

Thermoelectricity and Thermal Conductivity in the Lead Sulfide Group of Semiconductors

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The thermal conductivity and thermoelectric power of six specimens of PbS and one each of PbSe and PbTe have been measured at temperatures ranging from 4°K to 100°K. In the same temperature region the charge carrier mobility in these samples was determined from measurements of electrical resistivity and Hall coefficient. Four of the PbS samples were natural and *n* type, while the other specimens were synthetic and *p* type. The synthetic samples contained only a few single crystals but two of the natural specimens were highly polycrystalline.

At low temperatures the charge carrier mobilities tend to high constant values similar to those reported elsewhere in single

crystals of the same materials. From an estimate of the scattering cross section of the point defects we find evidence for explaining this behavior in terms of metallic rather than semiconducting properties.

Maxima attributed to phonon drag have been observed below 20°K in the thermoelectric power of the specimens of highest thermal conductivity. The thermal conductivity was similar in all samples at 100°K but varied by as much as two orders of magnitude at 10°K. In order to explain these results it is necessary to consider scattering of phonons by point imperfections, free electrons, and dislocations.

INTRODUCTION

IN recent years a great deal of work has been done in measuring the optical and galvanomagnetic properties of the lead sulfide group of semiconductors. These topics are discussed fully in the recent review article by Scanlon.¹ The thermal and thermoelectric properties on the other hand have received much less attention especially in the temperature range below 100°K. Devyatkov² measured the thermal conductivity of a series of PbTe samples at temperatures between 80°K and 450°K, and Finlayson and Greig³ measured the thermoelectric power of three specimens of natural galena down to liquid hydrogen temperatures.

We have now measured the thermal conductivity and thermoelectric power of a series of PbS, PbSe, and PbTe samples over the temperature range 4°K to 100°K, and their electrical resistivity from 4°K to room temperature. While previous measurements of thermoelectric power³ had given no indication of any phonon-drag maxima, the present investigation reveals pronounced maxima at about 10°K in several samples. From the extension of the thermal conductivity measurements to lower temperatures, information has been gained on the number and nature of the lattice imperfections which give rise to the thermal resistance. This information is all the more valuable as the observed thermal conductivity values in the lead salts are unusually small. A detailed knowledge of these imperfections also answers some of the questions which had been raised by previous analyses of mobility data.^{1,4}

SPECIMENS

The samples which were investigated are listed in Table I together with the room temperature values of their Hall constant *R*. If we assume that each of the samples investigated contains only charge carriers of one kind then their carrier concentrations *n* are given by

$$n = 1/Re. \quad (1)$$

The values of *n* calculated from (1) are listed in Table I. This table also contains the number of dislocations per unit area as determined from microscopic examination of etched cleavage planes. The etching agent for the sulfides was described by Scanlon⁵ and that for



FIG. 1. Etch pits on surface of sample 5. Linear magnification, 4600X.

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¹ W. W. Scanlon, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9, p. 83.

² E. D. Devyatkov, *Zhur. Tekh. Fiz.* **27**, 461 (1957) [translation: *Soviet Phys. (Tech. Phys.)* **2**, 414 (1957)].

³ D. M. Finlayson and D. Greig, *Proc. Phys. Soc. (London)* **73**, 49 (1959).

⁴ D. M. Finlayson and D. Greig, *Proc. Phys. Soc. (London)* **B69**, 796 (1956).

⁵ W. W. Scanlon, *Phys. Rev.* **106**, 718 (1957).

TABLE I. Source, crystalline state, crystallite size, dislocation density, Hall constant, and carrier density.

No.	Compound	Source	Crystalline state	Average crystallite size	Dislocation density (cm ⁻²)	R (cm ³ coulomb ⁻¹)	Sign of carriers	n (cm ⁻³)
1	PbS	Yukon	Schistose			a	—	7.5×10 ¹⁷ b
2	PbS	Yukon	Few single crystals		3 × 10 ⁷	−10.6	—	5.9×10 ¹⁷
3	PbS	Yukon	Polycrystalline		1.3×10 ⁷	−8.40	—	7.5×10 ¹⁷
4	PbS	Utah	Few single crystals		1.2×10 ⁷	−73.1	—	8.5×10 ¹⁶
5	PbS	Synthetic	Few single crystals	5 mm×1.5 mm	7.5×10 ⁶	+3.68	+	1.7×10 ¹⁸
6	PbS+Ag	Synthetic	Few single crystals	10 mm×3 mm	6.3×10 ⁶	+0.352	+	1.8×10 ¹⁹
7	PbSe	Synthetic	Few single crystals	3 mm×1 mm	1.9×10 ⁷	+1.16	+	5.4×10 ¹⁸
8	PbTe	Synthetic	Few single crystals	15 mm×2 mm	1.8×10 ⁶	+2.53	+	2.5×10 ¹⁸

^a The resistance of this sample was so high that we were unable to measure its Hall constant with the available equipment.

