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Thermal Conductivity of Potassium Chloride Crystals Containing Calcium*

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The details of the phonon scattering produced by point imperfections in insulating crystals has been determined from measurements of the thermal conductivity of six single crystals of KCl from 3°K to 30°K as a function of the concentration of point imperfections. These imperfections were produced by the addition of $CaCl_2$, which was incorporated into the KCl crystals as a substitutional impurity during growth from the melt. At temperatures above 15°K the mean free path of the phonons decreases inversely with increasing calcium concentration. The average scattering cross section of a calcium ion—potassium ion vacancy complex increases as the fourth power of the temperature for low temperatures, and becomes equal to the geometrical cross section of the vacancy at a temperature of about $\theta_D/6$. Below 15°K the phonon scattering by colloids of precipitated calcium chloride produces a large thermal resistivity in the impure crystals. The thermal conductivity of "pure" KCl at low temperatures is limited mainly by isotope and boundary scattering. The theoretical expressions as given by Klemens for combining thermal resistivities which possess different temperature dependences have been calculated, and have been applied to the present results. The agreement between Klemens' theory and the present experiment as to both the magnitude and the temperature dependence of the thermal resistivity is considered to be satisfactory.

I. INTRODUCTION

THE purpose of the present investigation is to determine the quantitative details of the phonon scattering from point imperfections in insulating crystals at low temperatures. One of the simplest and most attractive systems to study from a theoretical viewpoint is a neutral vacancy in an alkali halide crystal. The system of an associated calcium ion—potassium ion vacancy complex in a KCl crystal approaches this desired model quite closely. An analysis of the thermal conductivity of KCl as a function of the temperature and the calcium impurity concentration has been carried out in the present investigation. The magnitude of the scattering cross section for a single point imperfection has been determined as a function of the phonon wavelength. The thermal resistances produced by point imperfection scattering as well as by several other scattering mechanisms have been found to agree quite well with previous theoretical predictions.

The thermal conductivity of insulating single crystals has attracted attention since 1905 when Lees[1] established that the thermal conductivity increases with decreasing temperature. Since that time the theory of insulating crystals has been studied, and some of the experimental measurements have shown good agreement with the theory. Several review articles[2–4] have appeared recently which summarize both the experimental data and the theories. The present investigation is concerned with potassium chloride as a representative insulating crystal. Some of the first measurements of the low-temperature thermal conductivity of KCl crystals were made by Eucken[5] in 1911. He showed that the thermal conductivity was inversely proportional to temperature between 22°K and 273°K, but no absolute values of the conductivity were given. In 1928 Eucken and Kuhn[6] made further measurements on KCl crystals and on compressed powders of KCl–KBr mixtures at 83°K and 273°K. These results agreed with the previous work on KCl, and absolute values for the conductivity were given. They demonstrated further that at a given temperature the thermal resistivity, which is the reciprocal of the conductivity, increases linearly with increasing bromine (or chlorine) impurity content at low concentrations. The magnitude of this resistivity increase cannot readily be compared with theory since their dampened and compressed powders were probably not mixed on an atomic scale.

The thermal conductivities of pure KCl and also KBr were measured from 2°K to 5°K and from 15°K to 20°K by deHaas and Biermasz[7] in 1937. They discovered that at about 7°K KCl possesses a conductivity maximum which is caused by the onset of phonon reflection from the crystal walls. Later they[8] made an extensive study of the effect of crystal size on the thermal resistivity below 5°K, and concluded that at the very lowest temperature the thermal conductivity is nearly proportional to T^3 and to the smallest crystal dimension. A preliminary study of the effect of impurities on the thermal resistivity of KCl crystals was made by Devyatkova and Stilbans[9] in 1952. They measured the dependence of the thermal resistivity on the concentration of F centers produced by additive coloring in potassium vapor. Measurements were made

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* Supported in part by the National Science Foundation.

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[3] R. L. Powell and W. A. Blanpied, National Bureau of Standards, Circular 556, 1954 (unpublished).

[4] P. G. Klemens, *Handbuch der Physik* (Verlag-Julius Springer, Berlin, 1956), Vol. 14, No. 1, p. 198.

[5] A. Eucken, Ann. Physik **34**, 185 (1911).

[6] A. Eucken and G. Kuhn, Z. physik. Chem. **134**, 193 (1928).

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[8] W. J. deHaas and T. Biermasz, Physica **5**, 47 (1938).

[9] E. D. Devyatkova and L. S. Stilbans, J. Tech. Phys. (U.S.S.R.) **22**, 968 (1952).

at temperatures of 98, 200, and 298°K. Their data show that the resistivity of "pure" KCl increases linearly with temperature, and the resistivity produced by impurities increases linearly with impurity concentration at low concentrations. The phonon "scattering number" can be estimated from their data, as is shown later.

The thermal conductivity of an insulator can reach very high values at low temperature. In 1914 Debye[10] pointed out that a crystal lattice bound together with purely harmonic forces would have an infinite thermal conductivity at all temperatures. Anharmonic coupling is necessary to produce a finite conductivity. In 1929 Peierls[11] considered the discrete nature of the crystal lattice as well as its anharmonic coupling. He was able to show that at low temperatures the thermal conductivity rises exponentially with decreasing temperature, and becomes infinite at absolute zero. In 1938 both Casimir[12] and Makinson[13] calculated the effect of the external crystal boundaries on the measured thermal conductivity, and showed that the measured conductivity of a crystal of finite size will never really become infinite. The measured conductivity of a pure crystal of finite size, however, can become quite large. Artificial sapphire crystals[14] at 40°K may have a thermal conductivity as much as thirty-five times that of copper at room temperature.

Measurement of the thermal conductivity at low temperatures should be a very sensitive means of studying crystal imperfections since these high values of thermal conductivity are seriously reduced by anything which disturbs the lattice vibrations. Thus small amounts of chemical or structural disorder in the lattice will decrease the conductivity. Berman[15] has shown experimentally that the low-temperature conductivity of quartz crystals can be greatly reduced by neutron irradiation. The conductivity of potassium chloride should also be sensitive to small amounts of impurity. For example, a large, pure crystal of KCl should have a conductivity of about 250 watts/cm-deg at 10°K when only umklapp processes limit the conductivity; it would take only 4 parts per million (ppm) of calcium to reduce this conductivity by 10%. At 5°K the sensitivity to impurities would be still higher. Klemens[16] has developed the theory of the effects of small amounts of impurities and imperfections on the low-temperature thermal conductivity of insulating crystals. His theory[17] agrees qualitatively with Berman's data on quartz, and will be used extensively in analyzing the present results.

TABLE I. Data on the six different KCl crystals.

