

## Thermal Conductivity in Sodium Chloride Crystals Containing Silver Colloids\*

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(Received 3 February 1966)

Measurements are presented of the low-temperature thermal conductivity of crystals of sodium chloride containing colloidal particles of silver. It is found that parts per million of colloidal material can substantially reduce thermal conductivity in the temperature range below the peak conductivity. Comparison is made with crystals containing the same concentrations of unprecipitated silver chloride, and with pure crystals. In addition, the scattering of phonons at external crystal surfaces is discussed.

### I. INTRODUCTION

THE thermal conductivity of a pure nonmetallic single crystal reaches a maximum value at a temperature in the neighborhood of  $\Theta/25$ , where  $\Theta$  is the Debye temperature of the solid. Below and in the region of this maximum, the thermal conductivity is extremely sensitive to the chemical and structural perfection of the crystal. Above the maximum this sensitivity is reduced because the vibrational excitations, or phonons, which are responsible for heat flow, are more strongly scattered by the nonlinear interatomic forces than they are by crystalline defects.

Since the early 1950's, many studies have been made of the defect-sensitive thermal conductivity at low temperatures, with particular attention given to point defects. Since point defects might be expected to scatter phonons with a Rayleigh cross section,  $\sigma \propto \omega^4$ , ( $\omega$  = angular frequency of the phonon), the resistivity of a point defect should vanish at low temperatures, when only low-frequency phonons are present. However, several experiments on point defects have shown anomalously large resistivities at low temperatures.<sup>1</sup> It has occasionally been suggested that in such cases, the point defects might not be randomly distributed, but concentrated in certain regions, or even partially precipitated into small particles, or colloids, of a separate phase.

In an attempt to study the effect on the low-temperature conductivity of precipitation of point defects, Klein<sup>2</sup> measured the conductivity of crystals of NaCl containing  $\text{MnCl}_2$ , using the electron spin resonance of the Mn ion to observe the degree of precipitation. He found no striking change in the thermal conductivity upon precipitation, probably because the background of defects unaffected by the Mn precipitation was large enough to obscure the change sought.

\* This work was supported in part by the U. S. Atomic Energy Commission and the Advanced Research Projects Administration.  
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<sup>1</sup> R. Berman, E. L. Foster, and H. M. Rosenberg, in *Report of the Bristol Conference on Defects in Crystalline Solids* (The Physical Society, London, 1954); G. A. Slack, *Phys. Rev.* **105**, 832 (1957); R. O. Pohl, *ibid.* **118**, 1499 (1960); G. A. Slack, *ibid.* **126**, 427 (1962); M. L. Holland and L. J. Neuringer, *Proceedings of the International Conference Semiconductor Physics, Exeter, 1962* (The Institute of Physics and The Physical Society, London, 1963), p. 474.

<sup>2</sup> M. V. Klein, *Phys. Rev.* **123**, 1997 (1961).

The experiments described here were designed to fill the need for unequivocal information about thermal phonon scattering by colloidal particles. By a fortunate choice of precipitant and host lattice, we have been able to separate clearly the effects of dissolved and precipitated silver atoms in crystals of NaCl. The results show that a few parts per million of foreign material in colloidal form can substantially reduce the thermal conductivity, particularly at very low temperatures. In addition, the conductivity measurements, together with a knowledge of the solute concentration, have furnished estimates of particle size and concentration, and information concerning the mechanism of precipitation.

### II. EXPERIMENTAL APPARATUS

The experimental apparatus was designed to provide measurements of thermal conductivity of reasonable accuracy over the temperature range 1.2 to 100°K. The estimated absolute accuracy was better than 20% at the high temperature limit, and improved at lower temperatures, being better than 10% below about 40°K. The apparatus, described in detail elsewhere,<sup>3</sup> was in many respects similar to those of Slack, Williams, and Klein.<sup>4</sup> The only major departure was the use of helium exchange gas to obtain a reliable and simply operated thermal switch between the crystal and the helium bath. High conductance was available for fast initial cooling and fast response, and for making measurements only slightly above the liquid-helium bath temperature. Alternatively, low conductance was available for reaching moderately high temperature ( $\sim 25^\circ\text{K}$ ) without either (a) excessive power input and concomitant rapid loss of liquid helium, or (b) loss of the stabilizing influence of the bath.

