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Mobility of Electrons and Holes in PbS, PbSe, and PbTe between Room Temperature and 4.2°K*

ROBERT S. ALLGAIER, *United States Naval Ordnance Laboratory, White Oak, Maryland and University of Maryland, College Park, Maryland*

AND

WAYNE W. SCANLON, *United States Naval Ordnance Laboratory, White Oak, Maryland*

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Hall coefficient and resistivity measurements have been made on 29 single crystals (mostly synthetic) of PbS, PbSe, and PbTe between room temperature and 4.2°K. Almost all of the samples had extrinsic carrier concentrations of the order of 10^{18} per cm^3, as deduced from the Hall coefficients which were essentially constant over the entire temperature range investigated. Hall mobilities were calculated from the Hall and resistivity data, and were found to increase rapidly with decreasing temperature. Between room temperature and about 50°K the mobility behavior was essentially intrinsic and varied approximately as $T^{-2.2}$. Below 50°K the mobility curves turned gradually toward the horizontal in a manner resembling the residual resistance phenomenon observed in metals. Values as high as 800 000 cm^2/v-sec were attained at 4.2°K despite the large carrier concentrations present in all the samples. A simple experiment was performed which suggests that dislocations are the principal scattering mechanism below 50°K, rather than the charged point defects associated with the extrinsic carriers. The possibility that a high static dielectric constant could explain the large mobilities at low temperatures is discussed.

INTRODUCTION

THE main purpose of the work reported in this paper was to study the mobility of electrons and holes in the lead-salt semiconductors PbS, PbSe, and PbTe between room temperature and 4.2°K. The mobilities were derived from Hall-effect and resistivity data taken on 29 samples, most of which were synthetic single crystals grown at the Naval Ordnance Laboratory.

The lead salts are polar semiconductors which crystallize in the cubic NaCl structure. Thin films of these compounds are sensitive infrared detectors, and there is an extensive literature on them in this form. Much less work, however, has been reported on single crystals of the lead salts. Several review articles have been published[1–6] and a more detailed review is being prepared by one of us.[7]

The electronic mobilities of PbS, PbSe, and PbTe may be studied as an example of the polar interaction of charge carriers and optical-mode lattice vibrations. Such studies in the high-resistivity, low-mobility alkali halides are complicated by ionic conductivity, polarization effects, and noise. The lead salts, on the other hand, have small energy gaps (0.41, 0.29, and 0.32 ev at 300°K for PbS, PbSe, and PbTe[8]) low, resistivities (the intrinsic room temperature resistivity of PbS is about 2.5 ohm-cm, and is lower for PbSe and PbTe; typical crystals of the lead salts have room-temperature resistivities of 0.1 ohm-cm or less), and mobilities (500–2000 cm^2/v-sec at room temperature) which are easily measured.

Previous measurements of the Hall coefficient and resistivity of synthetic crystals of the lead salts have been confined to temperatures above 77.4°K,[9–18] with the exception of Putley's data at 20°K.[19,20] Measurements on 5 crystals of *natural* PbS down to 4.2°K have also been reported recently.[21] The published single-crystal measurements have generally revealed a constant Hall coefficient in the extrinsic temperature range, and a mobility which increased very rapidly with decreasing temperature. Frequently the mobility can be approximated by the formula $\mu=\mu_0T^{-n}$, where n is a constant for each sample with a value between 2 and 3. Several authors have concluded that $n=2.5$ is the most appropriate value,[16,19,21,22] although until

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[*] This paper is a portion of a thesis submitted by the first author to the University of Maryland in partial fulfillment of the requirements for the Doctor of Philosophy degree in physics. Copies of the complete thesis are available from the U. S. Naval Ordnance Laboratory.

[1] R. A. Smith, in *Semiconducting Materials* (Butterworths Scientific Publications, Ltd., London, 1951), p. 198.

[2] R. A. Smith, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1953), Vol. 2, p. 321.

[3] R. A. Smith, Physica **20**, 910 (1954).

[4] T. S. Moss, Proc. Inst. Radio Engrs. **43**, 1869 (1955).

[5] R. P. Chasmar, in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 463.

[6] Scanlon, Brebrick, and Petritz, in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 619.

[7] W. W. Scanlon, in *Solid State Physics* (Academic Press, Inc., New York), to be published.

[8] W. W. Scanlon, Phys. Rev. **109**, 47 (1958), for PbS value; PbSe and PbTe values to be published.

[9] K. Bauer, Ann. Physik **38**, 84 (1940).

[10] L. Eisenmann, Ann. Physik **38**, 121 (1940).

[11] J. A. Dunaev and J. P. Maslakovetz, J. Exptl. Theoret. Phys. U.S.S.R. **17**, 901 (1947).

[12] R. P. Chasmar and E. H. Putley, in *Semiconducting Materials* (Butterworths Scientific Publications, Ltd., London, 1951), p. 208.

[13] E. H. Putley, Proc. Phys. Soc. (London) **B65**, 993 (1952).

[14] R. F. Brebrick and W. W. Scanlon, Phys. Rev. **96**, 598 (1954).

[15] E. L. Brady, J. Electrochem. Soc. **101**, 466 (1954).

[16] S. J. Silverman and H. Levinstein, Phys. Rev. **94**, 871 (1954).

[17] E. Hirahara and M. Murakami, J. Phys. Soc. Japan **9**, 671 (1954).

[18] K. Shogenji and S. Uchiyama, J. Phys. Soc. Japan **12**, 252 (1957).