^b Estim. from Fig. 5.

the telluride by Houston and Norr.⁶ It was found that this latter could also be used to etch the selenide. Figure 1 is an electron microscope photograph of the etched surface of sample 5.

Silver and lead occur together in nature and it is rather difficult to obtain natural galena which does not contain silver. Spectrographic analysis⁷ has revealed the presence of at least 1% silver in all of the Yukon material, and also from 0.1% to 10% antimony, bismuth, copper, or iron in most of it. Typical results are given in Table II. According to the supplier, sample 4 contains very little silver but its rather low mobility (see Fig. 2) nevertheless indicates the presence of imperfections.

The synthetic specimens were prepared by melting the components together in sealed quartz tubes and then zone melting the resulting compound. It was necessary at all stages to control the vapour pressure of sulfur or selenium over the compounds. In sample 6 one atomic percent of the lead was replaced by silver in an attempt to induce properties similar to those of the Yukon material. However, although the properties of sample 6 were slightly different from those of the other synthetic samples they were still quite unlike those of the natural specimens.

MEASURING APPARATUS

The thermal conductivity was determined by measuring the equilibrium temperature gradient set up when a known and constant heat current flows along the sample. Since it was necessary to limit the heat input at the lowest temperatures it was found that the ratio of length to cross section had to be around 10 cm⁻¹ in order to establish a reasonable temperature gradient along the specimen. We therefore ground rectangular samples 40 mm by 10 mm by 3 mm.

Two narrow bands on the sample surface at about one quarter of the length from each end were copper plated. The end faces of the specimens were also copper plated and copper leads soldered to the plated areas. These leads were attached to the heat source, to the

heat sink, to the thermometers, and to the thermoelectric potential probes.

The cryostat was of the type described by White and Woods.⁸ Thermocouples consisting of a gold-cobalt alloy against copper were used to measure the temperature differences along the sample and between the sample and the helium bath. Around 4°K the thermoelectric power of the gold-cobalt, copper thermocouple is 3.34 μv per degree. In order to measure a temperature difference of 0.1° to an accuracy of 2% it was therefore necessary to measure voltages of the order of 0.01 μv.

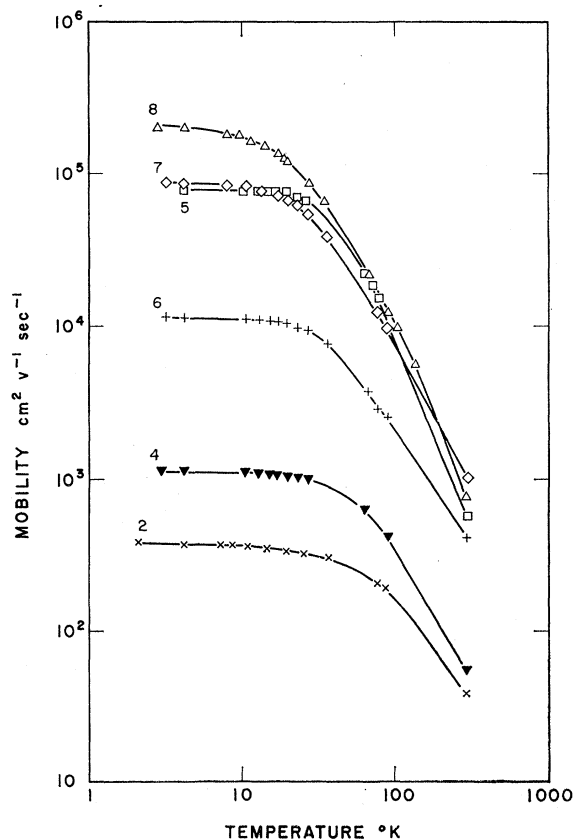


FIG. 2. Temperature dependence of mobility between 3°K and 295°K. The numbers refer to the sample numbers (see Table I).

⁶ B. B. Houston and M. K. Norr, J. Appl. Phys. **31**, 615 (1960).

⁷ R. W. Boyle, Geological Survey of Canada, Paper 55-30, 1956 (unpublished).

⁸ G. K. White and S. B. Woods, Can. J. Phys. **33**, 58 (1955).

TABLE II. Spectrographic analysis of Yukon galena.

Sample ^a	Percentage of metallic constituent						Not found
	100% to 10%	10% to 1%	1% to 0.1%	0.1% to 0.01%	0.01% to 0.001%		
1	Pb	Fe	Ag, Cu, Sb, Bi	Mg, Mn, Zn, Sn, Ca	Cd, Si, Al		
2, 3	Pb		Ag	Sb, Sn, Si, Al	Cu, Cr, Mn, Ca, Ba, Sr, Bi, Cd, Fe, Mg	Zn, As, Te	

^a The analysis relates to the lots from which the samples were cut.