Crystal	*A*	*K*	*N*	*Q*	*R*	*S*
Growth run No.	...	20	21	21	22	22
No. of ground faces	0	2	2	2	0	0
Cross sectional area, A, cm^2	0.45	0.44	0.41	0.43	0.43	0.42
Thermometer separation, b, cm	1.80	1.57	1.22	1.60	1.68	1.70
Calcium concentration, $G \times 10^4$	0.0	0.0	0.6	1.1	1.3	2.1
Isolated dislocation density, (lines/cm^2) $\times 10^{-4}$	...	40	4	7	9	5
Av distance between grain boundaries, cm	...	0.02	0.09	0.03	0.07	0.10
$K_{\max}$, watt/cm-deg	7.30	5.76	4.14	2.(3)	1.46	1.26
$T_{\max}$, °K	4.9	5.5	6.0	8.(1)	12.4	13.0
L, cm	2.3	1.3	0.70	0.16	0.028	0.021
$\Gamma \times 10^4$	1.1(0)	1.2(5)	1.5(3)	2.(1)	2.1(8)	2.4(0)

II. KCl CRYSTALS

Great care is needed to insure that the KCl used as starting material is as pure as possible, and that whatever background impurities are present in the KCl remain constant for all of the crystals. For this reason a large, single crystal of Harshaw[18] KCl was used as the starting material. It was then split into several pieces, remelted, and five different crystals were grown from these pieces (see Table I). Crystal *A* was taken from a different Harshaw single crystal and was measured after annealing, but it was not regrown. The other crystals were grown from the melt in a graphite crucible by using a modified Kyropoulos[19] technique at a growth rate of 1.4 cm/hr. A dried atmosphere of 10% H_2 and 90% N_2 was used to prevent hydrolysis of the salt and oxidation of the crucible. The sample crystals were cleaved by hand from the grown boules using a sharp razor blade. If these cleaved faces contained appreciable cleavage steps, the two opposing crystal faces were ground flat on No. 400 emery paper (see Table I).

Crystal *K* was grown without any added impurity. Calcium chloride was added to the melt during growth of the other four crystals. The amount of calcium in the grown crystal cannot be determined accurately from the concentration in the melt. Radioactive Ca^{45} was therefore used as a tracer to measure the absolute Ca concentration in the grown crystal. The ratio of Ca^{45} to nonradioactive Ca was about 1 atom in 10^6. The radiation damage inside the crystal from this amount of Ca^{45} is insignificant. The calcium concentration in the crystal was measured by placing a small unmasked area of the crystal surface over a thin mica end-window Geiger counter. This method allowed the average calcium concentration in the crystal to be measured to ±13%, and also permitted a measurement of the axial and radial concentration gradients in the crystal samples. The samples were all about 40 mm long by 6 mm square (see Fig. 2). The axial and radial variations were both about 5% throughout that portion of the sample across which the measured temperature

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[10] P. Debye, *Vorträge Über die Kinetische Theorie der Materie und der Electrizität* (B. G. Teubner, Berlin, 1914), p. 46.

[11] R. E. Peierls, Ann. Physik **3**, 1055 (1929); *Quantum Theory of Solids* (Oxford University Press, New York, 1955), p. 40.

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[13] R. E. B. Makinson, Proc. Cambridge Phil. Soc. **34**, 474 (1938).

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[17] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

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[19] S. Kyropoulos, Z. Physik **63**, 849 (1930).

drop occurred. The absolute calcium concentrations in the crystal are expressed in terms of

$$G=\frac{\text{number of Ca atoms per cm}^3}{\text{number of K atoms per cm}^3}.$$

After the crystal samples were shaved to size from the original boule and the radioactive counting was completed, they were annealed to remove any strains produced during growth and subsequent handling. The annealing was done in air at 700°C for $\frac{1}{2}$ hour, followed by programmed cooling to room temperature at a drop rate of 30°C per hour. The crystals were then placed between crossed polaroids in a beam of monochromatic light to check for birefringence caused by strain. The minimum detectable strain was about one percent of that necessary to break the crystal.[20] The strain was also checked after the copper thermal contacts were attached to the crystal, and was small in the region over which the thermal resistivity measurements were made. A further check was made of the strain introduced during cooling. No increase in strain was found in the mounted crystals when examined between crossed polaroids in a liquid nitrogen bath.

After the thermal resistivity of the crystal sample was measured, a 3-mm thick slab was cleaved from the end of each sample bar. These thin slabs were reannealed using the previous annealing cycle, and the surface layer was removed with a water plus ethyl alcohol rinse. The fresh surfaces were then etched for 40 seconds at room temperature in absolute ethyl alcohol which contained 25% of the saturation amount of $BaBr_2$ added as an inhibitor.[21] This technique forms etch pits at both edge and screw dislocations, and reveals both isolated dislocations and grain boundaries.[22] The results of the etch pit counting under a microscope are shown in Table I. The density of isolated dislocations is about as low as has been obtained for a well-annealed KCl crystal. The average number of grain (or mosaic) boundary lines per centimeter is also given. The grain-boundary angles were calculated from the number of etch pits per centimeter. The angles were between 5×10^{-5} and 10^{-3} radian. In all of the crystals the total number of dislocation lines per cm^2 that were present in the grain boundaries was within a factor of 3 of the density of the isolated dislocations.

Several analyses were made in order to determine the background impurity concentration in the pure crystals. Spectrochemical analyses were made[23] in order to check for metallic impurities. No heavy metals or sodium, beryllium, or magnesium were detected. Three of the alkaline earths were found and the upper limits on calcium, strontium, and barium were about 5, 10, and 5 ppm, respectively. The crystals containing intentionally added calcium were used to calibrate the sensitivity of the photographic plates. A wet chemistry analysis was made for bromine and iodine[24]; about 20 ppm of bromine were found. An upper limit on the iodine concentration was set at about 20 ppm, though none was definitely detected. A check was made with a microscope for graphite flakes which might have spalled off the walls of the crucible during growth. No graphite was found. If present, its concentration was less than 1 ppm.

III. IONIC CONDUCTIVITY

As a further check on the divalent impurity concentration in both the pure KCl and in those containing added calcium, the ionic conductivity of several crystals was measured. These measurements were made on small plates of KCl about 2 mm thick and 6 mm square. The measurements were made using a sensitive dc electrometer, and the charge transport was kept sufficiently small so that polarization effects could be neglected. The data are shown in Fig. 1. Crystals Q and L contained intentionally added calcium to the extent of $G=1.1\times10^{-4}$ and 0.5×10^{-4}, respectively. The variation of the ionic conductivity as a function of temperature and impurity concentration agree quite well with the

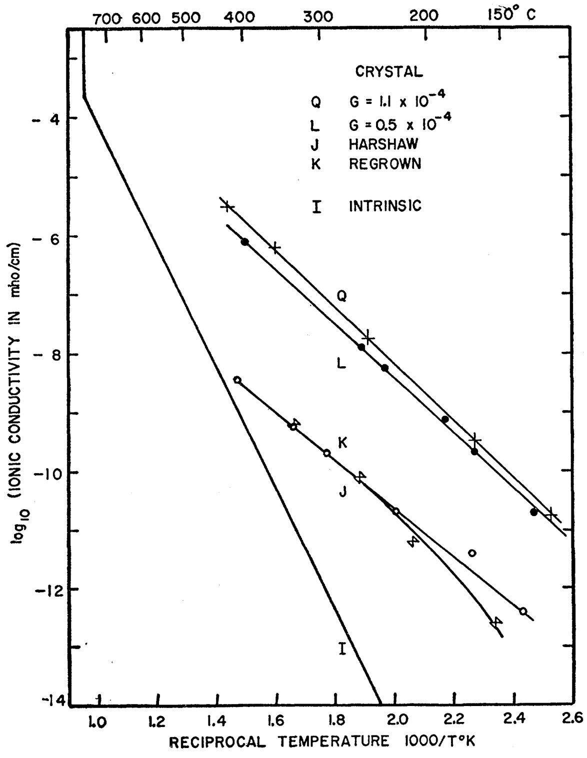

FIG. 1. The ionic conductivity of KCl crystals *versus* temperature for different impurity concentrations.