A variable-volume helium-gas thermometer and platinum resistance thermometer furnished measurements of absolute temperature. A single matched pair of carbon resistors in an ac bridge circuit with phase-sensitive detection provided measurements of the temperature

<sup>3</sup> J. M. Worlock, Ph.D. thesis, Cornell University, 1962 (unpublished).

<sup>4</sup> G. A. Slack, *Phys. Rev.* **105**, 832 (1957); Ph.D. thesis, Cornell University (unpublished); W. S. Williams, *Phys. Rev.* **119**, 1021 (1960); Ph.D. thesis, Cornell University, 1956 (unpublished); M. V. Klein, *Phys. Rev.* **122**, 1393 (1961); and Ph.D. thesis, Cornell University, 1961 (unpublished).

gradient over the whole temperature range. Measurements were made under steady-state conditions, with direct thermal current provided by an electrical heater.

### III. CRYSTALS

The crystals measured in these experiments were of three types: (a) pure NaCl; (b) NaCl containing AgCl in solution; and (c) NaCl containing metallic silver colloids.

This particular crystal system had several features which made it attractive for this study. First, the state of the impurity silver could be changed from complete solubility to complete insolubility by chemical means (reduction in alkali vapor). This made it possible to distinguish clearly the separate effects of dissolved and coagulated silver atoms on the thermal conductivity. Second, the precipitation reaction, once complete, was not reversible (except possibly in a strongly oxidizing atmosphere such as Cl<sub>2</sub> gas) and the crystals could be carefully annealed to remove excess reducing agent and reduce thermal strain. Third, both the dissolved and coagulated silver showed characteristic optical absorption bands which furnished valuable information concerning silver content and particle size. Fourth, the high electron density in the silver precipitates enhanced their observability by such techniques as transmission-electron microscopy.

This section contains a description of the crystals, the techniques used in their preparation, the studies made to determine their defect structures, and the conclusions drawn from these studies.

#### A. Pure NaCl

The "pure" NaCl crystal was grown by the Kyropoulos technique, from an alumina crucible, in an argon atmosphere. The salt was reagent-grade NaCl which had undergone several cycles of baking in a chlorine atmosphere at 700°C. Klein has shown that this chlorine treatment is effective in removing the ubiquitous ultraviolet absorption band at 1850 Å, as well as an associated impurity—probably OH<sup>-</sup>—which is extremely effective in scattering phonons.<sup>5</sup> Optical absorption measurements on this crystal gave no hint of defects other than the OH<sup>-</sup>, which was present in a concentration of 7.10<sup>14</sup> cm<sup>-3</sup>.<sup>6</sup> The thermal conductivity of this crystal is compared with Klein's thermal conductivity measurements in Sec. V.

#### B. NaCl:AgCl

The mixed crystals of NaCl and AgCl were grown in the same manner from the same chlorine-treated raw material. A small pellet of AgCl was added to the first charge, after which a piece from the bottom of each boule was used to dope the next charge with AgCl.

<sup>5</sup> M. V. Klein, Phys. Rev. **122**, 1393 (1961).

<sup>6</sup> Tan Ik Gie and M. V. Klein, Bull. Am. Phys. Soc. **8**, 230 (1963).

Transmission measurements in the near ultraviolet provided information about the actual Ag<sup>+</sup> concentrations in these crystals. There are two weak absorption bands, at 2170 and 2100 Å, which correspond to forbidden transitions of the 4*d* electrons on the silver ions. The relations between the mole fraction of silver *C* and the optical absorption constants  $\kappa$  at 20°C have been determined by Martienssen<sup>7</sup>:

$$C = 2.4 \times 10^{-5} \times \kappa \text{ (cm}^{-1}\text{) at 2170 Å,}$$

$$C = 1.9 \times 10^{-5} \times \kappa \text{ (cm}^{-1}\text{) at 2100 Å.}$$

AgCl is highly soluble in NaCl<sup>8</sup>: The two solids have identical crystal structures and nearly identical lattice constants. Therefore the silver ions have no tendency to cluster and can be considered to have a uniform random distribution, with a slight concentration gradient in the direction of growth.

Since the distribution coefficient for AgCl dissolved in NaCl is significantly less than 1, the concentration of AgCl in the boule increased with growing time, and the early part of the boule was more lightly doped than the late. As a result, each crystal measured contained a range of concentrations of AgCl. These concentrations and their ranges are shown in Table I.