[19] E. H. Putley, Proc. Phys. Soc. (London) **B65**, 388 (1952).

[20] E. H. Putley, Proc. Phys. Soc. (London) **B68**, 22 (1955).

[21] D. M. Finlayson and D. Greig, Proc. Phys. Soc. (London) **B69**, 796 (1956).

[22] R. L. Petritz and W. W. Scanlon, Phys. Rev. **97**, 1620 (1955).

recently there was no theoretical justification for this particular choice.

Since the lead salts are only partially ionic,[23] it might be anticipated that a combination of scattering by optical and by acoustical modes will be needed to explain the observed mobility behavior. Petritz and Scanlon[22] compared experimental mobility data on PbS in the temperature range from 77.4° to 500°K with the polar mobility theory of Howarth and Sondheimer,[24] and found that the agreement was considerably improved above room temperature if a contribution from acoustical scattering ($\mu=\mu_0 T^{-1.5}$) was included.

Theoretical low-temperature approximations to polar mobility[24–26] predict a value which increases exponentially with reciprocal temperature and which will therefore become large compared to any power-law mobility at sufficiently low temperatures. The published mobility data on the lead salts at 77.4°K and above do not show any tendency to change over to a $T^{-1.5}$ behavior at low temperatures. We decided to make a thorough study of the mobility between 77.4° and 4.2°K, to see if such an effect might be observed in this temperature range.

We were also interested in searching for the effects of scattering by ionized impurities. There appeared to be no published evidence that the low-temperature mobility in the lead salts was limited by ionized-impurity scattering. This was the case even for crystals containing more than 10^{18} carriers per cm^3 at low temperatures.

It should be emphasized that an impurity in the lead salts (as well as in other polar semiconductors) refers not only to an actual foreign atom, but also to a deviation from stoichiometry. For example, consider the effect of removing a sulfur *atom* from a perfect crystal of PbS consisting of equal numbers of Pb^{2+} and S^{2-} ions. An atom rather than an ion must be removed to preserve electrical neutrality. Consequently, two electrons are left behind in the crystal, and are attracted to the sulfur vacancy. These electrons form donor levels, just as an *n*-type impurity does in a nonpolar semiconductor. Similarly, an excess of sulfur in PbS produces acceptor levels and a *p*-type crystal. This simple discussion is not meant to imply that the deviation from stoichiometry cannot also occur by incorporation of interstitial atoms.

Finally, we wished to obtain data on a substantial number of crystals of consistent quality. Most of the previously published measurements on PbS, PbSe, and PbTe were confined to a few crystals, or else the results suggested that the samples were of variable quality.

APPARATUS AND EXPERIMENTAL PROCEDURE

A conventional dc apparatus was used for all the measurements. Special care was taken to minimize thermal potentials in the circuits, since preliminary investigation had shown the need for measuring voltages of the order of a few microvolts at the lowest temperature. Temperatures between 4.2° and 20 or 30°K were determined with a carbon resistor, and higher temperatures with a gold-silver or copper-constantan thermocouple. Further details of the apparatus are contained in the first author's thesis.[27]

The synthetic crystals used were grown at this Laboratory by modifications of the Bridgman-Stockbarger technique. The few natural crystals of PbS which were measured were single crystals from Joplin, Missouri. The compounds PbS and PbSe cleave easily along the planes determined by the cubic axes of these materials. With more care, PbTe will also cleave in this manner. All of the specimens measured were cleaved crystals, although occasionally some faces which had cleaved irregularly were smoothed by sanding.

Visual examination of the highly reflecting cleaved surfaces offered a simple means of determining that the samples selected were actually single crystals. Several low-angle grain boundaries were detected in a few of the samples, but this appeared to have no influence on the experimental results.

The compositions of the liquid and solid phases of the lead salts which are in equilibrium with each other are generally not the same.[28] As a consequence, the composition of a crystal grown from the melt was usually found to vary along the direction of growth. The samples were cleaved such that their lengths were as nearly as possible perpendicular to the composition gradient. The sample dimensions were generally about 1×1×3 or 4 mm. All samples used were checked for homogeneity by probing their surfaces with a thermoelectric test set. In this manner, crystals were selected in which the carrier concentration was constant to within about 15% or better.

The Hall-coefficient and resistivity measurements at 77.4° and 4.2°K were obtained by direct immersion of the sample in liquid nitrogen and liquid helium. Data at about 15 temperatures between 77.4°K and room temperature were obtained by positioning the sample at an appropriate level inside a Dewar partially filled with liquid nitrogen. For readings between 77.4° and 4.2°K, the sample was held in a fixed position, initially immersed in the helium in the inner Dewar of a double Dewar system (the annular region between the two Dewars was filled with liquid nitrogen). As the helium boiled away and the sample began to warm, readings were taken as quickly as possible. In this manner, data

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[23] W. W. Scanlon, Naval Ordnance Laboratory Report Navord-4262, 1955 (unpublished).

[24] D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

[25] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 496 (1939).

[26] F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1955).

[27] R. S. Allgaier, Naval Ordnance Laboratory Report Navord-6037, 1958 (unpublished).

[28] J. Bloem and F. A. Kröger, Z. physik. Chem. **7**, 1 (1956).

at an average of about 50 temperatures between 4.2° and 77.4°K were obtained. It normally took 4 to 6 hours for the sample to warm from 4.2° to 77.4°K.

This simple method of obtaining Hall-effect and resistivity measurements at many temperatures was practical because of the low resistivity of the samples, their small size, and the fact that they were mounted horizontally, perpendicular to the temperature gradient inside the Dewar.

