

where  $V_H$  is the Hall voltage,  $E_H$  is the Hall field,  $H$  is the magnetic field in gauss and  $E_L$  is the longitudinal field.  $E_L$  can be written as the product of  $I$  and the gradient of the resistance in the  $z$  direction. The latter, in turn, is given by

$$1 / \left( q \int_0^b \int_0^a \mu_D N dx dy \right),$$

so that

$$V_H \times 10^8 = HI \int_0^a \mu_H dx / \int_0^b \int_0^a \mu_D N dx dy. \quad (6A)$$

Substituting, as before, the value for  $N$  given by Eq. (1) of the text, integrating over  $y$ , and making the additional substitution  $u = \pi x/a$ , one can obtain

$$V_H \times 10^8 = \pi^2 HI / 4 N_m b K_2 (\mu_D / \mu_N), \quad (7A)$$

where

$$K_2 = \left( 1 + \int_0^{\pi/2} \frac{\Delta\mu}{\mu_m} \sin u du \right) / \left( 1 + 2/\pi \int_0^{\pi/2} \frac{\Delta\mu}{\mu_m} du \right),$$

the  $\mu$ 's in this expression being drift mobilities. As before,  $K_2$  has been evaluated graphically for  $n$ -type Si and the results are given in Fig. 1.

## Phonon Scattering in KCl-KBr Solid Solutions at Low Temperatures\*

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(Received March 31, 1960)

The scattering of phonons by point defects at liquid helium temperatures has been studied. Single crystals of KCl-KBr solid solutions were employed, since it is known that the  $\text{Cl}^-$  and  $\text{Br}^-$  ions are randomly distributed in the anion lattice sites. A 1 mole percent addition of KBr reduced the conductivity of KCl by a factor of three. For all the crystals measured, including pure KCl and pure KBr, the thermal conductivity showed a maximum at the same temperature (5°K). Hence, point defects reduce the conductivity on both the high- and low-temperature sides of the maximum. For the mixed crystals the thermal conductivity was found to be related to the absolute temperature by the empirical formula  $K = K_0 e^{-0.0087T}$  for the temperature interval 6°K to 16°K.

### INTRODUCTION

KLEMENS' theory of phonon scattering by crystal imperfections at low temperatures<sup>1-4</sup> has stimulated a great deal of experimental work but has not been well verified—especially in the case of high concentrations of imperfections. Klemens calculated an additive thermal resistance due to point defects and dislocations, and these predictions were tested experimentally by Slack,<sup>5</sup> Williams,<sup>6,7</sup> Toxen,<sup>8,9</sup> Sproull, Moss, and Weinstock,<sup>10</sup> Pohl,<sup>11</sup> and others. Pohl<sup>11</sup> could not fit his data

\* This work was supported in part by the National Science Foundation.

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<sup>1</sup> P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

<sup>2</sup> P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

<sup>3</sup> P. G. Klemens, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XIV, p. 198.

<sup>4</sup> P. G. Klemens in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

<sup>5</sup> G. A. Slack, Phys. Rev. **105**, 832 (1957).

<sup>6</sup> W. S. Williams, Ph.D. thesis, Cornell University, 1956 (unpublished).

<sup>7</sup> W. S. Williams, Bull. inst. intern. froid, Comm. 1 et 2, Louvain, 1956. Annexes, 1956-2, pg. 119.

<sup>8</sup> A. M. Toxen, Ph.D. thesis, Cornell University, 1958 (unpublished).

<sup>9</sup> A. M. Toxen, Phys. Rev. **110**, 585 (1958).

<sup>10</sup> R. L. Sproull, M. Moss, and H. Weinstock, J. Appl. Phys. **30**, 334 (1959).

<sup>11</sup> R. Pohl, Bull. Am. Phys. Soc. **5**, 49 (1960), and Phys. Rev. **118**, 1499 (1960).

on LiF containing  $F^-$  centers using Klemens' theory. Sproull et al.<sup>10</sup> found that dislocation scattering is much more significant than Klemens' theory predicts. Although Slack<sup>5</sup> obtained agreement within a factor of two for low concentrations of  $\text{Ca}^{++}$  in KCl, Williams<sup>6</sup> and Toxen<sup>8,9</sup> found that the Klemens formula did not give the right concentration dependence when extended to the range of up to 50% "impurity" (KCl-KBr and Ge-Si solid solutions, respectively).

Another theoretical treatment of low-temperature thermal conductivity has been given recently by Callaway.<sup>12</sup> Curves generated by his theory are in good agreement with the experimental data of Geballe and Hull<sup>13</sup> on isotopically-enriched and normal germanium, where the effect of isotopes on thermal conductivity is clearly shown but is substantially less than predicted by Klemens. Although the Callaway formulation is approximate, it proved successful in interpreting this critical experiment and has prompted this examination of Williams' data on KCl-KBr mixed crystals. The present discussion, then, is an account of the experimental procedures and results. An analysis of the data using the Callaway formulation will follow as a separate paper.