This was achieved by reducing the output from a Rubicon 622 potentiometer one hundred times and comparing this emf with that from the thermocouple by means of a dc amplifier and null detector system. To measure the mean temperature of the specimen, an accuracy of a hundred times less was quite adequate so that a direct reading of the potentiometer sufficed.

The electrical resistivity was measured during the same experimental runs as the thermal conductivity. However, it was necessary to remount the samples with point contact probes in order to measure the Hall voltage with the ac bridge described by Dauphinee and Mooser.⁹ Since previous measurements^{1,4} had shown that the Hall coefficient R is a constant over the entire temperature range 3°K to 300°K, it was sufficient to measure R at room temperature, although in the natural samples in which the electron mobility was unusually small, measurements were also made at 78°K.

RESULTS

In Figs. 2 and 3 the Hall mobilities μ_H , as determined from the experimental values of R and ρ according to

$$\mu_H = R/\rho, \quad (2)$$

are plotted against temperature.

In Figs. 4 and 5 we give the temperature variations of thermal conductivity and thermoelectric power, respectively. The thermoelectric power was measured against copper. Since the low-temperature thermoelectric power of copper is strongly dependent on impurity and can be as great as $-10 \mu\text{V deg}^{-1}$,¹⁰ we determined the thermoelectric power of the Formel H.F. 38 enamelled copper wire by replacing the semiconductor by superconducting niobium tin. Immediately below the transition point of the superconductor (17.5°K) the thermoelectric power of the copper wire was still only $0.24 \mu\text{V deg}^{-1}$. As this is two orders of magnitude less than the thermoelectric power of the lead salts measured against copper we conclude that our measurements refer to the absolute thermoelectric powers of the various specimens.

Since all the measurements of current, voltage, and length were read to an accuracy of 2% or better, the limit to the overall accuracy of the results was determined by the degree of inhomogeneity of the specimens.

In spite of the size of the samples the variations of the resistivity at different points along them were no greater than the 10–20% reported elsewhere.^{4,11}

DISCUSSION OF MOBILITY

From Figs. 2 and 3 it is clear that the spread in the charge carrier mobilities even at room temperature is enormous. Between 80°K and 300°K the values and temperature dependence ($\mu_H \sim T^{-2.2}$) of the mobilities of the synthetic samples 5, 7, and 8 are representative of the intrinsic behavior reported elsewhere.^{4,11,12} The somewhat lower mobility values found in sample 6 are probably caused by the addition of silver to this sample. In the natural sample 1 the temperature dependence is reversed (see Fig. 3). In view of the highly polycrystalline nature of this sample this is perhaps not surprising because mobilities increasing with T have been observed¹³ in synthetic sintered PbS where they were interpreted as being due to grain boundary scat-

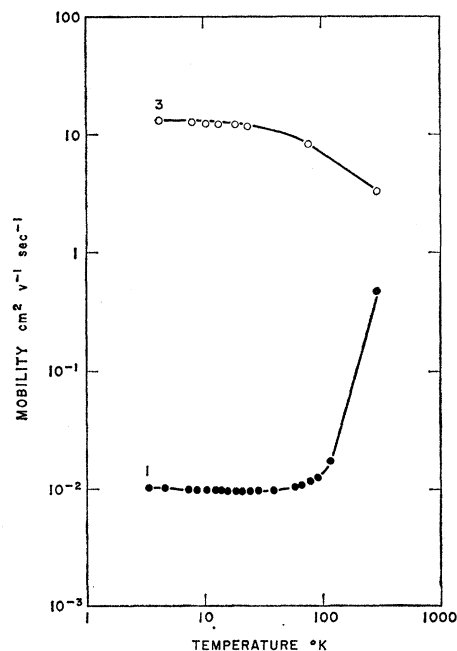


FIG. 3. Temperature dependence of mobility in two samples in which it is unusually small. The numbers refer to the sample numbers (see Table I).

⁹ T. M. Dauphinee and E. Mooser, *Rev. Sci. Instr.* **26**, 660 (1955).

¹⁰ D. K. C. MacDonald and W. B. Pearson, *Proc. Roy. Soc. (London)* **A219**, 373 (1953).

¹¹ R. S. Allgaier and W. W. Scanlon, *Phys. Rev.* **111**, 1029 (1958).

¹² E. H. Putley, *Proc. Phys. Soc. (London)* **B68**, 22 (1955).

¹³ E. H. Putley, *Proc. Phys. Soc. (London)* **B65**, 736 (1952).

TABLE III. Fermi energy, Fermi velocity, and experimental mobility at 4°K. Density of imperfections N from scattering cross section compared with carrier density n .