In calculating the resistivity, an average of the voltages across the resistivity probes with the sample current in either direction was used. To obtain the Hall coefficient, an appropriate average was taken of the voltages across the Hall probes for the four combinations of sample current and magnetic field directions.

Several samples were checked at 77.4°K and at 4.2°K to see if the resistivity depended on the sample current and to see if the Hall coefficient depended on the sample current or magnetic field strength. Only in one case was any significant dependence noted. For a sample having a very high mobility at 4.2°K, a 10% decrease in resistivity occurred for a current three times larger than the value used for the measurements. This was not accompanied by a change in the Hall effect.

RESULTS

Five of the 29 samples investigated were *n*-type crystals of natural PbS; the remainder were synthetic, and included 7 PbS, 5 PbSe, and 12 PbTe specimens. The Hall coefficient and resistivity were measured as a quasi-continuous function of temperature between 4.2° and 295°K for 17 of the 29 samples. These 17 will be hereinafter referred to as the *principal* group of samples. The Hall coefficient and resistivity of the remaining samples were measured only at one or more of the temperatures 4.2°, 77.4°, and 295°K.

Figures 1 and 2 show the Hall coefficient as a function of reciprocal temperature for 7 of the crystals from the principal group in the temperature ranges 40°–295°K and 4.2°–50°K. These results are typical of those found for all of the crystals examined.[27] Figures 3 and 4 show the resistivity *versus* reciprocal temperature for the same crystals and temperature ranges. Table I lists the Hall coefficients and resistivities of all 29 samples at 295°, 77.4°, and 4.2°K.

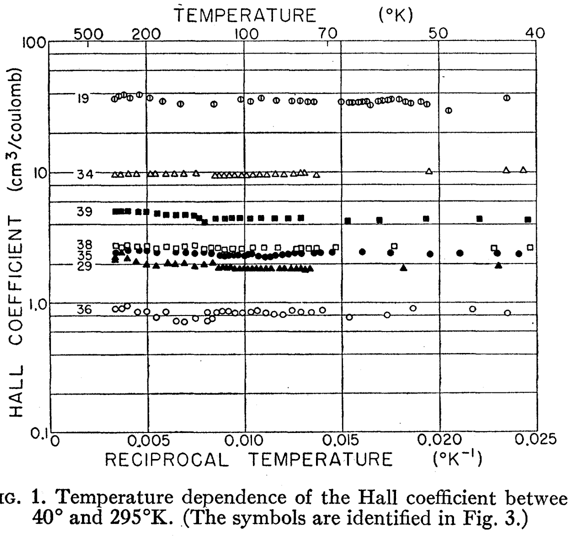

FIG. 1. Temperature dependence of the Hall coefficient between 40° and 295°K. (The symbols are identified in Fig. 3.)

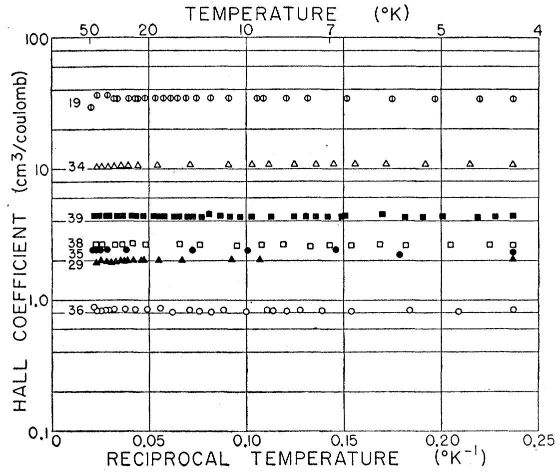

FIG. 2. Temperature dependence of the Hall coefficient between 4.2° and 50°K. (The symbols are identified in Fig. 3.)

Figure 5 contains a log-log plot of the Hall mobility data *versus* reciprocal temperature for two typical samples, showing the individual data points calculated from the Hall coefficient and resistivity measurements.[29] The purpose of this figure is to illustrate the density and precision of the mobility data. From such data as these,

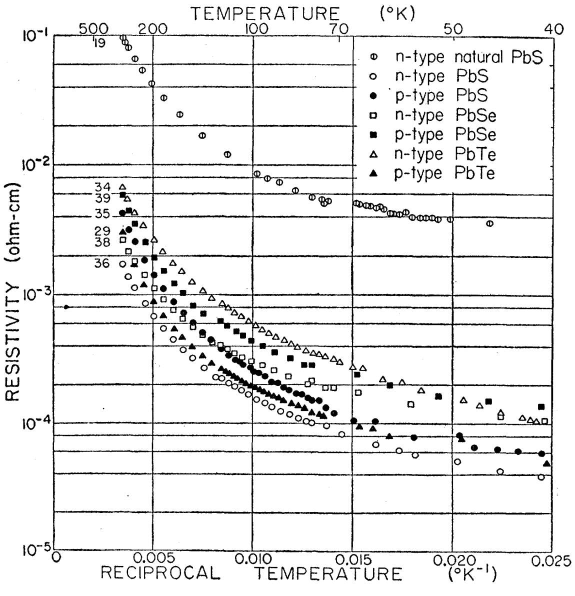

FIG. 3. Temperature dependence of the resistivity between 40° and 295°K.

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[29] See reference 27 for similar figures for the remaining samples of the principal group.

TABLE I. Hall coefficient and resistivity at 295°, 77.4°, and 4.2°K.

