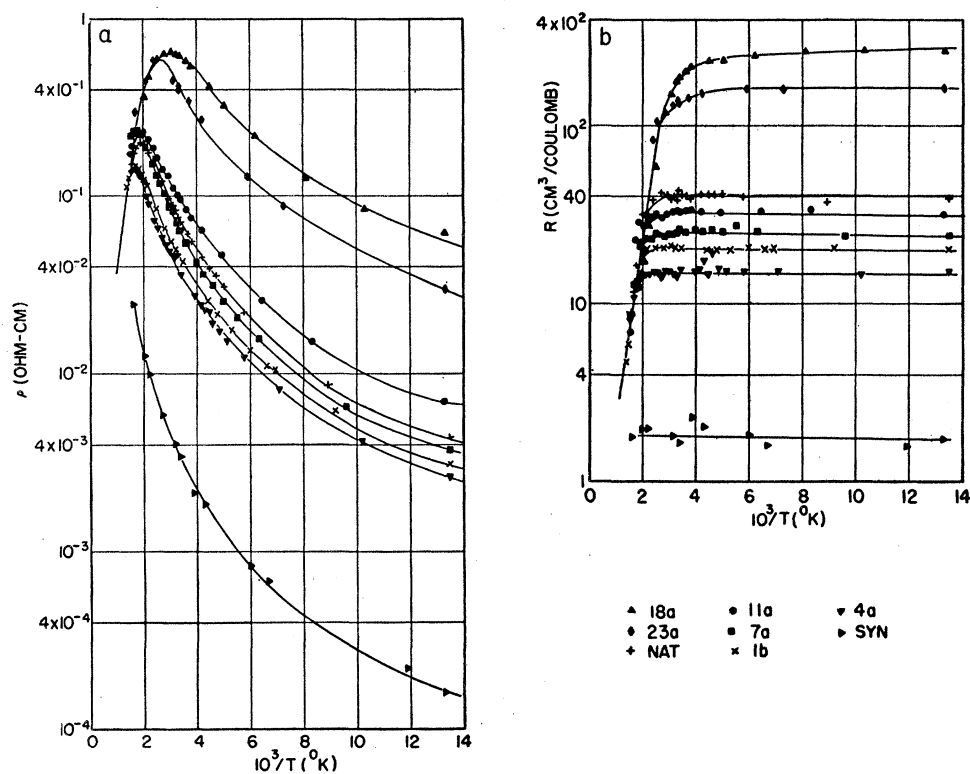
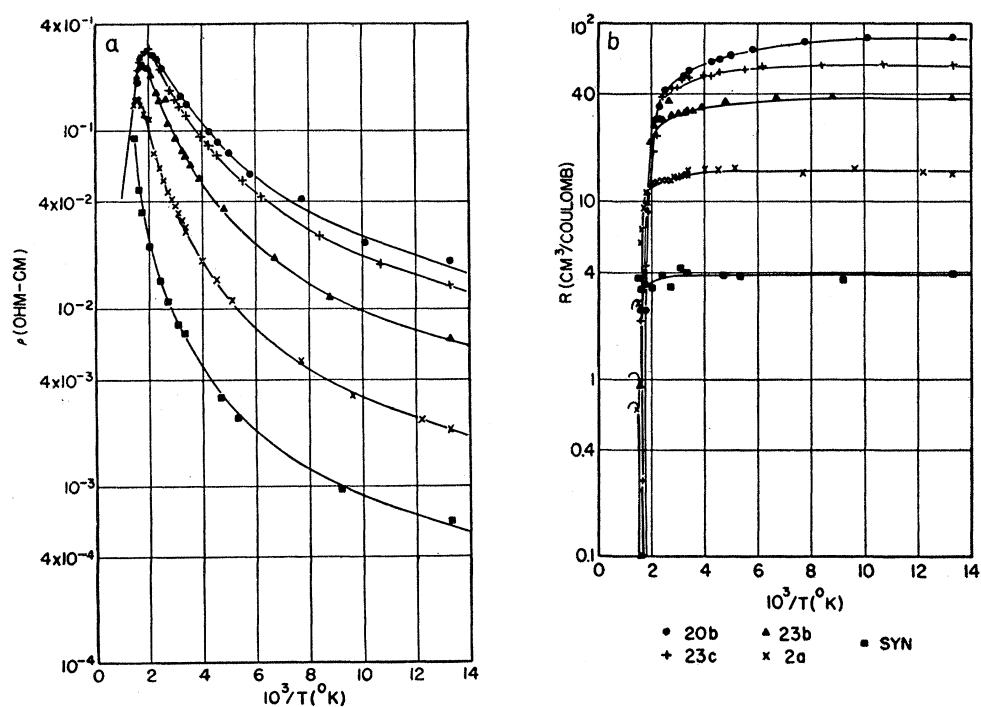
Small natural crystals of PbS, 2 mm or less thick, were exposed at 500°C to various fixed pressures of sulfur vapor for 20 hours and then quenched to room temperature. The apparatus used is shown in Fig. 1. The sulfur temperatures used ranged from 50°C to 160°C corresponding to a range of sulfur pressures from 3×10^{-5} mm Hg to 3×10^{-1} mm Hg. A thin surface layer, probably formed in the quenching process, could be removed by grinding approximately one mil from each crystal face. The Hall coefficients and resistivities of these crystals were then measured by the standard dc method. The results of such measurements are summarized in Fig. 3 where the room temperature values of the Hall coefficient and resistivity are plotted as a function of the sulfur reservoir temperature. The treatment was reversible in so far that crystals could be changed from n to p and back to n type. As a rule, crystals were used only once. The reproducibility of the treatment was checked by running two or more crystals simultaneously. The electrical properties agreed to within 10 percent in such cases.