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[20] E. Schmid and W. Boas, *Kristallplastizität* (Verlag-Julius Springer, Berlin, 1935), Chap. 7.

[21] This etching technique was developed by Dr. W. G. Johnston of the General Electric Research Laboratory, Schenectady, New York.

[22] S. Amelinckx, Acta Metallurgica **2**, 848 (1954).

[23] Courtesy of W. D. Cooke, Chemistry Department, Cornell University, Ithaca, New York.

[24] V. A. Stenger and I. M. Kolthoff, J. Am. Chem. Soc. **57**, 831 (1935).

data of Kelting and Witt.[25] Crystals J and K were both from the same original single crystal of Harshaw KCl. Crystal K was taken from a regrown crystal which contained no added calcium (see Table I), whereas crystal J was a piece of the unmelted Harshaw stock crystal. A comparison of crystals J and K shows that the regrowth does not appreciably alter the divalent impurity concentration. The limiting Curve I shown in Fig. 1 is the intrinsic ionic conductivity of KCl.

The ionic conductivities of crystals J and K indicate[25] an electrically active divalent impurity concentration in the vicinity of 0.4 ppm. This is lower than the upper limit set by spectroscopic analysis by a factor of 50. The low concentration of electrically active (i.e., atomically dispersed) calcium could be caused by association of the calcium ions with potassium ion vacancies. Most of the inactive calcium, however, is probably present as a precipitated phase along grain boundaries. The effects of this association and precipitation at higher calcium concentrations is discussed later.

IV. APPARATUS

The thermal conductivity was measured by using a steady-state heat flow method. Two carbon resistance thermometers[26] (Allen Bradley 56 ohm, $\frac{1}{2}$ w) were placed along the length of the crystal in order to measure the average temperature and the temperature gradient (see Fig. 2). Heat was supplied at the top of the crystal by a Nichrome heater wound on a copper clamp, and extracted at the bottom by a large copper plate which acted as a heat sink. The temperature of the copper plate at the base of the crystal was adjusted with respect to the helium bath by means of an auxiliary heater and a fixed thermal leakage resistance. The liquid helium bath provided the final heat sink. The bath temperature was varied between 1.9°K and 4.2°K, depending on the temperature range desired.

The thermal contacts at the top and bottom of the crystal between the KCl and the copper were held together during thermal cycling by a C-clamp arrangement which maintained a nearly constant pressure of 200 lb/in.^{2}. A piece of pure indium foil 0.25 mm thick was used to make good thermal contact between the copper and the KCl. The maximum temperature drop between the crystal and either the heat source or sink was 1°K. The two carbon thermometers used to measure the temperature gradient were cemented into copper yokes which surrounded the crystal. These yokes were also held in place by spring tension, and the 1.0 mm wide contact ridge was covered with indium foil. The average vertical spacing between the centers of the contact ridges was 1.6 cm, although it varied somewhat from crystal to crystal (see Table I).

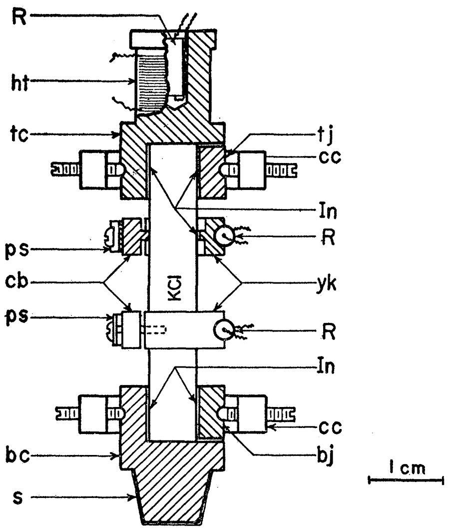

FIG. 2. The arrangement of the KCl crystal with heater, clamps, and thermometers: bc = bottom cap, bj = bottom jaw, cb = crossbar, cc = c-clamp, ht = heater, In = indium foil, ps = phosphor-bronze spring, R = carbon thermomenter, s = Cerrolow 117 solder, tc = top cap, tj = top jaw, and yk = copper yoke.

The crystal, heaters, thermometers, and heat sink were all placed inside an evacuated copper can which was submerged in the liquid helium bath. A helium gas thermometer attached to the copper plate served as a standard thermometer against which all of the carbon thermometers were calibrated.

V. THERMAL CONDUCTIVITY

The determination of the thermal conductivity at a temperature, T, depends on: Q, the heat input to the crystal; ΔT, the temperature difference between the carbon thermometers; b, the distance between the thermometers; and A, the cross-sectional area of the crystal (see Table I).

$$K(T)=Qb/A\Delta T. \tag{1}$$

Here T is the arithmetic average of the temperatures of the two carbon thermometers. The values of ΔT varied between 0.01 and 1.0 degree Kelvin, and the values of Q between 10 and 200 milliwatts. With these small power inputs and temperature differences, care is required to keep heat leak losses very small. The only leads attached to the sample were made of 0.1-mm advance wire about 15 cm long. The helium gas pressure inside the experimental chamber was constantly checked with a special gauge[27] and was always less than 10^{-6} mm Hg. The data for crystal Q, however, exhibits more scatter than those for the other crystals. This was caused by a helium leak, and the pressure was about 10^{-3} mm Hg during the experiment. Other corrections due to thermal radiation, mechanical vibration, and room temperature gas molecules were negligible. It is believed that the relative values of the thermal conduc-

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[25] H. Kelting and H. Witt, Z. Physik **126**, 697 (1949).

[26] J. Clement and E. Quinell, Rev. Sci. Instr. **23**, 213 (1952); R. Berman, Rev. Sci. Instr. **25**, 94 (1954); Hoare, Matthews, and Yates, Proc. Phys. Soc. (London) **B68**, 388 (1955).

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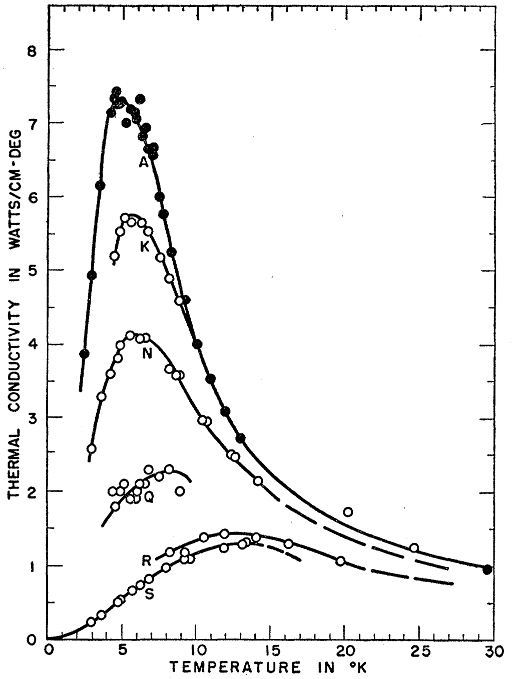

FIG. 3. The thermal conductivities of the six different KCl crystals as a function of temperature.

tivity data points for any one crystal are reliable to ±4%, the absolute thermal conductivity values to ±10%, and the absolute temperatures to ±1%.