<sup>12</sup> J. Callaway, Phys. Rev. **113**, 1046 (1959).

<sup>13</sup> T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

## DESCRIPTION OF EXPERIMENT

Since KCl and KBr are available in reasonable purity, form a complete range of solid solutions, and can be pulled from the melt into single crystals, this alloy system is an attractive one to study. Also, an extensive literature exists on KCl-KBr mixed crystals and provides answers to questions about the variation of crystallographic properties with composition. X-ray analysis<sup>14</sup> and *F*-center studies<sup>15</sup> have shown that the Br<sup>-</sup> and Cl<sup>-</sup> are randomly distributed among anion sites. Thus, the system can be regarded as an extreme case of substitutional doping, or as a substance with two anion "isotopes" of very different mass. The first point of view makes the experiment relevant to considerations of efficiency in thermoelectric cooling or power generation, where ways are sought to reduce lattice thermal conduction in semiconductors. The second way of viewing the experiment relates it to the isotope effect in thermal conductivity. Both interpretations were motivations for initiating the experiment, but because of the inadequacy of the Klemens-type analysis, only a brief report of the experimental results was published.<sup>7</sup>

## EXPERIMENTAL APPARATUS

The apparatus used for the measurement of thermal conductivity employed the constant heat flow method and is shown schematically in Fig. 1. The apparatus is similar to that used by Slack,<sup>5</sup> except that differential thermocouples were used as thermometers. The thermocouples, of Au+2.1 at. % Co versus constantan, were calibrated against the temperature differential between the helium bath and a variable-volume helium gas

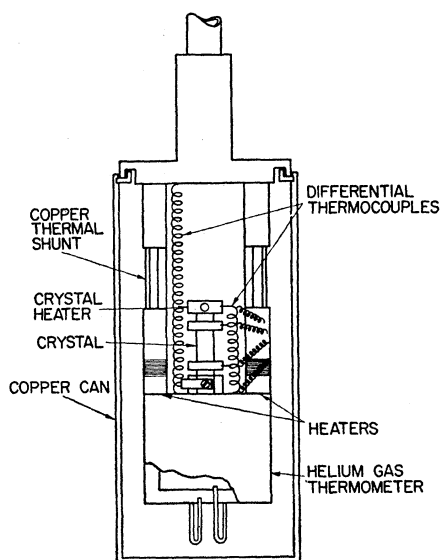


FIG. 1. Experimental chamber, showing location of crystal, differential thermocouples, and helium gas thermometer.

<sup>14</sup> L. Vegard, *Z. Physik* 5, 17 (1921).

<sup>15</sup> G. Miessner, *Z. Physik* 134, 576 (1953).

thermometer built into the apparatus. A Liston-Becker dc breaker amplifier served as a detector. For the thermal resistivity versus temperature characteristics of the mixed crystals, the differential thermocouples had sufficient sensitivity down to 3°K. The thermoelectric power of the couple is approximately  $0.86T$  microvolts per °K, where  $T$ =absolute temperature in °K, in the liquid helium range. The thermocouple junctions were inserted and pinched in copper foil tubes. These were soldered with a low melting point indium alloy to OFHC copper clamps making contact to the crystal through indium facings. Good crystal contact was thus maintained even at liquid helium temperatures. By scanning the thermocouples with an *L* & *N* multiple position switch, temperature differences between various points in the system could be quickly estimated during a run. Temperatures below the normal helium boiling point were obtained by pumping on the bath, and higher temperatures were reached by passing a heat current through a thermal resistance between the crystal and the bath.

Power inputs to the crystal heater—nichrome wound on a copper spool clamped to the top of the crystal—were obtained directly from current and voltage measurements and were reliable to better than 1%. Crystal cross sections,  $A$ , and thermometer spacings,  $\Delta l$ , were measured with a traveling microscope; because of some irregularity in crystal cross section, the geometrical factor  $\Delta l/A$  is known to only  $\pm 5\%$ .

Measurements of thermal conductivity as a function of temperature from 3°K to 16°K were taken on pure KCl, pure KBr and four mixed crystals. The conductivities obtained are believed accurate to  $\pm 10\%$ , and the temperatures to  $\pm 1\%$ .

## KCl-KBr MIXED CRYSTALS

The mixed single crystals of KCl-KBr were pulled from the melt. Optical grade Harshaw crystals of KCl and KBr were used as the starting material. Melts of approximately the desired composition were contained in high-purity graphite crucibles. The pulling rate was 1.3 cm/hr and the crystals were rotated during growth. The operation was carried out in a slightly reducing atmosphere: 92% nitrogen, 8% hydrogen. To prevent the crystals from cracking from thermal shock, it was necessary to pull them from the crucible into a hot zone provided by a heated chimney. The crystals were annealed after growth by heating to 75°C below the melting point, holding for 1½ hours, and cooling to room temperature over a period of 15 hours. A similar schedule was followed after the crystals were cleaved to size:  $\frac{1}{4}$  in.  $\times$   $\frac{1}{4}$  in.  $\times$   $\frac{3}{4}$  in.