The Hall coefficient and resistivity for several crystals treated by this method are shown as a function of temperature from -190°C to 250°C in Fig. 4 (n type) and Fig. 5 (p type). The corresponding curves for two un-

TABLE I. Estimated rate of approach to equilibrium at 500°C for a 2-mm thick crystal.

D_0	E (kcal)	$D(500^\circ)$	t (hr)	$\frac{C - C_i}{C_s - C_i}$
2×10^{-4}	7.58	1.5×10^{-6}	5	0.998
2	23	0.81×10^{-6}	9.3	0.998
200	30.3	0.61×10^{-6}	12.3	0.998

⁴ See reference 3, p. 137.

FIG. 4. (a) Resistivity and (b) Hall coefficient for *n*-type PbS crystals as a function of temperature.FIG. 5. (a) Resistivity and (b) Hall coefficient for *p*-type PbS crystals as a function of temperature.

treated synthetic crystals are also included. The curves labeled "nat" in Fig. 4 are for the untreated natural PbS. Below 250°C, diffusion is slow enough that the crystals did not change composition during the course of the measurements as was evidenced by the reversibility of the Hall coefficient and resistivity with temperature cycling. This is not the case at higher temperatures as has been pointed out previously.⁶

IV. DISCUSSION

a. Diffusion

Eisenmann⁶ observed that at 600°C, four hours was sufficient for the electrical properties of 1-mm thick, synthetic PbS crystals to reach steady values. By assuming that the composition change was between 70 and 99.9 percent complete at the center of these crystals after four hours, a corresponding range of 10^{-7} to 5×10^{-7} cm²/sec is obtained from Eq. (2) for the diffusion constant at 600°C.

The diffusion constant reported for radioactive lead in pressed PbS powders is 2×10^{-11} cm²/sec at 550°C and 5×10^{-11} cm²/sec at 600°C.⁷ The average diffusion constant for a *p*-type powder was three times as large as that for one that changed from *p* to *n* type during the course of the diffusion.

Synthetic crystals prepared thus far in this Laboratory, both from fusion of the element and from remelted natural PbS crystals, have a diffusion constant considerably smaller than that found for the natural crystals used here. The synthetic crystals remained unchanged except for a surface layer 0.1 mm thick or less when exposed to various pressures of sulfur vapor at 500°C for twenty hours. However, when run simultaneously for four hours at 850°C, natural crystals, *p*-type synthetic crystals, and *n*-type synthetic crystals all reached essentially the same composition.

In view of the experiments with superficially oxidized natural crystals mentioned above, it is possible that the synthetic crystals used here contain oxygen, probably as oxygen ions on sulfide ion sites, which slows the diffusion rate. Since the crystals were grown in sealed quartz or Vycor tubes that had to be heated over 1120°C, the melting point of PbS, it was difficult to insure

an oxygen-free, water-free atmosphere. At these temperatures, PbS is unstable relative to oxidation products such as PbSO₄, PbO, etc., at almost any partial pressure of oxygen⁸ and probably is also unstable relative to incipient oxidation products such as mixed PbS—PbO crystals, which presumably would form if the oxygen supply were limited.

b. Equilibrium

As seen in Fig. 3, the Hall coefficient and resistivity change rapidly in the neighborhood of 104°C, and the scatter of experimental points is therefore more pronounced. Experiments on thin evaporated films of PbS in which the films were heated successively to different temperatures in vacuum and in sulfur atmospheres yield curves with similar characteristics.⁹

From the high-temperature slope of the Hall curves in Fig. 4, the intrinsic energy gap was calculated using the intrinsic Hall equation. The mean value was found to be 0.37 ± 0.01 eV and is in accord with the values obtained from optical data, but is about one-third the value previously derived from Hall data.¹⁰

The reasons for this difference have been discussed elsewhere⁵ and are based upon the change of composition of PbS at elevated temperatures.

The impurity energy gap obtained from the low-temperature Hall curves for the present materials were 0.03 eV for the *n*-type crystals and 0.001 eV for the *p*-type crystal.

The Hall coefficients of the *p*-type crystals, Fig. 5, became negative at higher temperatures, indicating an electron to hole mobility ratio greater than one. From the temperatures at which the Hall coefficient changed sign this ratio was calculated to be 1.4. From the extrapolated resistivity data, the estimated room-temperature resistivity of intrinsic PbS is about 3 ohm-cm. The highest value achieved in the equilibrium experiments was 1.3 ohm-cm.

The resistivity in the impurity range does not show the effects of impurity scattering usually found in non-polar crystals such as germanium and silicon. Further details on the mobility and the theory of scattering in PbS will appear in a separate article.

⁵ W. W. Scanlon, Phys. Rev. **92**, 1573 (1953).

⁶ L. Eisenmann, Ann. Physik **38**, 121 (1940).

⁷ J. S. Anderson and J. R. Richards, J. Chem. Soc. **1946**, 537.

⁸ Bureau of Mines, Bulletin 406, 1937 (unpublished).

⁹ H. Hintenberger, Z. Physik **119**, 1 (1942).

¹⁰ E. H. Putley and J. B. Arthur, Proc. Phys. Soc. (London) **B64**, 616 (1951).