Sample Type and material	No.	Hall coefficient (cm^3/coulomb) 295°K	77.4°K	4.2°K	Resistivity (ohm-cm) 295°K	77.4°K	4.2°K
n PbS (natural)	3	−40.4	−39.4	−38.3	9.38×10^{-2}	6.53×10^{-3}	2.67×10^{-3}
	19	−37.2	−35.5	−34.1	9.64×10^{-2}	5.89×10^{-3}	2.22×10^{-3}
	20	−32.8			6.70×10^{-2}		
	4	−20.4			4.42×10^{-2}		
	5	−5.5			1.37×10^{-2}		
n PbS	13	−1.67			2.72×10^{-3}		
	17	−1.40	−1.47	−1.47	2.72×10^{-3}	1.34×10^{-4}	2.15×10^{-5}
	26	−1.55	−1.40	−1.35	2.71×10^{-3}	1.60×10^{-4}	3.36×10^{-5}
	36	−0.910	−0.850	−0.840	1.74×10^{-3}	9.98×10^{-5}	1.51×10^{-5}
	16	−0.240	−0.232	−0.230	4.80×10^{-4}	5.57×10^{-5}	8.59×10^{-6}
p PbS	41	2.76			4.65×10^{-3}		
	35	2.62	2.45	2.35	4.22×10^{-3}	1.63×10^{-4}	2.94×10^{-5}
n PbSe	38	−2.80	−2.68	−2.62	2.68×10^{-3}	2.11×10^{-4}	6.87×10^{-5}
	27	−1.87	−1.77	−1.75	1.87×10^{-3}	1.07×10^{-4}	1.26×10^{-5}
p PbSe	39	5.10	4.53	4.35	5.90×10^{-3}	2.86×10^{-4}	9.05×10^{-5}
	24	2.62	1.78	1.68	2.85×10^{-3}	1.39×10^{-4}	3.81×10^{-5}
	37	1.92	1.52	1.46	1.93×10^{-3}	1.11×10^{-4}	2.52×10^{-5}
n PbTe	34	−9.70	−9.80	−10.8	6.71×10^{-3}	3.54×10^{-4}	2.40×10^{-5}
	9	−5.67	−5.44	−5.78	3.28×10^{-3}	1.72×10^{-4}	7.23×10^{-6}
	32	−1.95	−1.82	−2.01	1.17×10^{-3}	8.66×10^{-5}	8.68×10^{-6}
	33	−2.03	−1.90	−1.94	1.24×10^{-3}	9.13×10^{-5}	1.58×10^{-5}
	30	−0.723	−0.660	−0.660	5.38×10^{-4}	6.15×10^{-5}	9.93×10^{-6}
p PbTe	1	20.5	18.8		2.44×10^{-2}	9.35×10^{-4}	
	1a	7.93	6.56		1.04×10^{-2}	3.03×10^{-4}	
	12	3.45	2.62		5.03×10^{-3}	1.62×10^{-4}	
	8	3.20	2.58	2.95	4.11×10^{-3}	1.59×10^{-4}	1.15×10^{-5}
	11	2.79			3.56×10^{-3}		
	10	2.74			3.94×10^{-3}		
	29	2.20	1.85	2.07	3.04×10^{-3}	1.27×10^{-4}	1.08×10^{-5}

the smooth mobility curves of Figs. 6, 7, and 8 were obtained for the 17 principal samples. Table II lists the Hall mobilities at 295°, 77.4°, and 4.2°K, and the carrier concentrations in the 29 samples, and also the average slope between 295° and 100°K for the mobility curves of the principal samples. The carrier concentrations were calculated from the formula $R=1/ne$ (R=Hall coefficient, e=electronic charge, n=carrier concentration), using the Hall coefficient value at 4.2°K, or at the lowest temperature at which it was obtained.

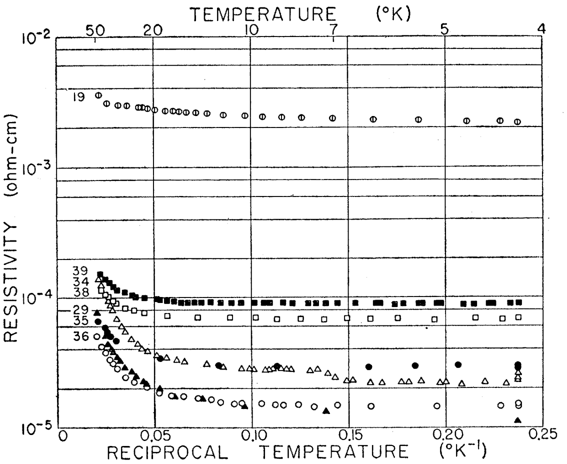

FIG. 4. Temperature dependence of the resistivity between 4.2° and 50°K. (The symbols are identified in Fig. 3.)

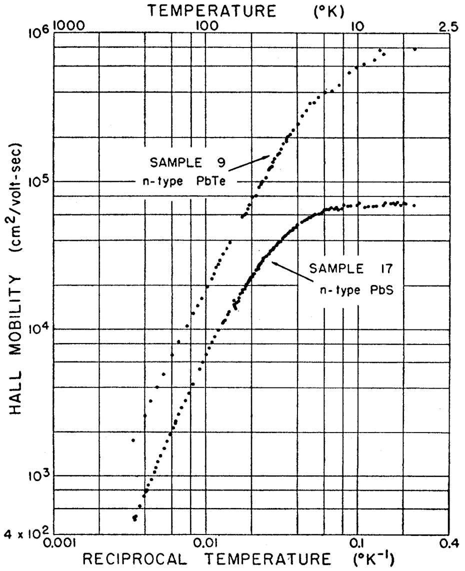

FIG. 5. Mobility data obtained for two typical samples between 4.2° and 295°K.