The measured values of the thermal conductivity for the six different crystals are plotted in Fig. 3 as a function of temperature. The important features of this set of curves are the occurrence of a conductivity maximum, $1/T$ decrease in the conductivity of a given crystal at temperatures above the maxima, and the monotonic decrease in conductivity with increasing calcium concentration at all temperatures.

VI. THEORY

The theory of the thermal conductivity of nonmetallic solids can explain in a reasonably quantitative way all of the features of the curves in Fig. 3. No attempt will be made to present an exhaustive coverage of the theory, since this has been published by other authors.[4,10–13,16,17,28–31]

The simplest approach to the problem was suggested by Debye[10] in 1914 when he showed that thermal conductivity of an insulator can be represented by

$$K = lvC_v/3, \tag{2}$$

where K = thermal conductivity, l = average mean free path of a phonon, v = average phonon velocity, and C_v = specific heat per unit volume at constant volume.

The values of v and C_v in Eq. (2) are usually known for a given material.[32,33] The main problem in the theory is the calculation of l. In an insulating solid such as KCl the following scattering mechanisms may all contribute to the determination of the mean free path: external crystal boundaries, internal grain boundaries, colloidal particles, dislocations, point imperfections, and umklapp collisions. Usually only one or two of these mechanisms are important at any one temperature. The resultant mean free path for a given phonon wavelength when two or more mechanisms are present is given by

$$l_{\text{tot}}^{-1} = \textstyle\sum_i l_i^{-1}, \tag{3}$$

where l_i in general depends on the phonon wavelength. The additive resistance approximation Eq. (3B) follows from Eqs. (2) and (3) and the assumption that l_i is wavelength-independent:

$$W_{\text{tot}} = \textstyle\sum_i W_i, \quad \text{where} \quad W_i = K_i^{-1}. \tag{3B}$$

The values of l_i for the several scattering mechanisms depend in different ways on the phonon wavelengths, and Eq. (3B) is strictly valid only when the wavelength dependences of the two mechanisms are the same. The approximation is, for example, valid when two types of point imperfections are being considered, and very poor when, for example, point imperfections and crystal boundaries are both important.

In order to make a more accurate analysis of the contributions of the various scattering mechanisms to the mean free path of the phonons, the more exact theory of Klemens[16,17] will be used. Equation (2) in its general form is given by Klemens as

$$K = \tfrac{1}{3} \sum_j \int l(\kappa) v_g(\kappa) \left[\frac{\partial}{\partial T} E(\kappa,T)_j \right] d\kappa,$$

where l is now the effective relaxation length of a phonon of wave vector κ and polarization j, v_g is the group velocity of the above phonon, and E is its energy. The calculation of $l(\kappa)$ involves considerations of the selection rules for phonon interaction, equilibration among the various phonon populations by ordinary three phonon collisions, and the dependence of the various scattering mechanisms on both the phonon momentum and polarization. These details are given by Klemens.

Single-Scattering Mechanisms

For the present purpose only temperatures below one-tenth of the Debye temperature (θ_D) are of interest. Thus the formulas given below are applicable to this temperature region. When only one scattering mecha-

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[28] I. Pomeranchuk, J. Phys. (U.S.S.R.) **6**, 237 (1942).

[29] C. Herring, Phys. Rev. **95**, 954 (1954).

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[31] J. Frenkel, *Wave Mechanics—Elementary Theory* (Oxford University Press, New York, 1932), p. 266.

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[33] P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1354 (1953); J. R. Clement, Phys. Rev. **93**, 1420 (1954).

nism is present at a time, the following expressions may be used to compute the thermal conductivity[16,17]:

External crystal boundaries.—

$$K_B=\frac{4\pi k^4LT^3}{v^2h^3}\int_0^\infty\frac{x^4e^xdx}{(e^x-1)^2}, \tag{4}$$

where k = Boltzmann's constant, h = Planck's constant, L = smallest crystal dimension, v = average phonon velocity, and $x=h\nu/kT$.

Internal grain boundaries.—

$$K_G=\frac{144\pi k^4T^3}{\epsilon_G\gamma^2\theta^2v^2h^3}\int_0^\infty\frac{x^4e^xdx}{(e^x-1)^2}, \tag{5}$$

where ϵ_G = number of grain boundaries per unit distance, γ = Gruneisen's constant, and θ = the misfit angle.

Dislocations.—

$$K_D=\frac{60k^3T^2}{B\epsilon_Dvb^2\gamma^2h^2}\left[\int_0^1\frac{x^4e^xdx}{(e^x-1)^2}+\int_1^\infty\frac{x^3e^xdx}{(e^x-1)^2}\right], \tag{6}$$

where ϵ_D = number of dislocation lines per unit area, b = length of the Burger's vector of the dislocation, and B is a factor depending on the type of dislocation. The value of B is 1.00 for all screw dislocations, and for an edge dislocation in KCl the value of B is 1.10.

Point imperfections.—

$$K_P=\frac{4\pi k^4T^3l_{P0}}{v^2h^3}\left[\int_0^1\frac{x^4e^xdx}{(e^x-1)^2}+\int_1^\infty\frac{e^xdx}{(e^x-1)^2}\right]. \tag{7}$$

Here l_P is the mean free path of the phonons for scattering by point imperfections. Its value is given by

$$l_P=\frac{1}{48\pi^3V_0\Gamma}\left(\frac{vh}{kTx}\right)^4,\quad \Gamma=\sum_j V_0\epsilon_{Pj}S_j^2,$$

where V_0 = average volume occupied by one atom of the crystal, ϵ_{Pj} = number of point impurities of type j per unit volume, and S_j^2 = total scattering number for the jth type of point imperfection. When $x=1$, then l_P equals l_{P0}.

Umklapp processes.—

$$K_U=\frac{4\pi k^4T^3l_{U0}}{v^2h^3}\left[\int_0^1\frac{x^4e^xdx}{(e^x-1)^2}+\int_1^\infty\frac{x^2e^xdx}{(e^x-1)^2}\right]. \tag{8}$$

Here l_U is the mean free path of the phonons for scattering via umklapp processes; its value is given by

$$l_U=\frac{U}{V_0^{\frac{1}{3}}}\left(\frac{vh}{2\pi kTx}\right)^2e^{\theta_D/2T},$$

where U is some arbitrary constant. When $x=1$, l_U equals l_{U0}.