Concentrations of Br<sup>-</sup> in the KCl-KBr crystals were obtained by measuring densities and using the additivity of specific volumes, known as Retgers' rule,<sup>16</sup> which

<sup>16</sup> W. Retgers, *Z. physik. Chem.* 3, 497 (1889).

has been found to apply to KCl-KBr solid solutions.<sup>17</sup> Densities were measured by a weight-loss method with 1, 3-dibromopropane as the flotation liquid. Compositions so determined expressed in mole percent KBr in KCl, were 1.00, 8.75, 26.64, and 47.84, each with an uncertainty of  $\pm 0.10$  mole percent. As mentioned above, the  $\text{Br}^-$  ions were randomly located in the anion lattice sites.

### RESULTS OF MEASUREMENTS

From measurements of the power input  $Q$ , the geometrical factor  $\Delta l/A$ , and the temperature drop  $\Delta T$  across  $\Delta l$ , the thermal conductivity  $K$  corresponding to the average crystal temperature  $T$  is found using  $K = (Q/\Delta T)(\Delta l/A)$ . Values of  $\log K$  versus  $\log T$  for pure (Harshaw) KCl are plotted in Fig. 2, with the curve obtained by Slack on a crystal cleaved from the same boule shown for comparison. Data are also plotted for measurements on two (Harshaw) KBr crystals. With the high conductivity KCl and KBr crystals, values near the maxima are unobtainable with this apparatus since the small  $\Delta T$ 's give differential thermocouple emf's of the level of background fluctuations (a few hundredths of a microvolt). Even though the KBr data are not as accurate as those for the mixed crystals, the curve is included here since no other thermal conductivity measurements have been reported on KBr in the temperature range between liquid helium and liquid hydrogen. At 16°K the present value is 2.5 times higher than that given by de Haas and Biermasz,<sup>18</sup> but their crystal was thought to have a high impurity content.

The curves of log thermal conductivity versus temperature for the four mixed crystals are also presented in Fig. 2 along with those for the pure crystals. As expected, the thermal conductivities of the KCl-KBr mixed crystals were substantially less than either of the two pure components. A one mole percent KBr addition

reduced the conductivity of KCl by a factor of three. The curve for the 26% KBr crystal has been corrected for the effect of a helium leak in the evacuated sample chamber by reducing the calculated  $K$  by 20%, a value based on other measurements made during the run. All the curves are found to have a similar shape: a maximum at 5°K and with the conductivity falling off as  $e^{-aT}$  for temperatures between 6°K and 16°K. The parameter  $a$  has the value  $0.099 \pm 0.002$ , so in this temperature interval the conductivity of each crystal decreases by approximately the factor  $e$ .

### DISCUSSION

The similarity in curve shape is to be contrasted with Slack's results<sup>5</sup> on Ca-doped KCl. He found a flattening of the curve and shift in the position of the conductivity maximum to higher temperatures with increasing calcium content. The explanation for this behavior was thought to be increasing precipitation of  $\text{KCl} \cdot \text{CaCl}_2$  colloids with increasing concentration. These colloids would scatter long-wavelength phonons more effectively than would point defects of atomic size.

The retention of the point character of the doping agent in KCl-KBr crystals is established by x-ray and  $F$ -center studies even up to 50% KCl-50%KBr. Thus for an experiment involving only point defects, the maximum did not shift to higher temperatures. We note that the experimental data of Geballe and Hull<sup>13</sup> show no shift in the maximum when normal Ge is compared with isotopically enriched material. The additional phonon scattering centers in normal Ge (isotopes) are, as in KCl-KBr, randomly-located point defects. The fact that these point defects do not shift the maxima to lower temperatures shows that considerable phonon scattering occurs even on the low-temperature side of the maximum, an effect included in Callaway's formulation<sup>12</sup> and also in one by Carruthers.<sup>19</sup> (A maximum exists in a pure crystal because at very low temperatures the phonon mean free path eventually becomes limited by the finite size of the sample.)

A Klemens-type analysis of the present data would discuss the reduction of thermal conductivity in KCl produced by adding KBr in terms of three perturbations in the total crystal energy: a kinetic energy perturbation resulting from the difference in mass between  $\text{Cl}^-$  and  $\text{Br}^-$ , and two potential energy perturbations, one from increased anharmonicity produced by the difference in ionic radii, and one from the difference in elastic linkages. Klemens calculated approximate values for each term. In his formulation, the mass-difference effect dominates. The difference in masses is 125%, leading to a value of the parameter  $\Gamma = \sum_i f_i [1 - (M_i/\bar{M})^2] = 5.39 \times 10^{-2}$  for 47.8% KBr. ( $M_i$  = mass of  $i$ th species, of relative abundance  $f_i$ .) This value is very large compared with that for naturally occurring isotopes ( $1.77 \times 10^{-4}$  for KCl).