Sample	$E_F(0)$ (ergs)	v (cm sec ⁻¹)	μ_H at 4°K (cm ² volt ⁻¹ sec ⁻¹)	N (cm ⁻³)	n (cm ⁻³)
5	6.88×10^{-14}	3.55×10^7	7.85×10^4	4.74×10^{18}	1.70×10^{18}
6	4.17×10^{-13}	9.81×10^7	1.15×10^4	1.48×10^{19}	1.78×10^{19}
7	1.62×10^{-13}	5.68×10^7	8.40×10^4	2.79×10^{18}	5.38×10^{18}
8	9.25×10^{-14}	4.2×10^7	2.09×10^5	1.30×10^{18}	2.47×10^{18}

tering. Sample 3 contained relatively few crystallites compared to sample 1 while samples 2 and 4 appeared to be single crystals. However on cleaving any of these three samples we found traces of impurity (see Table II) on the surfaces thus exposed. It would appear from the results that such impurity layers have a marked influence on both the charge carrier mobility and the thermal conductivity.

Scanlon¹ remarks that "the behavior of the mobility in the liquid helium range is characteristic of the phenomena associated with the residual resistance observed in metals." The residual resistance in metals is normally attributed to the scattering of the charge carriers by chemical and physical imperfections.¹⁴ A simple calculation shows that scattering on point

defects does indeed account for the mobilities found at low temperatures. The mobility μ is given by

$$\mu = (e/m^*) (\Lambda/v), \quad (3)$$

where m^* is the effective mass of the charge carriers and Λ their mean free path.

In a degenerate gas the velocity v of the particles can, to a first approximation, be derived from

$$\frac{1}{2} m^* v^2 = E_F(T) \simeq E_F(0) = (h^2/2m^*) (3n/8\pi)^{2/3}, \quad (4)$$

where $E_F(T)$ is the Fermi level at temperature T . Thus if m^* , n , and μ are known, it is possible from (3) and (4) to calculate the mean free path at any temperature. Once the mean free path is known one can calculate the number of scattering point defects, N , from

$$\Lambda = 1/(N\pi r^2), \quad (5)$$

where r is the scattering radius of the point defects. We have calculated N assuming an effective mass ratio of between 0.11 and 0.17 depending on the charge carrier concentration,³ and taking r equal to the average atomic radii. The results are given in Table III together with n , the carrier concentration as determined from the Hall effect. There is rather good agreement between N and n indicating that the free charge carriers originate from the impurities which act as scattering centers. We have found a similar correspondence in Allgaier and Scanlon's¹¹ samples. However, it should be pointed out that these authors reported a decrease in the low temperature mobility after they deformed a sample mechanically. This suggests that the charge carriers are also scattered by dislocations although it would seem from the above analysis that this is only a secondary process.

DISCUSSION OF THERMAL CONDUCTIVITY

In metals and semiconductors heat is transported by both the charge carriers and the lattice. The total thermal conductivity is therefore composed of two parts,

$$\mathcal{K}_{\text{total}} = \mathcal{K}_{\text{electron}} + \mathcal{K}_{\text{lattice}}. \quad (6)$$

The electronic contribution was obtained from the Wiedemann-Franz law

$$\mathcal{K}_{\text{electron}} = LT/\rho, \quad (7)$$

with an appropriate Lorenz number L . For metals above their Debye temperatures the theoretical value

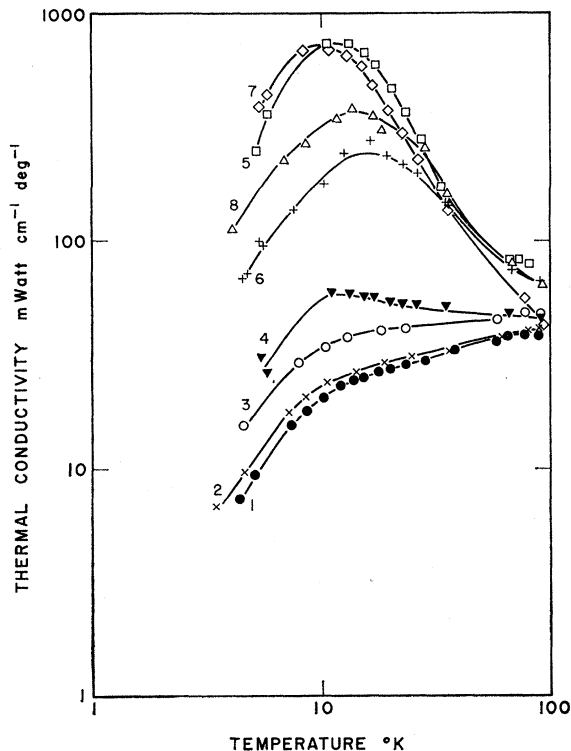


FIG. 4. Temperature dependence of thermal conductivity between 4°K and 100°K. The numbers refer to the sample numbers (see Table I).

¹⁴ For a recent discussion, see D. K. C. MacDonald, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, No. 1, p. 137.