#### C. NaCl with Ag Colloids

Crystals of NaCl containing metallic silver colloids were produced from the mixed crystals by reduction of the silver in an atmosphere of alkali (potassium) vapor. Sealed Pyrex bombs containing mixed crystals and triply distilled potassium metal were held at temperatures of about 600°C for times up to 48 h. At the end of this precipitation period, the crystals were removed from the bombs and annealed in an argon atmosphere at 600°C for 24 h, after which they were cooled slowly to room temperature in another 24 h. This anneal was designed to allow any excess alkali metal to diffuse out, and to reduce the thermal strains resulting from differential thermal contraction of silver and NaCl. The single exception to this rule is noted in Table I.

*The precipitation process.* In the precipitation process, potassium atoms arriving at the surface of the NaCl crystal provided a sink for cation (Na<sup>+</sup>) vacancies diffusing to the surface, gave up their electrons, and became incorporated onto the crystal as KCl. In an undoped crystal, the electrons would be trapped at anion (Cl<sup>-</sup>) vacancies, which thus become *F* centers. In the doped crystals, electrons were trapped also by silver ions, the most stable combination being a silver ion, a nearest neighbor anion vacancy, and an electron: the *B* center of Etzel and Schulman.<sup>9</sup> At elevated temperatures the neutral silver was able to diffuse, and coagulated into metallic silver particles.

<sup>7</sup> W. Martienssen (private communication).

<sup>8</sup> R. J. Stokes and C. H. Li, Acta Met. **10**, 535 (1962).

<sup>9</sup> H. W. Etzel and J. H. Schulman, J. Chem. Phys. **22**, 1549 (1954).

TABLE I. Silver content.

Crystal	Average	Range	Remarks
1	...	...	Pure
2	$2.5 \times 10^{-5}$ (mole fraction)	$2 \times 10^{-5}$ to $3 \times 10^{-5}$	Dissolved AgCl
3	$4 \times 10^{-4}$ (mole fraction)	$3 \times 10^{-4}$ to $5 \times 10^{-4}$	Dissolved AgCl
4	$8 \times 10^{-4}$ (mole fraction)	$5 \times 10^{-4}$ to $14 \times 10^{-4}$	Dissolved AgCl
5	$9 \times 10^{-6}$ (volume fraction)	$7 \times 10^{-6}$ to $11 \times 10^{-6}$	Precipitated Ag metal. Unannealed. Contained colloidal Na and $F$ centers
6	$1.8 \times 10^{-5}$ (volume fraction)	$1.4 \times 10^{-5}$ to $2.3 \times 10^{-5}$	Precipitated Ag metal
7	$1.5 \times 10^{-4}$ (volume fraction)	$1.1 \times 10^{-4}$ to $1.8 \times 10^{-4}$	Precipitated Ag metal
8	$3.0 \times 10^{-4}$ (volume fraction)	$1.8 \times 10^{-4}$ to $5.1 \times 10^{-4}$	Precipitated Ag metal

Two arguments are here adduced to show that the coagulation was complete and no appreciable amount of silver was left in solution, either as dissolved silver ions or as  $B$  centers. (1) The exothermic reaction,  $K + AgCl \rightarrow KCl + Ag$ , once complete, cannot be reversed at ordinary temperatures because the heat evolved in the reaction is too great. Amelinckx and others<sup>10</sup> who have studied the colloidal decoration of dislocations in alkali halides report that silver colloids remain intact up to the melting point of the crystals. (2) The rate at which the reaction took place was limited primarily by the availability of electrons liberated at the surface, which in turn was controlled by the diffusion of cation vacancies to the surface from the interior. This is deduced from the fact that there was a sharp (less than  $1 \mu$  thick) boundary between colored and uncolored material which moved slowly ( $\sim \frac{1}{10}$  mm/h in a crystal containing  $2 \times 10^{19}$  silver ions per cc) into the crystal from the surface. The reaction proceeded to its conclusion in a given region of the crystal before the electrons were allowed to pass through the region to begin the coloration of the next layer.

Since the reaction was complete, it is possible to compute the fractional volume of each crystal which was occupied by colloidal material, from the data on the initial  $Ag^+$  concentrations. These figures are shown in Table I.