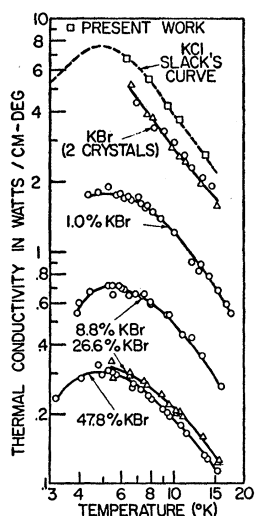


FIG. 2. Log thermal conductivity versus log temperature for pure KCl, pure KBr, and four KCl-KBr mixed crystals.

<sup>17</sup> M. Kantola, State Inst. Tech. Research, Finland No. 2 (1947).

<sup>18</sup> W. J. deHaas and T. Biermasz, *Physica* 4, 752 (1937).

<sup>19</sup> P. Carruthers, *Bull. Am. Phys. Soc.* 5, 48 (1960).

TABLE I. Comparison of KCl-KBr thermal resistivities with values calculated from Klemens' theory. Linear interpolations used for  $V_0$ ,  $v$ , and  $\bar{M}$ , and for background  $W$  used to obtain  $\Delta W_{\text{exp}}$ . Temperature = 13°K.

$N$ mole fraction KBr	$V_0$ in $10^{-24}$ $\text{cm}^3$	$v$ in $10^5$ $\text{cm/sec}$	$\bar{M}$ in g	$\Gamma$ in $10^{-4}$	$W$		
					$W_{\text{exp}}$	$\Delta W_{\text{exp}}$ in $\text{cm-deg/watt}$	$\Delta W_{\text{Klemens}}$
0.000 <sub>0</sub>	62.0	1.88	74.6	(1.77) <sup>a</sup>	0.369	...	
0.010 <sub>0</sub>	62.1	1.87 <sub>5</sub>	75.0	34.8	1.14	0.77	1.33
0.087 <sub>5</sub>	62.8	1.83 <sub>9</sub>	78.4	257	2.76	2.38	10.3
0.266 <sub>4</sub>	64.5	1.75 <sub>5</sub>	86.3	517	6.21	5.81	23.2
0.478 <sub>4</sub>	66.4	1.65 <sub>5</sub>	95.8	539	7.09	6.67	28.2
1.000 <sub>0</sub>	71.8	1.41	119.0	(.878) <sup>a</sup>	0.480	...	

<sup>a</sup> Refers to naturally-occurring isotopes, ignored in the mixed crystals.

Klemens' formula for the added thermal resistivity due to mass differences is

$$\Delta W = (\pi^2 V_0 / 0.897 h v^2) \Gamma T,$$

where  $V_0$  = volume of unit cell,  $h$  = Planck's constant,  $T$  = absolute temperature, and  $v$  = sound velocity. The parameter  $\Gamma$  defined above has the form  $\Gamma = N(1-N) \times (\Delta M)^2 / (\bar{M})^2$  for the special case of only two different masses, here the molecular weights of KCl and KBr. ( $N$  = mole fraction KBr in KCl.) The values of the added thermal resistivity calculated from this formula are shown in Table I along with the measured values. It is seen that the Klemens formula overestimates the effect of mixing by factors ranging from 2 to 4, even including only one of the three scattering terms. Because the values of  $\Gamma$  used in this experiment are all relatively large, the deviation from a linear dependence of  $\Delta W$  on  $\Gamma$  is only suggested by the data. The plot of collected data presented by Toxen<sup>9</sup> offers more convincing evidence for this nonlinearity.

Thus both the form of the Klemens expression and the magnitude are seen to be in disagreement with the

data, and in fact even the use of an additive resistance approximation has been found by Callaway<sup>12</sup> and Carruthers<sup>19</sup> to be improper. Consequently the Klemens-type analysis will not be pursued here, but the introduction of it does lend some physical plausibility to the experimental results.

#### SUMMARY

The thermal conductivities of KCl-KBr mixed crystals have been measured in the liquid helium region. Differential thermocouples were used after calibration *in situ* against a helium gas thermometer. Phonon scattering by ions of like charge but different mass and size decreases the thermal conductivity substantially, but the effect is not adequately described by Klemens' theory.

#### ACKNOWLEDGMENTS

The author wishes to thank the following: R. L. Sproull for guidance and suggestions; G. A. Slack for advice during the early part of the work; and M. Moss for growing the crystals.