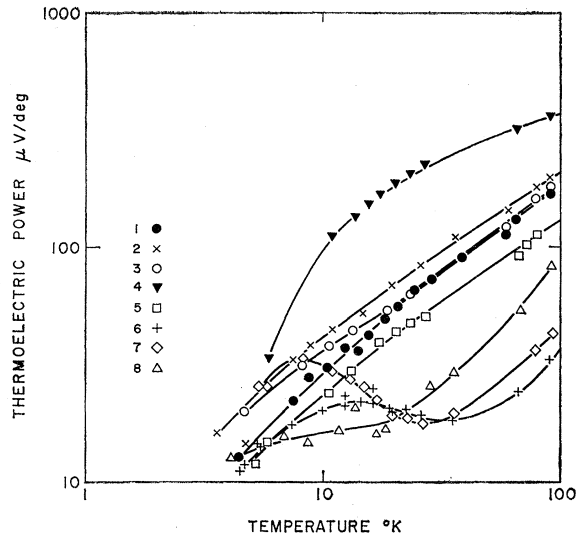


FIG. 5. Temperature dependence of thermoelectric power between 4°K and 100°K. The numbers refer to the sample numbers (see Table I).

of $L = (\pi^2/3)(k/e)^2$. Devyatkova² found by experiment that in lead telluride at room temperature

$$L = 2(k/e)^2 = 1.49 \times 10^{-8} \text{ watt ohm deg}^{-2}. \quad (8)$$

At low temperatures L decreases in general so that substituting (8) in (7) will give the upper limit of $\mathcal{K}_{\text{electron}}(T)$. From this upper limit we estimate $\mathcal{K}_{\text{electron}}$ at 100°K to be at most 20% of $\mathcal{K}_{\text{total}}$. At lower temperatures the estimated contribution of $\mathcal{K}_{\text{electron}}$ to $\mathcal{K}_{\text{total}}$ decreases rapidly and we shall therefore neglect $\mathcal{K}_{\text{electron}}$ from this point onwards.

As in the case of the mobilities, the thermal conductivities of the natural and synthetic materials are markedly different at low temperatures. Although all samples have similar conductivities at 100°K, the conductivities of the natural ones do not show the pronounced maxima found at 10°K to 20°K in the synthetic specimens. A possible explanation of this is that in the natural samples grain boundary scattering becomes important at comparatively high temperatures. However, it should be pointed out that for grain boundary scattering to remain the dominant scattering mechanism up to 100°K, grains of only a few tens of angstroms would be required. In view of the fact that even in the schistose sample 1 grain diameters of the order of 10^{-3} -cm diameter or greater are observed, other scattering mechanisms must come into play.

A more detailed analysis can be given for the synthetic specimens. It is often assumed¹⁵ that the total thermal resistivity of a solid is the sum of different resistivities each arising from a possible phonon scat-

¹⁵ For a full discussion of this approximation, see, for example, P. G. Klemens, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, No. 1, p. 220.

tering process, so that,

$$W_{\text{total}} = W_{\text{umk}} + W_{\text{isot}} + W_{\text{imp}} + W_{\text{bound}} + W_{\text{disloc}} + W_{\text{osc.disloc}} + W_{\text{electron}}. \quad (9)$$

Here we have included Umklapp processes (W_{umk}) and scattering by point imperfections (W_{isot} , W_{imp}), boundaries (W_{bound}), dislocations (W_{disloc}),¹⁶ oscillating dislocations ($W_{\text{osc.disloc}}$),¹⁷ and electrons (W_{electron})¹⁸ as the mechanisms which inhibit the flow of phonons.

The first four terms in (9) have recently been discussed in detail by Mielczarek and Frederikse¹⁹ in a paper on the thermal conductivity of InSb. Using their expressions we have calculated W_{umk} , W_{isot} , W_{bound} with the parameters appropriate to sample 5 (see Table IV). The calculated curves $W_{\text{umk}}(T)$, $W_{\text{isot}}(T)$, $W_{\text{bound}}(T)$ are plotted in Fig. 6 as curves C, B, and G. In the temperature region above 15°K where scattering on dislocations and by electrons is unimportant (see below) agreement with the experimental data (curve A) can only be obtained if impurity scattering is dominant and as big as indicated by curve D. This

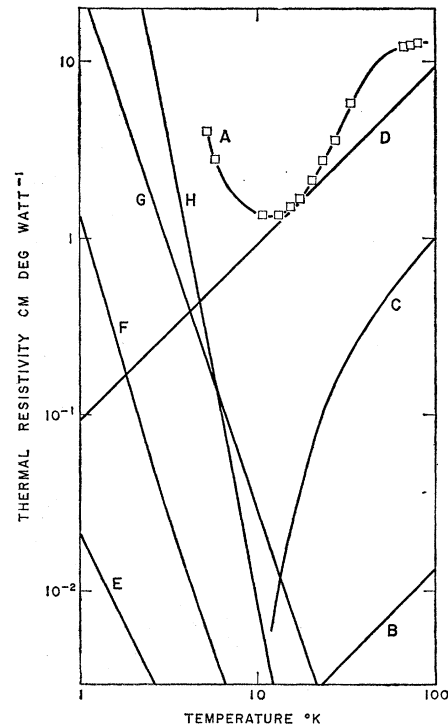


FIG. 6. Curve A, experimental thermal resistivity in sample 5; curves B, C, D, E, F, G, and H represent the contributions to thermal resistance from isotope, umklapp, point imperfection, dislocation, oscillating dislocation, boundary, and electron scattering effects, respectively.