In all of the preceding expressions for the thermal conductivity, five different integrals appear. These may be evaluated from published tables.[34]

$$\int_0^1\frac{x^4e^xdx}{(e^x-1)^2}=0.317,\quad \int_1^\infty\frac{x^ne^xdx}{(e^x-1)^2}=\begin{cases}0.583 & \text{for } n=0,\\ 2.317 & \text{for } n=2,\\ 6.733 & \text{for } n=3,\\ 25.658 & \text{for } n=4.\end{cases}$$

Two Scattering Mechanisms

Over most of the temperature region in which measurements were made on KCl, two different scattering mechanisms are important at any given temperature. The resultant mean free path for a given phonon frequency is then given by Eq. (3). The expressions for l_i and l_j will in general depend in different ways on the phonon frequency. One such important case occurs when both boundary and point-imperfection scattering are important. The expression for the thermal conductivity then becomes

$$\begin{aligned}K_{BP}(R_4)&=K_{\max}\frac{R_4^{-\frac{3}{4}}}{0.619}\left[\frac{0.317R_4}{R_4+1}+I_4(R_4)\right],\\ T(R_4)&=T_{\max}R_4^{-\frac{1}{4}},\end{aligned} \tag{9}$$

where $K_{\max}$ is the maximum thermal conductivity and $T_{\max}$ is the temperature at which this maximum occurs. Furthermore

$$R_4\equiv\frac{l_{P0}}{L},\quad I_4(R_4)\equiv\int_1^\infty\frac{x^4e^xdx}{[1+(x^4/R_4)](e^x-1)^2},$$

and

$$\begin{aligned}K_{\max}&=\frac{0.310vkL}{\pi^2}\left(\frac{\pi}{3LV_0\Gamma}\right)^{\frac{3}{4}},\\ T_{\max}&=\frac{hv}{2\pi k}\left(\frac{\pi}{3LV_0\Gamma}\right)^{\frac{1}{4}}.\end{aligned} \tag{10}$$

The function $I_4(R)$ is given in Fig. 4. The values were obtained by graphical integration and are probably accurate to a few percent. Once I_4 is known, it is possible to compute $K_{BP}/K_{\max}$ *versus* $T/T_{\max}$. Thus all thermal conductivity curves taken in the region where only crystal boundary (or grain boundary) scattering and point-imperfection scattering are important should have the same shape. Values of $K_{BP}/K_{\max}$ *versus* $T/T_{\max}$ are given in Table II. This table can be extended by using the following limiting equations:

$$I_4(R_4)=0.583R_4 \quad \text{for} \quad R_4\leq 10^{-2},$$
$$I_4(R_4)=25.66 \quad \text{for} \quad R_4\geq 10^5.$$

The expression for $K_{BP}(T)$ in Eq. (9) has been matched to the experimental data for crystals A and S at the conductivity maxima. The agreement between the

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[34] D. K. C. MacDonald and L. T. Towle, Can. J. Phys. 34, 418 (1956).

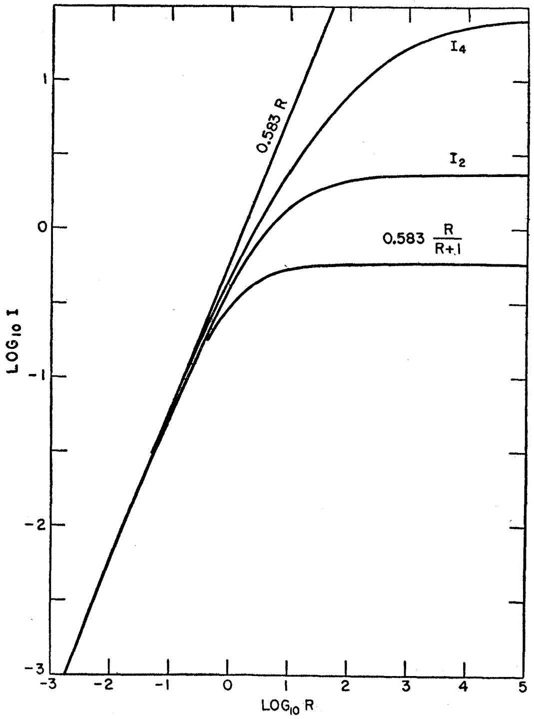

FIG. 4. The integrals $I_2(R)$ and $I_4(R)$ as a function of R. The two limiting cases $I_0(R)$ and $I_\infty(R)$ are also shown.

computed resistivity (W_{BP}) and the experimental curves is shown in Fig. 5. At temperatures below the minimum the agreement between theory and experiment is good. The curve predicted by a simple additive resistance approximation ($W_B+W_P+W_U$) is seen to give a very poor fit to the experimental data (crystal S).

Another rather interesting result can be obtained from Table II. It can be seen that the effect of point-imperfection scattering extends to temperatures well below $T_{\max}$. The conductivity does not reach a simple T^3 dependence, as expected for boundary scattering alone, until temperatures below $0.1T_{\max}$. In fact the conductivity becomes a T^2 dependence only at a temperature of $0.2T_{\max}$. This explains why de Haas and Biermasz[8] did not find a pure T^3 dependence for KCl as predicted by Casimir,[12] since their measurements extended only to 1.9°K.

TABLE II. Thermal conductivity *versus* temperature as determined by boundary and point-imperfection scattering.

$T/T_{\max}$	$K/K_{\max}$	$T/T_{\max}$	$K/K_{\max}$
0.0	0.00	1.2	0.98
0.1	0.04	1.3	0.95
0.2	0.19	1.4	0.92
0.3	0.38	1.6	0.84
0.4	0.55	1.8	0.77
0.5	0.71	2.0	0.71
0.6	0.82	2.5	0.57
0.7	0.92	3.0	0.48
0.8	0.98	3.5	0.41
0.9	0.99	4.0	0.37
1.0	1.00	4.5	0.33
1.1	0.99	5.0	0.30

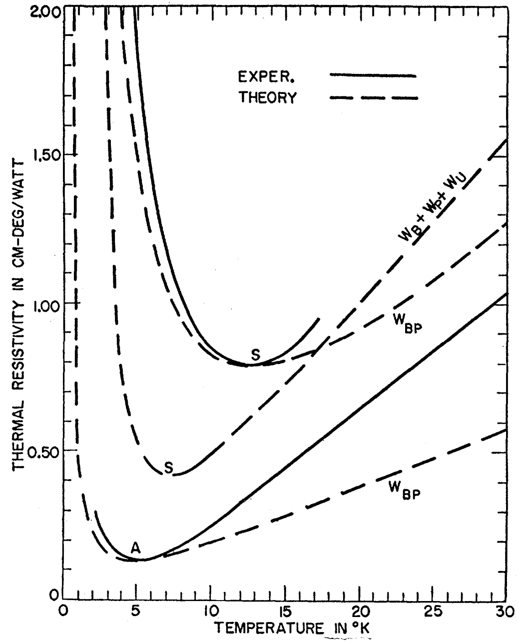

FIG. 5. The comparison of the thermal resistivities of KCl crystals A and S with the theory. W_{BP} is the correct combination of boundary and point impurity scattering. The additive resistance approximation for crystal S is given by $W_B+W_P+W_U$.