*Optical transmission studies.* The presence of colloidal silver in these crystals was demonstrated by an optical extinction band with a peak near  $4500 \text{ \AA}$ . This band was observed much earlier by Blau<sup>11</sup> who produced it by electrolytic coloration of mixed crystals  $NaCl: AgCl$ .

The absorption and scattering of light occur in a resonant interaction of the electron plasma in the silver particles with the high-frequency electric field of the light. Figures 1(a)–1(c) show measurements of the optical extinction bands in crystals taken from the same boules as conductivity samples 5, 6, and 7, respectively. These measurements are to be compared with the theoretical extinction bands shown in Fig. 2. The small temperature dependence of the height of the band in the

unannealed crystal, Fig. 1(a), was probably caused by a small concentration of  $F$  centers (a few times  $10^{16} \text{ cm}^{-3}$ ) produced in the coloring process. The colloid band itself is temperature independent. Both  $F$  centers and  $B$  centers were absent in annealed crystals. The shift of the peak of the band to higher energies upon annealing, Figs. 1(b) and 1(c), was probably a result of the purification of the silver as the more volatile sodium evaporated from the colloid.

Figure 2 shows theoretical extinction bands, calculated for  $NaCl$  crystals containing one part per million by volume of monodisperse silver spheres with several different radii. A formula for the total cross section (absorption and scattering) for a sphere in a dielectric medium<sup>12</sup> was evaluated numerically, using the optical constants of bulk silver obtained by Schulz<sup>13</sup> and the refractive index of  $NaCl$  given in the International Critical Tables.<sup>14</sup>

Comparison of the observed extinction bands with the theoretical bands provides an estimate of the size of the silver particles. The general shapes (i.e., half-widths and relative heights of the main peak and the shoulder peak) indicate particle radii of about  $250 \text{ \AA}$ . The positions of the peaks indicate particle radii somewhat less than  $200 \text{ \AA}$ . Qualitative measurements of the optical scattering cross sections of the particles also are consistent with particle radii less than  $200 \text{ \AA}$ .

This comparison between theoretical and observed extinction bands, however, cannot be made precise for the following reasons: (1) The particles were not necessarily monodisperse, but may have had a distribution of sizes. Part of the breadth of the measured curves may be ascribed to this size distribution. (2) The particles were not necessarily spheres, but may possibly have been oblate or prolate with extinction curves differing from those calculated for spheres, as shown by Gans.<sup>15</sup> (3) The purity of the metal in the particles is also capable of affecting the size, shape, and position of the extinction curve.<sup>16</sup>

<sup>12</sup> J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), p. 563.

<sup>13</sup> L. G. Schulz, *J. Opt. Soc. Am.* **44**, 357 (1954); L. G. Schulz and F. R. Tangherlini, *ibid.* **44**, 362 (1954).

<sup>14</sup> *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1930), p. 14.

<sup>15</sup> R. Gans, *Ann. Physik* **47**, 270 (1915).

<sup>16</sup> S. Nakashima, *J. Phys. Soc. Japan* **16**, 1650 (1961).

<sup>10</sup> S. Amelinckx in *Dislocations and Mechanical Properties of Crystals, Lake Placid Conference* (John Wiley & Sons, Inc., New York, 1956), p. 4; W. Van der Vorst and W. Dekeyser, *Phil. Mag.* **1**, 822 (1956).

<sup>11</sup> M. Blau, *Nachr. Akad. Wiss. Göttingen, II Math.-Physik. Kl.* **401** (1933).

*Optical microscopy.* All of the thermal conductivity specimens which contained colloids were examined in dark field optical microscopy, at a magnification of 560, in an attempt to see the light scattered from individual silver colloids. No such light was observed, for several probable reasons. (1) The eye is not very sensitive at a wavelength of 4500 Å, where the scattering was