¹⁶ P. G. Klemens, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, No. 1, p. 198.

¹⁷ A. Granato, *Phys. Rev.* **111**, 740 (1958).

¹⁸ J. M. Ziman, *Phil. Mag.* **8**, 1, 191 (1956).

¹⁹ E. V. Mielczarek and H. P. R. Frederikse, *Phys. Rev.* **115**, 888 (1959).

TABLE IV. Parameters of sample 5.

Debye temperature θ , 194°K
Velocity of sound u , 3.4×10^8 cm sec ⁻¹
Grüneisen constant γ (estimated), 2
Diameter of crystallites, 0.15 cm
Volume of unit cell V_0 , 5.21×10^{-23} cm ³

curve has been calculated according to Mielczarek and Frederikse from

$$W_{\text{imp}} = \frac{T(2\pi)^3 V_0 S^2 N}{hu^2 1.72 \times 10^{22}} \text{ cm deg/watt}, \quad (10)$$

with a scattering parameter $S=1$ and a density of point defects $N=2 \times 10^{19}$ cm⁻³. This value, which is of the order of the maximum possible number of point imperfections²⁰ in lead sulfide, differs somewhat from the density of point imperfections obtained from mobility data and listed in Table III (4.74×10^{18} cm⁻³). While both values are based on rather crude approximations we believe that the value obtained from (10) is the less reliable because (1) the method of summing thermal resistivities is inaccurate; (2) curves *B* and *D* in Fig. 6 will only have unit slope in the region in which the specific heat is proportional to T^3 ; for $T \gtrsim \theta$ the two curves should level off; (3) the scattering parameter S of the impurities is not known accurately; (4) when the number of point defects becomes large W_{imp} ceases to be proportional to N ²¹ and the expression (10) is no longer valid.

Below 15°K we have to consider rather different effects. In addition to scattering on boundaries, scattering on dislocations becomes important in this temperature range. Klemens¹⁶ has given an expression for this part of the thermal resistivity,

$$T^2 W_{\text{dis}} = (\gamma^2 u b^2 N_D / 1.68) \text{ cm deg}^{-1} / \text{watt}, \quad (11)$$

where γ is the Grüneisen constant, u the velocity of sound, b the magnitude of the Burgers vector, and N_D the number of dislocation lines per cm². With b equal to 6×10^{-8} cm and N_D equal to 7.5×10^6 cm⁻² (Table I), we have calculated $W_{\text{dis}}(T)$ from Eq. (11) and included the result in Fig. 6 as curve *E*. As seen from this figure, the calculated values are much too small to account for the experimental results; but Carruthers²² has recently shown that if one includes the long-range effects of the strain fields surrounding the dislocations, the calculated values of W_{dis} are increased by a factor of order 1000.

Granato¹⁷ has also shown that the scattering by dislocations can be much greater than predicted by Klemens if one accepts that the dislocations oscillate under stress and re-emit energy. Granato's estimate for

the thermal resistivity originating from such oscillating dislocations is

$$W_{\text{osc.dis}} \sim a^2 u N_D / 5.7 \theta^2 F(T/\theta) \text{ cm deg/watt}, \quad (12)$$

where $F(T/\theta) = (T/\theta)^4 [\ln(\theta/5T)]^2$. Here a is the lattice spacing along a dislocation line. We have again taken N_D to be 7.5×10^6 cm⁻² and have plotted $W_{\text{osc.dis}}$ in Fig. 6 (curve *F*). It will be seen that this mechanism again does not account quantitatively for the measured values but a more sophisticated theory including perhaps a combination of Carruthers' and Granato's models might improve the agreement.

However, scattering on dislocations alone cannot account for the fact that while at the lowest temperatures the thermal conductivity of sample 6 is five times smaller than that of sample 5, microscopic examination revealed approximately the same number of dislocations in both these samples (see Table I). The carrier concentration of sample 6 is ten times larger than that of sample 5 so that this behavior may perhaps be best explained by the scattering of phonons by free charge carriers. In the temperature range with which we are concerned Ziman¹⁸ calculated the mean free path l of phonons scattered by free charge carriers. His result is

$$l = \frac{\pi^5 \hbar^4 \rho T^2}{20 C^2 (m^*)^3 T_F^{\frac{1}{2}} T_S^{\frac{1}{2}}} \left[1 + \frac{4}{\sqrt{\pi}} \left(\frac{T_S}{T} \right)^{\frac{1}{2}} \right]^{-1} \text{ cm}, \quad (13)$$