At temperatures above $T_{\max}$, point-imperfection scattering is much greater than boundary scattering. In this temperature range the point-imperfection resistivity is, however, not sufficient to explain the experimental results. Some other source of phonon scattering is also present. This extra thermal resistivity above that caused by the point imperfections is presumably due to umklapp scattering. The magnitude of the umklapp scattering in KCl can be computed from the difference between the measured resistivity and the resistivity (W_{BP}) calculated from boundary plus point-imperfection scattering. Let us consider the data for crystal A. It can be seen from Fig. 5 that at a temperature of twice $T_{\max}$ the value of W_{BP} is very nearly equal to W_P; the boundary resistivity contribution has disappeared. Thus from 10°K to 30°K the observed resistivity is a combination of point-imperfection and umklapp resistivity (W_{PU}). To a first approximation,

$$W_{PU}=W_P+W_U.$$

This additive approximation is not strictly true. When both point imperfection and umklapp processes are present, the conductivity is given by

$$K_{PU}=\frac{4\pi k^4T^3l_{U0}}{h^3v^2}\left[\frac{0.317R_2}{1+R_2}+I_2(R_2)\right], \tag{11}$$

where

$$R_2 \equiv l_{P0}/l_{U0}, \quad \text{and} \quad I_2(R_2) \equiv \int_1^\infty \frac{x^2 e^x dx}{[1+(x^2/R_2)](e^x-1)^2}.$$

The integral I_2 is given as a function of R_2 in Fig. 4. A general integral $I_n(R)$ can be defined as

$$I_n(R) = \int_1^\infty \frac{x^n e^x dx}{[1+(x^n/R)](e^x-1)^2}.$$

The two limiting cases, $I_0(R) = R/[(e-1)(R+1)]$ and $I_\infty(R) = R/(e-1)$, are also shown in Fig. 4. From Eqs. (7) and (8) it follows that for point imperfection and umklapp processes separately, the resistivities are related to R_2 by

$$R_2 = 2.634 W_U/(0.900 W_p).$$

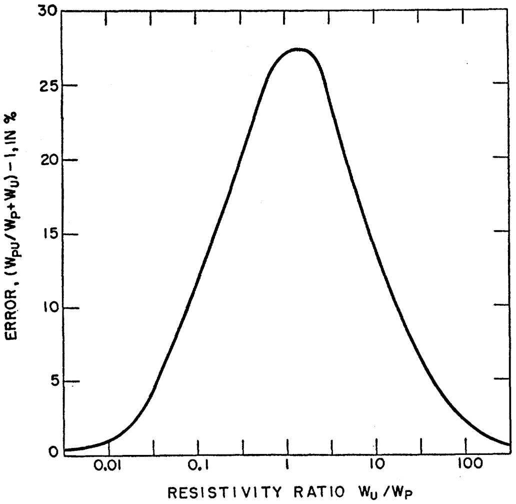

FIG. 6. The percentage error in the additive resistance approximation when used to combine umklapp and point imperfection scattering, as a function of W_U/W_P.

Consequently the ratio of the correct combination of W_P and W_U to the additive resistance approximation is

$$\frac{W_{PU}}{W_P+W_U} = \frac{0.900(1+R_2)}{[1+(R_2/2.93)][0.317+[1+(1/R_2)]I_2(R_2)]}. \qquad (12)$$

In Fig. 6 a plot of $[W_{PU}/(W_P+W_U)]-1$ is given as a function of W_U/W_P. When $W_P \simeq W_U$ the additive resistance approximation produces the largest error, and it predicts a value which is too low by 28%.

When W_{PU} and W_P are known at any given temperature, the value of W_U may be computed from Eq. (12). An experimental value of W_U has been determined from the data for Crystal A over the temperature range from 10°K to 30°K. The results are shown in Fig. 7. A quasi-theoretical estimate of W_U at low temperatures may be obtained from the measured resistivity of KCl at the Debye temperature (W_θ). Leibfried and Schlömann[30] have shown that W_U/W_θ is a function of T/θ_D, and this function is approximately the same for all crystals. This function has not been calculated theoretically, but its value may be found experimentally from measurements on solid helium[35] and artificial sapphire crystals.[14] The Debye temperature of KCl has been found to approach 233°K at absolute zero.[33] The value of W_θ at 233°K can be estimated from the data in Fig. 8 as 8.3 cm-deg/watt. The value of W_U computed by this method is also shown in Fig. 7. The agreement between the magnitude of the experimental and theoretical values of W_U is reasonable. The somewhat different temperature dependences may be an experimental error since only a few points determine the resistivity curve above 13°K.

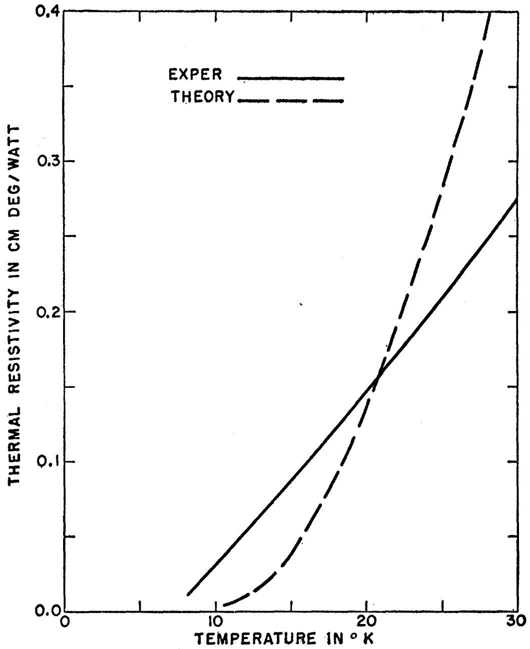

FIG. 7. Comparison of the experimental and theoretical values for the umklapp resistivity of KCl as a function of temperature.

The data given by different authors[6,7,9,36] for the thermal resistivity of KCl are plotted in Fig. 8. The average curve drawn through the points is designated as the total resistivity. This total resistivity is a combination of umklapp and point-imperfection scattering plus a small contribution from boundary scattering at very low temperatures. An attempt has been made to estimate the magnitude of the two major terms. The number of point imperfections is assumed constant, although the scatter in the data is probably caused by varying amounts of chemical impurity. The average phonon wavelength is comparable to or less than the

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[35] Webb, Wilkinson, and Wilks, Proc. Roy. Soc. (London) A214, 546 (1952).

[36] Ballard, McCarthy, and Davis, Rev. Sci. Instr. 21, 905 (1950).

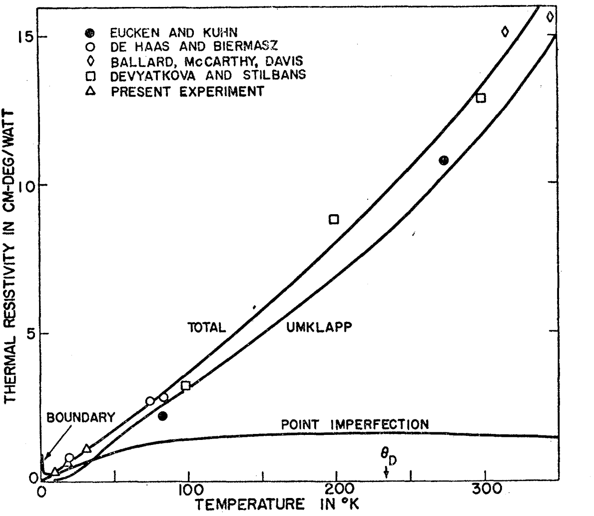

FIG. 8. The temperature variations of the contributions of boundary, point imperfection, and umklapp resistivities to the total thermal resistivity of KCl.

size of a point imperfection for all temperatures above about $\theta_D/2$. For this reason the scattering cross section for a point imperfection is nearly constant above $\theta_D/2$. Since C_v is also nearly constant above $\theta_D/2$, it follows from Eq. (2) that the point-imperfection resistivity is approximately constant above $\theta_D/2$. The point-imperfection scattering in crystal A has been extrapolated to high temperatures by using this assumption. There is also experimental justification for this extrapolation since the data of Eucken and Kuhn[6] and of Devyatkova and Stilbans[9] show that the resistivity increase produced by a given concentration of added point impurities remains nearly constant from 80°K to 300°K. The umklapp resistivity has been calculated from the theory of Leibfried and Schlömann using as the value for W_θ the difference between the total resistivity and the point-imperfection resistivity at the Debye temperature.