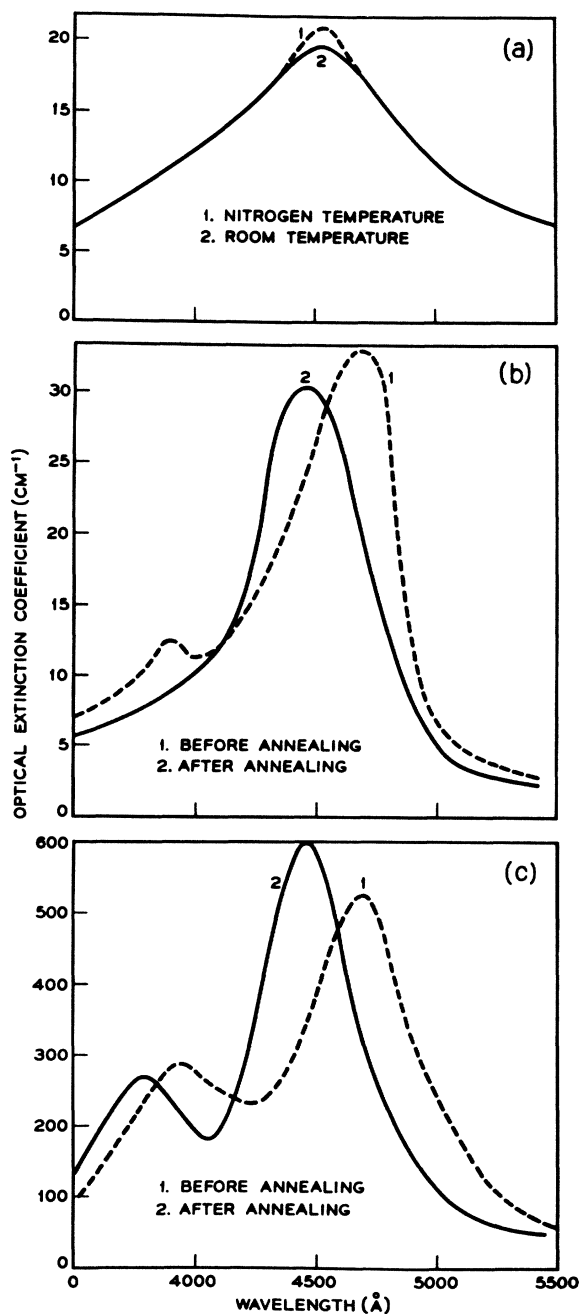


FIG. 1. Optical-extinction curves for crystals containing silver colloids. (a) NaCl with 7.10<sup>-6</sup> silver (by volume) unannealed; (b) NaCl with 15.10<sup>-6</sup> silver (by volume); (c) NaCl with 150 × 10<sup>-6</sup> silver (by volume).

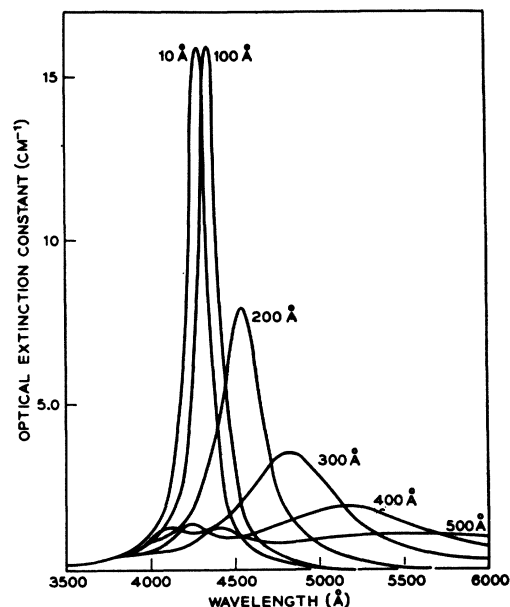


FIG. 2. Calculated optical extinction curves for NaCl containing 1 ppm of colloidal silver (by volume). Calculations made for monodisperse spheres with radii as shown.

strongest. (2) The particles may have been too small to scatter effectively. The scattering cross section is proportional to the square of the colloid volume, and hence total scattering for a given amount of colloidal material is strongly size dependent. The absorption cross section dominates the scattering cross section for spherical particles smaller than 150 Å in radius. (3) The particles may have been too close together to be resolved with light of wavelength 4500 Å. With 10 ppm of colloidal material in particles with a linear dimension of 200 Å, the separation between particles would be of the order of two wavelengths of blue light.

These negative observations are consistent with the preceding estimates of particle size.

*Electron microscopy.* Preliminary studies by D. Walton using transmission electron microscopy<sup>17</sup> have given strong support to the size estimates above, although the replication of cleavage surfaces<sup>18</sup> has produced no reliable micrographs.