The accuracy of the results is estimated to be 10–20%. Thus the principal source of uncertainty in many cases is the nonuniform composition of the crystal. The numerous factors which determine the accuracy of the data have been considered in detail elsewhere.[27]

DISCUSSION

Hall Effect and Resistivity

As is evident from Figs. 1 and 2, the Hall coefficient for every sample varied only slightly over the entire temperature range from 4.2° to 295°K. Generally, the Hall coefficient slowly decreased with decreasing temperature, and was 10 to 20% lower at 4.2°K than at 295°K (see Table I). However, the Hall coefficients of all except one of the 5 PbTe samples of the principal group increased again between 77.4° and 4.2°K by as much as 15%.

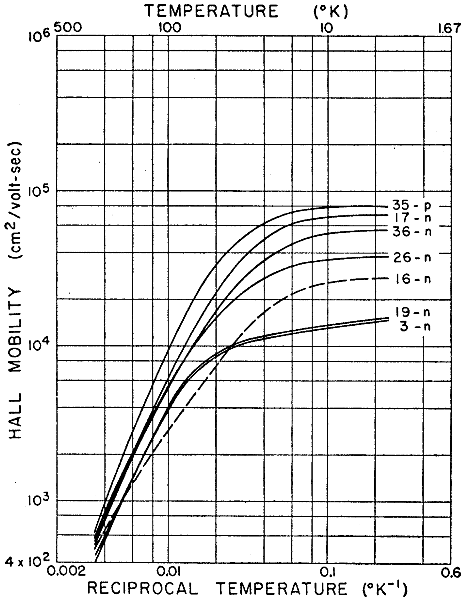

FIG. 6. Mobility in 7 PbS samples between 4.2° and 295°K.

The values of the Hall coefficient correspond to carrier concentrations of the order of 10^{18} per cm^3 (see Table I). A few samples, especially the natural PbS crystals, had carrier concentrations as small as about 10^{17} per cm^3. The care used in preparing the synthetic crystals makes it probable that most of the carriers present were due to deviations from stoichiometry rather than to the presence of impurities. Because of the large carrier concentrations occurring in the crystals, the essentially constant Hall coefficient is not surprising. Such behavior has been observed in many other semiconductors with similar carrier concentrations, and is generally ascribed to impurity bands which have broadened and overlapped the adjacent conduction or valence band.

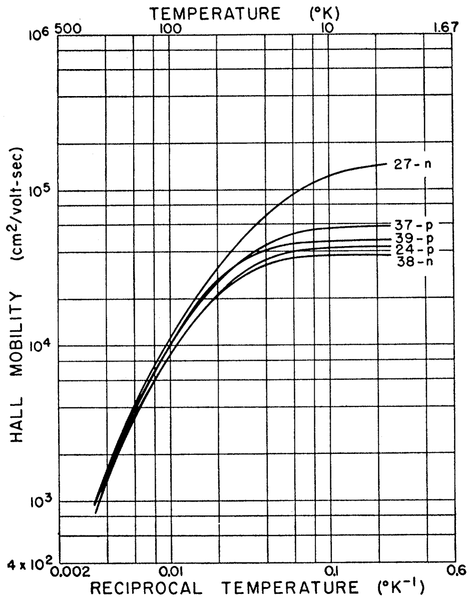

FIG. 7. Mobility in 5 PbSe samples between 4.2° and 295°K.

The decrease of the Hall coefficient with falling temperature could be due to changing statistics. The degeneracy temperature of a conductor with 10^{18} carriers per cm^3 is $(42/m^*)$°K, where m^* is the ratio of effective to free electron mass. There have not been any precise determinations of the effective masses of electrons or holes in the lead salts, but most of the estimates for m^* lie in the range 0.1–0.5.[3,22,30–32] For

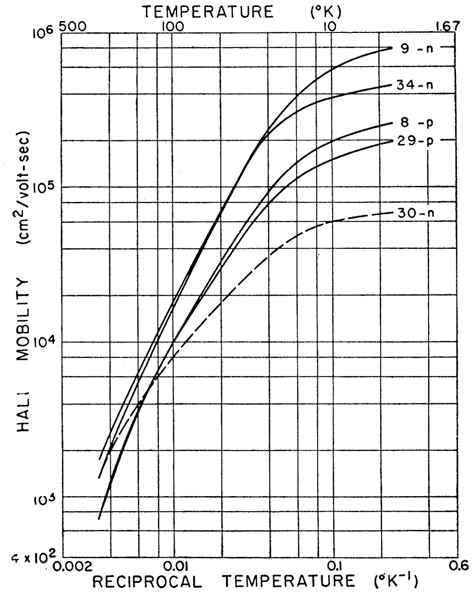

FIG. 8. Mobility in 5 PbTe samples between 4.2° and 295°K.

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[30] E. H. Putley, Proc. Phys. Soc. (London) **B68**, 35 (1955).

[31] Bloem, Kröger, and Vink, in *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 273.

[32] G. G. Macfarlane and L. Pincherle (unpublished), quoted in reference 4.

$m^*=0.25$, the degeneracy temperature is about 170°K, and thus the observed decrease in the Hall coefficient does occur in an appropriate temperature range.