VII. ANALYSIS OF THE RESULTS

Scattering Cross Section for a Calcium-Vacancy Complex

The experimental data can be fitted quite well with curves whose shape has been predicted by theory. From Figs. 3 and 7 it can be seen that W_U is an unimportant contribution to W_{tot} at temperatures at or below the maximum in the conductivity curves. Equation (10), therefore, may be applied at the conductivity maxima. The parameters L and Γ can be computed from Eq. (10) once $K_{\max}$ and $T_{\max}$ are known. The values of these four quantities are given in Table I. The value of Γ increases monotonically with increasing calcium content (G), but Γ is not zero when $G=0$. The experimental value of Γ may be set equal to

$$\Gamma=\tfrac{1}{2}GS_{\text{Ca}}^2+\Gamma_0,$$

where S_{Ca}^2 = total scattering number for one calcium atom in the lattice, and Γ_0 refers to the background impurities. A plot of Γ *versus* $G/2$ is shown in Fig. 9. The $\frac{1}{2}$ in $\frac{1}{2}G$ is necessary to reduce the calcium concentration to terms of the number of calcium atoms per lattice atom. Figure 9 shows that

$$S_{\text{Ca}}^2=1.4, \quad \text{and} \quad \Gamma_0=1.15\times10^{-4}.$$

The exact value of S^2 depends on the nature of the scattering center. The calcium atoms are incorporated substitutionally into the crystal.[37] For each divalent calcium ion in the crystal, there is also a potassium-ion vacancy. At the melting point of KCl these are unassociated, but a Ca^{++} ion–K^+ ion vacancy complex has a binding energy of about 0.32 ev.[38] Thus, if the crystal is at equilibrium at room temperature, about 90% of these complexes will be associated.[39] Since the crystals were cooled slowly to room temperature during the annealing process, and since they remained at room temperature at least several weeks before the measurements were made, probably 90% (or more) of the complexes are associated at liquid helium temperatures. Thus the experimental value of S_{Ca}^2 refers to an associated complex. Klemens has calculated that, for an unassociated Ca^{++} ion and K^+ ion vacancy in KCl, $S^2\geq1.2$. Klemens' theory would predict a value of perhaps $S^2=0.8$ for an associated complex. The agreement between theory and experiment is considered to be satisfactory in view of the fact that the physical constants relevant to the theoretical calculations are not well known. If the average mean free path of a

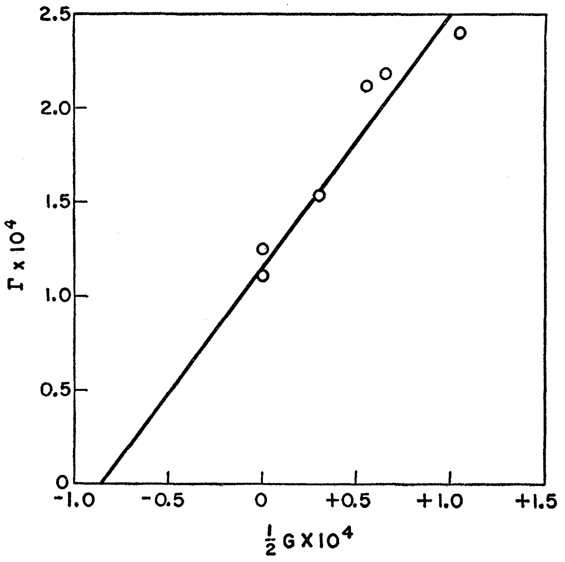

FIG. 9. Γ as a function of G for the six different KCl crystals. The slope of the line determines S_{Ca}^2, and its intercept the background impurity concentration.

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[37] H. Pick and H. Weber, Z. Physik **128**, 409 (1950).

[38] F. Bassani and G. Fumi, Nuovo cimento **11**, 274 (1954).

[39] A. B. Lidiard, Phys. Rev. 94, 29 (1954); Camagni, Chiarotti, Fumi, and Giulotto, Nuovo cimento **11**, 1 (1954).

phonon is l_{P0}, the experimental value of $S_{\mathrm{Ca}}{}^2$ corresponds to a scattering cross section equal to the area of a lattice vacancy at a temperature of $\theta_D/6$. This cross section is calculated from $\sigma^{-1}=l_{P0}\epsilon_P$.

Background Impurities

The background impurity concentration in the crystal corresponds to an equivalent calcium concentration of $G_0=1.7\times10^{-4}$. This is only an equivalent calcium concentration since both the spectrochemical analysis and ionic conductivity measurements indicate a much lower calcium concentration. Indeed no single impurity, or even the sum of all of the impurities found in the crystal, appears to be sufficiently abundant to explain such a large background resistivity. It is, of course, possible that some impurity, which is not easily checked for, is present in sufficiently large concentration to produce this background thermal resistivity.

It is also plausible that the background thermal resistivity in these relatively pure KCl crystals is caused by some intrinsic mechanism. In 1942 Pomeranchuk[28] pointed out that the naturally occurring isotopes in a crystal will destroy the perfect periodicity of the lattice and thus produce a thermal resistance. This suggestion has been compared[40,41] with the experimental results obtained for a number of different crystals. From this comparison it appears that the isotopes of K and Cl are sufficient to produce almost all of the background resistivity observed. The occurrence of such a large background resistivity limits the maximum thermal conductivity of KCl crystals to the order of 10 watts/cm-deg at 5°K. Thus the very high sensitivity to impurities suggested earlier does not occur in KCl. An isotopically pure crystal such as NaF would be much more sensitive to small amounts of foreign impurities or lattice imperfections.

Dislocations and Grain Boundaries

One of the other interesting features of the results is that the value of L decreases markedly with increasing calcium concentration (see Table I). This particular feature is not associated with phonon scattering by isolated dislocations. Equation (6) can be used to compute the dislocation resistivity. For 10^5 dislocation lines/cm^2 of either edge or screw type and a temperature of 5°K, the dislocation resistivity is only 2×10^{-6} cm-deg/watt. Thus the number of dislocations in the crystal is too small by a factor of about 10^5 to account for the observed resistivity. The grain boundaries in the crystal will also produce a very small thermal resistivity. If the maximum number of grain boundaries per centimeter occurring in Table I and the maximum grain-boundary angle is used, then the thermal resistivity at 5°K calculated from Eq. (5) is 2×10^{-8} cm-deg/watt. The phonon mean free path for grain boundary scattering is independent of wavelength and, for the grain-boundary concentration present, is equal to 4×10^5 cm. Therefore, grain-boundary scattering in the pure crystals is unimportant. Some calcium precipitation has been found to occur along the grain boundaries and also in the bulk of KCl crystals with a G greater than about 2×10^{-4}. This type of grain-boundary precipitation has also been observed[42] in NaCl containing excess $\mathrm{BaCl_2}$. Some calcium precipitation probably also occurs in the KCl crystal for $G\leq2\times10^{-4}$. This precipitation along grain boundaries, however, is not the major factor which limits the thermal conductivity at temperatures below the maximum. If it were, the experimental value of L in Table I would be somewhat larger than, or perhaps equal to, the average distance between grain boundaries. There is no such correlation in the crystals measured.