where ρ is the density, $T_S = \frac{1}{2} m^* u^2$, T_F the degeneracy temperature, and C represents a coupling factor between the carriers and the lattice. We have calculated l from (13) with $C=16$ ev, $m^*/m_0=0.15$ and have determined the corresponding thermal resistance from

$$1/W = \frac{1}{3} C_e u l. \quad (14)$$

The specific heat per unit volume $C_v(T)$ was extrapolated from measurements by Parkinson and Quarrington.²³ The result is plotted in Fig. 6 (curve *H*). Once more the theoretical values do not compare too well with experiment but it must be pointed out that Ziman's theory is in an early stage of development. In germanium, for example, Ziman finds his theory applicable only in rather restricted ranges of temperatures and carrier concentration.²⁴ Nevertheless, in view of the behavior of samples 5 and 6 we feel that the scattering of phonons by electrons is of importance in the lead salts.

DISCUSSION OF THERMOELECTRIC POWER

In contrast to the mobility and thermal conductivity results, there is no marked difference in the thermoelectric powers of the natural and synthetic specimens (Fig. 5). As there is no flow of electric current asso-

²⁰ J. Bloem, Philips Research Repts. **11**, 273 (1956).

²¹ See R. Berman, P. T. Nettle, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, Proc. Roy. Soc. (London) **A253**, 403 (1959).

²² P. Carruthers, Phys. Rev. **114**, 995 (1959).

²³ D. H. Parkinson and J. E. Quarrington, Proc. Phys. Soc. (London) **A67**, 569 (1954).

²⁴ J. A. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. M. Ziman, Proc. Roy. Soc. (London) **A238**, 502 (1957).

ciated with the thermoelectric power if there is only one kind of charge carrier present, this result is not unexpected.

Between 20°K and 100°K the results are similar to previous measurements.³ Below that, however, we found pronounced maxima in the thermoelectric powers of three samples with high thermal conductivities. These maxima can be explained by the phonon drag effect²⁵⁻²⁸ according to which the charge carriers are pushed towards the cold end of the sample by the phonon flow. Herring²⁶ has estimated the phonon drag contribution to the thermoelectric power to be

$$S_{ph} = u f \bar{l} / T \mu, \quad (15)$$

where f is the fraction of the crystal momentum lost by the charge carriers to the lattice vibrations and \bar{l} is the mean free path of those phonons which interact with the carriers.

If the experimentally observed decrease of the mobilities in a series of different samples at any given temperature can be attributed to a gradual increase of the importance of scattering mechanisms other than lattice vibrations, it is reasonable to assume that such a decrease of the mobilities is accompanied by a similar decrease of f . In fact Herring has shown that if μ_L is the mobility arising from the interaction of the carriers with low-energy lattice vibrations, then $\mu_L f / \mu$ is always close to unity. We therefore have

$$S_{ph} = u \bar{l} / T \mu_L. \quad (16)$$

Since μ_L is an intrinsic property of the material, S_{ph} is proportional to \bar{l} at any temperature. If \bar{l} is of the same order as the phonon mean free paths l derived from the thermal conductivities (in fact l is always smaller than \bar{l}), it follows that in the samples in which the thermal conductivity is low, the phonon drag effect will contribute only little to the thermoelectric power. It is not surprising therefore that the natural samples show no maxima in the thermoelectric power.

We have seen that in the synthetic samples at temperatures above 20°K the thermal conductivity is governed by scattering on point imperfections. In this case l is inversely proportional to the fourth power of the angular frequency ω of the lattice modes, and since ω is of the order $3kT/\hbar$ it follows that

$$\bar{l} \sim l \propto T^{-4}. \quad (17)$$

Taking μ_L to be equal to μ in the region of intrinsic behavior of the synthetic samples (80°K to 300°K) we have $\mu \propto T^{-2.2}$. If this relation can be extrapolated to the lowest temperatures, we obtain from (17)

$$S_{ph} \propto T^{-2.8}. \quad (18)$$

However at temperatures near and below the maxima of the thermal conductivities, different phonon scattering mechanisms are operative and the temperature dependence of \bar{l} will no longer be given by (17) [e.g., for boundary scattering $\bar{l} = \text{const}$] and no matter which mechanism predominates S_{ph} will now depend on a positive power of temperature. This explains why the maxima in thermoelectric power occur at the same temperature as the maxima in the thermal conductivity.