It is well known that the Hall coefficient for acoustical scattering in a parabolic band with spherical energy surfaces and with $\tau=l/E^{\frac{1}{2}}$ (τ= mean free time, l= constant, E= energy) is given by $R=(3\pi/8)/ne=1.18/ne$ for the case of classical statistics. As the statistics become completely degenerate, the factor 1.18 goes to unity. For the three cubically symmetric models treated by Abeles and Meiboom[33] and Shibuya,[34] the Hall coefficient is given by

$$R=\frac{3\pi}{8}\frac{1}{ne}\left[\frac{3K(K+2)}{(2K+1)^2}\right] \tag{1}$$

(where K is the ratio of effective masses characterizing the energy ellipsoids) for the case of classical statistics. We have calculated the Hall coefficient for these models using completely degenerate statistics and find that the only change is to replace $3\pi/8$ by 1, just as in the simple model.

For a polar crystal at high temperatures, $\tau=lE^{\frac{1}{2}}$.[24] In this case, $R=1.10/ne$ for classical statistics and the simple band, and again the numerical factor decreases to unity as the statistics become completely degenerate. At low temperature, the factor is essentially unity regardless of the statistics.[35] From the manner in which the relation of τ to E enters the calculations of Abeles and Meiboom and of Shibuya, it is clear that applying the polar scattering approximations to their models will again produce the simple band results, multiplied by the bracketed function in Eq. (1). Thus a decrease of 20% or less due to changing statistics is to be expected under quite general assumptions regarding the scattering mechanisms and band models.

The exact behavior of the Hall coefficient as a function of temperature could in principle be predicted if the precise form of $\tau=\tau(E,T)$ were known. This information is lacking, but it seems reasonable to ascribe the observed decrease in the Hall coefficient to changing statistics, since the above discussion shows that it is of the right order of magnitude and occurs in an appropriate temperature range.

The observed low-temperature increase in the Hall coefficient occurring in the PbTe samples may be due to the presence of impurity levels. However, this increase is partially obscured by the decrease discussed above, and this made it impractical to calculate an activation energy for the supposed impurity levels.

The resistivity is reciprocally related to the mobility because of the constant carrier concentration of the samples and will not be discussed separately.

Mobility between 50° and 295°K

As shown in Figs. 6, 7, and 8, the mobilities in the 17 principal samples increased rapidly with decreasing temperature down to about 50°K. The mobility behavior in this temperature range was essentially the same for all of the crystals of a given material and carrier type, with the following exceptions: the mobilities in the two natural PbS crystals (Samples 3 and 19) leveled off rather abruptly at about 60°K. Also, samples 16 (*n*-type PbS) and 30 (*n*-type PbTe) had mobilities which increased less rapidly with decreasing temperature over the entire temperature range from 295° to 50°K, so that they were less than half as large at 77.4°K as other samples of the same type. It was because of this important difference that the mobilities in samples 16 and 30 are shown as dashed curves in Figs. 6 and 8.

The averages of the mobilities at 295° and at 77.4°K, calculated from the values listed in Table II, are given in Table III. These values agree well with the more recent of the previously published measurements.[15,16,18–20,22] The average values for PbS at room

TABLE II. Hall mobility at 295°, 77.4°, and 4.2°K, carrier concentration, and average slope of mobility curve between 295° and 100°K.

Sample		Carrier concentration (cm^{-3})	Hall mobility $(\mathrm{cm}^2/\mathrm{volt\text{-}sec})$			Average slope of mobility curve between 295° and 100°K
Type and material	No.		295°K	77.4°K	4.2°K	
n PbS	3	0.164×10^{18}	431	6040	14 400	2.1
(natural)	19	0.184	386	6030	15 400	2.2
	20	0.191	490			
	4	0.306	462			
	5	1.14	402			
n PbS	13	3.74	614			
	17	4.25	515	11 000	68 500	2.3
	26	4.63	572	8750	40 200	2.1
	36	7.45	523	8520	55 600	2.2
	16	27.2	500	4160	26 800	1.6
p PbS	41	2.27	594			
	35	2.66	621	15 000	80 000	2.4
n PbSe	38	2.38	1045	12 700	38 200	2.0
	27	3.57	1000	16 500	139 000	2.3
p PbSe	39	1.44	865	15 800	48 100	2.3
	24	3.72	920	12 800	44 100	2.1
	37	4.28	995	13 700	57 900	2.1
n PbTe	34	0.579	1450	27 700	450 000	2.2
	9	1.08	1730	31 600	800 000	2.2
	32	3.11	1670	21 000	231 000	
	33	3.22	1640	20 800	123 000	
	30	9.48	1340	10 700	66 500	1.6
p PbTe	1	0.332	839	20 100		
	1a	0.952	763	21 600		
	12	2.39	686	16 200		
	8	2.12	780	16 200	256 000	2.4
	11	2.24	784			
	10	2.28	695			
	29	3.02	724	14 600	192 000	2.3

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[33] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).

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temperature suggest that *p*-type crystals have a higher carrier mobility than *n* type. Unfortunately, only one *p*-type ingot of PbS was available for study. Putley[19] also observed a higher mobility in *p*-type PbS. This is a puzzling result since intrinsic PbS at elevated temperatures is known to be *n* type. In fact, an *n*-type natural PbS crystal with only 6×10^{15} electrons per cm^3 measured recently[21] shows signs of becoming intrinsic at room temperature. More precise measurements on better materials are needed to resolve these contradictory results.