Colloidal Particles

The precipitation of excess calcium in the bulk of crystals which have been supersaturated produces a milky white color. The calcium probably precipitates as small particles of $\mathrm{KCl\cdot CaCl_2}$.[43] These particles are too small to be resolved with a light microscope. Miyake and Suzuki[44] have used x-ray scattering to measure the size of the calcium precipitates in supersaturated mixed crystals of NaCl and $\mathrm{CaCl_2}$. They conclude that the precipitated phase was in the form of platelets about 100 A in diameter and 15 A thick. Seitz[45] has given a similar size estimate for $\mathrm{CaCl_2}$ colloids in KCl. Crystals of KCl which contain less than 2.1×10^{-4} Ca/K do not possess sufficient bulk or grain boundary precipitation to appear milky. Pick and Weber,[37] from their density measurements on KCl containing excess calcium, have suggested that even for concentrations of $G<2\times10^{-4}$ about 20% of the added calcium precipitates out as a separate phase. If 20% of the calcium in crystal S precipitates out as colloids of $\mathrm{KCl\cdot CaCl_2}$ which are 100 A in diameter, there will be 1.6×10^{14} such colloids per cm^3.

The scattering cross section of these colloids will depend upon their size in comparison with the average phonon wavelength. At temperatures much below the Debye temperature (θ_D), the most numerous phonons in a Debye distribution have a frequency corresponding to

$$\bar{\nu}=1.6kT/h.$$

The wavelength of these phonons is approximately

$$\bar{\lambda}=\frac{d}{1.6}\left(\frac{4\pi}{3}\right)^{\frac{1}{3}}\left(\frac{\theta_D}{T}\right)=d\left(\frac{\theta_D}{T}\right),$$

where $d^3=V_0$. At 10°K the average phonon wavelength

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[40] G. A. Slack, preceding paper [Phys. Rev. **105**, 829 (1957)].

[41] Berman, Foster, and Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956).

[42] Amelinckx, Van der Vorst, Gevers, and Dekeyser, Phil. Mag. **46**, 450 (1955).

[43] O. Menge, Z. anorg. Chem. **72**, 162 (1911).

[44] S. Miyake and K. Suzuki, J. Phys. Soc. Japan **9**, 702 (1954).

[45] F. Seitz, Revs. Modern Phys. **26**, 21 (1954).

in KCl is about 75 A. The colloid diameter is, therefore, comparable to the average phonon wavelength at temperatures between 3°K and 15°K. Thus the colloid scattering cross section is nearly independent of frequency and Eq. (4) can be used to determine the value of L. The scattering cross section can be taken as the geometrical cross section. At $G=2.1\times10^{-4}$ the calculated mean free path is 0.008 cm, which compares favorably with the value of $L=0.021$ cm for crystal S. The value of L in Table I increases faster than linearly with G, perhaps as G^2 or G^3, which indicates that the precipitation process is probably self-nucleated rather than depending on sites already present in the crystal.

The measured value of L for crystals K and A is 2 to 3 times as large as the smallest crystal dimension. The phonon reflection from the external crystal boundaries does, however, limit the mean free path. A value of L larger than the smallest crystal dimensions indicates that some fraction of the phonon reflection from the crystal walls is specular. From the calculations of Berman, Simon, and Ziman,[46] it follows that about 50% of the reflections are specular in crystal K and about 75% in crystal A. The difference between the two crystals probably is due to the different surface treatment (see Table I). The four faces of crystal A were cleaved, whereas two faces of crystal K were cleaved and the other two were microscopically roughened by grinding.

VIII. EARLIER EXPERIMENTS

Numerical values of the thermal resistivity at low temperatures were measured by deHaas and Biermasz[7] in 1937. Their measurements did not cover the temperature range between 5 and 15°K. However, at higher and lower temperatures their results agree quite well with those obtained for crystal N. This indicates that their crystals were not so pure as crystals A and K.

In 1952 Devyatkova and Stilbans[9] measured the thermal resistivity of KCl crystals containing F centers produced by additive coloring. The measurements were made at 98°K, 200°K, and 298°K, and their data exhibited a rather large amount of scatter. They gave only a sketchy analysis of their results. But they found that, for F-center concentrations up to 1×10^{-4} F centers per potassium atom, the thermal resistivity increased linearly with increasing F-center concentration. Also the resistivity increase caused by the introduction of 1×10^{-4} F centers per potassium atom was nearly the same at all three temperatures and equal to $\Delta W=1.4$ cm-deg/watt. The temperature dependence of this thermal resistivity increase should be the same as that given in Fig. 8 for point-imperfection scattering. On this basis the resistivity increase at low temperatures caused by these F-centers becomes $\Delta W=0.018T$ cm-deg/watt, which is equivalent to an S^2 value of 2. An F center and an associated calcium ion–potassium ion vacancy complex both possess the same mass defect, both are electrically neutral, and their strain fields at large distances are comparable. Thus their scattering numbers at low temperatures should be nearly the same. In view of the approximations involved in determining S^2 for an F center, the agreement with the value of 1.4 for an associated complex is considered satisfactory.

IX. SUMMARY

The thermal conductivity of pure KCl crystals below 30°K is determined mainly by a combination of boundary and point imperfection scattering. Umklapp processes produce a measureable reduction in conductivity at temperatures between 10°K and 30°K. The temperature dependence of the boundary scattering is in good agreement with the theory of Klemens, and its magnitude in a crystal with cleaved faces indicates that about 75% of the phonon reflections at the boundary are specular. The background point imperfection scattering in a pure crystal may be caused by some unknown impurity, but the intrinsic resistivity produced by the naturally occurring isotopes appears to be a more plausible explanation. Thus the thermal conductivity of KCl is sensitive only to concentrations of divalent point impurities greater than 25 ppm (its sensitivity[16] to monovalent impurities is still less). The umklapp resistivity contribution agrees in magnitude with that proposed by Leibfried and Schlömann, but its temperature dependence is still in question.

The thermal resistivity of crystals containing added $CaCl_2$ is increased by the presence of precipitated colloidal particles about 100 A in diameter, and by associated calcium ion–potassium ion vacancy complexes. The experimental value of the scattering number of an associated complex is $S^2=1.4$. This is somewhat larger than the value predicted by Klemens, but the agreement is considered satisfactory.

X. ACKNOWLEDGMENTS

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[46] Berman, Simon, and Ziman, Proc. Roy. Soc. (London) **A208**, 90 (1951).