Following Herring we can make numerical estimates of S_{ph} by introducing into (16) the maximum and minimum values which \bar{l} can take at any given temperature. The maximum value of \bar{l} is determined by the grain size (10^{-1} cm in the smallest grained, synthetic sample 6). The lower limit of \bar{l} is given by the mean free path as determined from the thermal conductivity (10^{-4} cm in sample 6 at 10°K). With an extrapolated value for μ_L of 10^6 cm² volt⁻¹ sec⁻¹ at 10°K, we then find that at this temperature S_{ph} must lie between 3 and 3000 $\mu\text{V deg}^{-1}$. The experimental values of thermoelectric power lie far below 3000 $\mu\text{V deg}^{-1}$ which seems to confirm the findings of the last section that phonon scattering on boundaries is not important. However, it must be pointed out that if phonon scattering on free charge carriers becomes important as was suggested in that section then formula (15) must be modified. Herring has discussed the influence of phonon scattering by charge carriers upon the phonon drag effect. He found that at sufficiently high carrier densities such as are met in the lead salts the phonon current is reduced. The phonons will therefore exert less drag on the carriers and S_{ph} will be smaller than expected from (15).

SUMMARY

We have concentrated our discussion on the results from the four synthetic samples since the unusually low electrical and thermal conductivities in the natural galena specimens suggested the presence of high numbers of impurities and imperfections.

The charge carrier mobilities in the synthetic samples are similar to those reported elsewhere in single crystals of the same materials. The mobilities tend to high constant values at low temperatures and from an estimate of the scattering cross section of the point defects we find that this behavior can be explained in terms of metallic rather than semiconducting properties.

The thermal conductivity in the temperature range 20°K to 100°K is characterized by point-defect scattering processes, but a detailed comparison between theory and experiment is not possible at present. At lower temperatures it appears that the scattering of phonons by electrons is the most important process but again agreement with existing theory is rather poor and one ought not to discount the role played by dislocations.

Maxima attributed to phonon drag have been observed in the thermoelectric power around 10°K. These maxima occur at approximately the same tem-

²⁵ H. P. R. Frederikse, Phys. Rev. **92**, 248 (1953).

²⁶ C. Herring, Phys. Rev. **96**, 1163 (1954).

²⁷ D. K. C. MacDonald, Physica **20**, 996 (1954).

²⁸ V. A. Johnson, *Progress in Semiconductors* (Heywood, London, 1956), Vol. 1.

peratures as the maxima in the thermal conductivity, and indeed, only appear at all in the samples which are among the best conductors of heat.

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Selective Spin Excitation and Relaxation in Nuclear Quadrupole Resonance*

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Nuclear relaxation in a quadrupolar spin system has been investigated by selectively exciting nuclei into particular magnetic levels and observing the transient recovery of the spin system toward an equilibrium population distribution. Selective excitation is achieved by correlating the frequency and precessional behavior of nuclei in certain states with applied elliptically and linearly polarized, pulsed radio-frequency fields. A quantum-mechanical analysis is presented to describe the excitation of a quadrupolar spin system produced by a pulsed, elliptically polarized rf field. Using selective excitation techniques, several new modes of longitudinal relaxation are observed. Experiments using the chlorine quadrupole resonance in a single crystal of

KClO₃ demonstrate how these new relaxation modes are used (1) to study dynamic spin-spin interactions and cross relaxation between overlapping resonance lines, and (2) to determine the individual $\Delta m = \pm 1$ and ± 2 quadrupolar spin-lattice relaxation transition probabilities. A method is introduced by which the magnetic dipole-dipole contribution to the resonance linewidth can be determined independently of static quadrupole broadening, by observing the decay of the beat modulation of certain free-induction signals caused by precession in a small magnetic field. The measured magnetic linewidth of Cl³⁵ in KClO₃ is in good agreement with the value obtained from a second-moment calculation.

I. INTRODUCTION

PULSED nuclear magnetic induction techniques^{1,2} are a convenient means for study of the direct transient recovery of a spin system toward thermal equilibrium. Thermal equilibrium among the spins is established by spin-spin interactions, if a spin temperature can be defined; and also a spin-lattice thermal equilibrium is established if a lattice temperature can be defined. The present paper describes the application of transient resonance techniques to the study of nuclear spin relaxation in quadrupolar spin systems. By means of selectively exciting nuclei into particular magnetic substates, additional important information about spin-spin cross-relaxation effects, quadrupolar spin-

lattice relaxation, and pure magnetic line broadening can be obtained.

In solids having noncubic symmetry, the interaction between the nuclear electric quadrupole moment and the crystalline electric field gradient can establish a system of well-defined quadrupole energy levels.³ In zero magnetic field these energy states exhibit a characteristic twofold Kramer's degeneracy of $\pm m$, where m is the magnetic quantum number. Although spins in $+m$ and $-m$ states have the same energy, they precess in opposite directions about the electric field gradient as a result of the quadrupole coupling. Therefore, when a linearly polarized rf field is used to excite a quadrupole resonance, both oppositely rotating circularly polarized components of the field are active in inducing transitions. One circularly polarized component excites spins in $+m$ states while the other excites spins in $-m$ states. The action of the rf magnetic field leads to an observable linearly polarized magnetization, oscillating in the direction of the exciting

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FIG. 1. Etch pits on surface of sample 5.
Linear magnification, 4600X.