The mobility behavior in the measured samples appears to be an intrinsic property down to about 50°K. This is quite remarkable, considering that most of the crystals have carrier concentrations of the order of 10^{18} per cm^3. In germanium, the effects of scattering by 10^{18} ionized impurities are evident even at room temperature, and completely determine the mobility below room temperature.[36]

The average slopes of the $\log\mu-\log(1/T)$ curves between room temperature and 100°K (see Table II) of 15 of the 17 principal samples had values between 2.0 and 2.4, with an average of 2.2. (The two abnormal synthetic crystals, Samples 16 and 30, had slopes of 1.6.) There appears to be no difference in the slopes among PbS, PbSe, and PbTe, or between *n*- and *p*-type crystals. The slope values would have been higher had we extended the measurements to higher temperatures, since our mobility curves are generally slightly concave downward.

It seems quite probable that the intrinsic mobility behavior observed in the range 50–295°K is due to lattice scattering by a combination of optical- and acoustical-mode vibrations. Unfortunately, the lack of any detailed information on the band structure of the lead salts makes it impractical to make a quantitative analysis of the experimental data in terms of the numerous theoretical treatments of mobility presently available. However, we will make a few general remarks about several theories.

Herring,[37] by considering both intravalley and intervalley scattering in multiple energy-ellipsoid models, has shown that the slope of the $\log\mu-\log(1/T)$ curve for acoustical scattering can be increased to values considerably higher than the 1.5 which results from the simple theory. Ehrenreich and Overhauser[38] have calculated a mobility which varies approximately as $T^{-2.3}$ by considering nonpolar scattering from both acoustical and optical phonons in a crystal having two atoms per unit cell. Either of these theories, if treated phenomenologically, could provide a reasonable approximation to the observed mobilities in the lead salts.

TABLE III. Average mobilities at 295° and 77.4°K.

Material and type	Hall mobility (cm^2/volt-sec) 295°K	77.4°K	Number of samples averaged 295°K	77.4°K
n PbS (natural)	434	6035	5	2
n PbS	556	9420	4	3
p PbS	608	15 000	2	1
n PbSe	1023	14 600	2	2
p PbSe	927	14 100	3	3
n PbTe	1623	25 300	4	4
p PbTe	753	17 700	7	5

The low-temperature approximations to the mobility for various theories of polar scattering[24–26] predict a mobility proportional to $\exp(\theta/T)-1$, where θ is a characteristic temperature. This form of a mobility curve is decidedly concave upward on a log–log scale, and can be combined with a power law mobility to produce a concave downward curve only over a limited temperature range. Recently, however, Ehrenreich[39] considered the mobility of electrons in InSb, and showed that the mobility due to polar scattering (Howarth and Sondheimer theory[24]) did become concave downward if a nonparabolic band model was used. Another interesting development has been the derivation of a theoretical mobility which is proportional to $T^{-2.5}$.[40,41]

A distinguishing feature of the two synthetic samples which exhibited the much less rapid increase in their mobilities in the temperature range 50–295°K is that they were both *n*-type crystals (excess Pb) and had the highest carrier concentrations of any of the 29 samples measured. Bloem and Kröger[28] have investigated the phase diagram of PbS and found that not more than about 10^{19} excess lead ions per cm^3 can exist in equilibrium in solid PbS. Houston[42] observed the formation of a lead phase when he attempted to grow lead rich PbTe crystals with more than about 10^{19} excess lead ions per cm^3. It is therefore quite possible that the unusual mobility behavior in these two crystals is due to the presence of an interspersed lead phase.

The abrupt flattening of the mobility curves of the two natural PbS crystals of the principal group was rather surprising. These specimens were considered to be of high quality, as judged by lifetime measurements and etch pit counting.[43] A large variation in mobility behavior in natural PbS at low temperatures has been observed,[21] and since we were primarily interested in the synthetic crystals, we made no further attempt to account for the particular behavior noted in the two natural crystals.

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Mobility, 4.2° to 50°K

Below 50°K, the mobility curves of the principal samples turned gradually toward the horizontal, and in most cases had become constant at 4.2°K. The mobilities in a few samples (principally the PbTe crystals) were still increasing at 4.2°K, but in no case was a significant decrease observed. The mobilities at 4.2°K varied greatly from sample to sample: the ranges of measured values were 14 400–15 400 (natural PbS), 26 800–80 000 (PbS), 38 200–139 000 (PbSe), and 66 500–800 000 cm²/v-sec (PbTe).

The gradual turn of the mobility curves toward the horizontal below 50°K masks any acoustical lattice scattering ($\mu \propto T^{-1.5}$) which might otherwise have predominated in this temperature region. The behavior of the mobility in the liquid helium temperature range is characteristic of the residual resistance phenomenon observed in metals: the mobilities become temperature independent and their values vary from one sample to the next in a manner unrelated to the carrier concentration. The temperature-independent scattering suggests that the samples are statistically degenerate. This is indeed the case; for example, the Fermi level equals $170kT$ at 4.2°K for a simple band containing 10^{18} carriers per cm³ with $m^* = 0.25$.

There are many kinds of crystal defects which could limit the mobilities at low temperatures. One type of defect which must be present is the ionized "impurity" associated with each of the 10^{18} extrinsic carriers. Theoretical expressions for scattering by ionized impurities have been derived by Conwell and Weisskopf[44] and by Brooks[45] and Herring[46] for the case of classical statistics. Although the validity of these formulas for low temperatures and large carrier concentrations is questionable,[47,48] they have predicted correct order-of-magnitude results over a wide range of conditions, including carrier concentrations of 10^{18} in the liquid helium temperature range.[36]

The Brooks-Herring theory was extended to degenerate statistics by Dingle[49] and by Mansfield,[50] and the result was shown to be essentially the same as an earlier derivation by Mott[51] for dilute solid solutions of metals. This formula may be written as

$$\mu = \frac{6}{(3\pi^2)^{\frac{2}{3}}}\left(\frac{e}{h}\right)\frac{n^{\frac{1}{3}}}{N}\left[\frac{x^2/2}{f(x)}\right], \tag{2}$$

where

$$f(x) = \log(1+x) - x/(1+x), \tag{3}$$

$$x = \tfrac{1}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\left(\frac{h}{e}\right)^2\left(\frac{\kappa}{m_e}\right)n^{\frac{1}{3}}, \tag{4}$$

and μ, n, e, and m_e are the mobility, concentration, charge, and effective mass of the current carriers, h is Planck's constant, N is the concentration of scatterers, and κ is the static dielectric constant. The bracket in Eq. (2) equals unity for small x; for larger x, it increases monotonically with increasing x, and for very large x varies essentially as x^2. For fixed carrier concentration, x is proportional to κ/m_e.

The Conwell-Weisskopf formula was extended to degenerate statistics by Johnson and Lark-Horovitz[52] who found the familiar result

$$\rho = (6270/n^{\frac{1}{3}}) \text{ ohm-cm}, \tag{5}$$

where ρ is the resistivity. This result predicts a mobility of the order of 1000 cm²/v-sec for *all* materials with 10^{18} carriers per cm³. This is correct for germanium, but is in error by factors as large as 800 for the values for the lead salts listed in Table II. However, as one of us has shown elsewhere,[27] the Johnson-Lark-Horovitz formula may be generalized, and the result is then quite similar to Eq. (2).

If we use $m^* = 0.1$ and $n = N = 10^{18}$ in the modified Johnson-Lark-Horovitz and the Mott-Dingle-Mansfield formulas, mobilities of 50 000 and 500 000 cm²/v-sec require static dielectric constants of the order of 100 and 400, respectively. These are unusually high values for nonferroelectric materials. The International Critical Tables list a static dielectric constant of 17.9 for PbS from a measurement made in 1894. Burstein and Egli,[53] however, using a formula due to Szigeti,[54] have calculated that the static dielectric constant of PbS is about 70, and Burstein[55] has suggested that the values are even higher for PbSe and PbTe.

It should be mentioned that metals having many more than 10^{18} carriers per cm³ often have low-temperature mobilities considerably greater than 1000 cm²/v-sec, despite small dielectric constants. For example, at 15°K the mobility of electrons in copper and silver is about 5000 and 12 000 cm²/v-sec (assuming one carrier per atom). It may be that the "semiconductor viewpoint" is not appropriate for interpreting the low-temperature behavior of statistically degenerate samples of the lead salts.

Although a high dielectric constant indicates the possibility of a high mobility at low temperatures, it does not explain the extremely wide variation in the mobility values at 4.2°K. If ionized impurities determine these values, a high degree of compensation would be required to explain the results in some cases; this seems unlikely since the uncompensated carriers already number 10^{18} per cm³.

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Since the point defects do not appear to be an important scattering mechanism at low temperatures, it is natural to suspect dislocations or other gross defects. To identify further these scatterers is a formidable problem; however, we have performed the following simple experiment:

The Hall coefficient, resistivity, and mobility of a PbSe and a PbTe crystal at room temperature, 77.4°, and 4.2°K were determined in the usual way. The results were typical of the values reported above. Then the crystals were tapped several hundred times with a sharp instrument at various positions distributed over the crystal faces. The Hall coefficient, resistivity, and mobility were again determined. It was found that the room temperature mobilities were essentially unchanged; at 77.4°K they had decreased by 10%, and at 4.2°K they had decreased by 20% and 30%. The Hall coefficients changed at most by 5%. This experiment suggests that dislocations are an important low-temperature scattering mechanism in most of the crystals we have examined, even though 10^{18} extrinsic carriers per cm^3 are present. A similar experiment, also resulting in lowered mobilities, has been performed on germanium.[56]

CONCLUSIONS

We have reported Hall effect and resistivity measurements, and the Hall mobilities derived therefrom, for 29 crystals of PbS, PbSe, and PbTe between 4.2° and 295°K. The essentially constant Hall coefficient which was observed over the entire temperature range is usual for semiconductors containing 10^{18} carriers per cm^3. The mobility, however, which increased rapidly with decreasing temperature, was unique for semiconductors with such large carrier concentrations. The mobilities at 4.2°K became as large as 800 000 $\text{cm}^2/\text{v-sec}$, which is probably the highest mobility measured to date in any semiconductor at this temperature.

It is possible that unusually high static dielectric constants can explain the unimportance of low-temperature scattering by point defects in the lead salts. Another approach (not requiring a high dielectric constant) might be to treat the lead salts as metals rather than semiconductors, since many metals have rather high mobilities at low temperatures, despite carrier concentrations of the order of 10^{22} per cm^3. In any case, the lack of point-defect scattering in the lead salts resulted in a mobility which was an essentially intrinsic property down to about 50°K.

Theories are available to compare with the experimental results, but corroborative information is needed on the band structure of the lead salts from other types of measurements. Conventional cyclotron resonance is probably not useful for this purpose because of the very low resistance occurring in the samples; however, the recent proposals for observing cyclotron resonance in metals may well provide the needed technique.

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