#### D. Conclusions

Information concerning the impurity and defect concentrations of the thermal conductivity samples is presented in Table I. It is possible to place an upper limit on the particle size for the crystals which contained silver colloids. From optical and microscopic observations we conclude that the particles had linear dimensions of the order of 200 Å or less.

<sup>17</sup> Derek Walton (private communication).

<sup>18</sup> R. E. Simon and R. L. Sproull, *J. Appl. Phys.* **31**, 2224, (1960) were able to observe *K* colloids in a cleavage plane of KCl by vacuum cleaving and replication.

#### IV. THEORETICAL BACKGROUND

A simple argument from kinetic theory gives an expression for the thermal conductivity of a gas of carriers all of which travel at speed  $v$ , and possess a mean free path  $\lambda$  between collisions which result in complete loss of memory of direction. This expression is

$$K = \frac{1}{3} C v \lambda, \quad (1)$$

where  $C$  is the heat capacity per unit volume of the gas. This is easily generalized to the case of many groups of carriers, each possessing its heat capacity, speed and mean free path.

$$K = \frac{1}{3} \sum_i C_i v_i \lambda_i. \quad (2)$$

Since we shall be discussing the thermal conductivity of a gas of phonons at low temperatures, it is reasonable to make use of the Debye phonon spectrum. All acoustic phonons are taken to have the same speed, regardless of wavelength and direction. Finally, in all cases of present quantitative interest, the mean free path is determined by scattering at external or internal boundaries, and can be taken to be independent of wavelength and direction. Thus both  $v$  and  $\lambda$  can be taken out of the sum, and the original expression is restored to validity.

The heat capacity per unit volume, in the Debye approximation, for a solid with Debye temperature  $\Theta$ , is

$$C = \frac{3k}{2\pi^2} \left( \frac{kT}{nv} \right)^3 \int_0^{\Theta/T} \frac{x^4 e^x dx}{(e^x - 1)^2}. \quad (3)$$

For low temperatures,  $\Theta/T > 10$ , negligible error is incurred by setting the upper limit of the integral at infinity. The result is the well-known  $T^3$  dependence of the heat capacity, which leads, according to (1), to a similar temperature dependence for the thermal conductivity:

$$K = 2.60 \frac{k}{2\pi^2} \left( \frac{kT}{n} \right)^3 \frac{1}{v^2} \lambda. \quad (4)$$

The conditions for the validity of this argument are quite often met in good crystals at low temperatures, where intrinsic anharmonic scattering and point-defect scattering have become impotent because of the low frequencies and long wavelengths of the phonons present. In such cases, a measurement of  $K$  is a direct measurement of  $\lambda$ .

In an otherwise perfect crystal in which phonons are scattered diffusely at the surfaces, Casimir<sup>19</sup> has calculated that  $\lambda = d$  for longitudinal heat flow in a right circular cylinder of diameter  $d$ , and  $\lambda = 1.12d$  for a crystal of square cross section of side  $d$ . Ziman<sup>20</sup> has generalized Casimir's treatment to include a fraction,  $P$ , of specularly reflected phonons, and has found that the mean free path is increased by the factor  $(1+P)/(1-P)$ .

We shall be interested in a case in which there are internal defects scattering phonons with cross sections which are independent of phonon frequency. Colloids with dimensions larger than phonon wavelengths are such defects. For wavelengths much smaller than particle size, all the arguments of geometrical optics will apply, and the scattering occurs by reflection and refraction at the surface of the colloid, and is patently wavelength independent. For wavelengths much larger than particle size, analogous arguments of physical or wave optics apply, and the cross section must, in the Rayleigh limit, fall off as (wavelength)<sup>-4</sup>. In the intermediate region, the cross section can only be calculated numerically, and depends on details of acoustic mismatch and particle shape. By analogy with available numerical calculations,<sup>21</sup> we expect that the cross section will remain substantially constant until wavelength divided by  $2\pi$  becomes at least as large as the radius of the particle.

If we assign our scatterers a constant cross section  $\sigma$ , and a concentration  $\eta$ , then the mean free path appropriate to the conductivity calculation is given by

$$1/\lambda = \alpha \sigma \eta, \quad (5)$$

where  $\alpha$  is a number of order of magnitude 1 which accounts for the fact that the scattered wave may have some angular correlation with the incident wave. For example,  $(1-P)/(1+P)$  is just such a factor for the case of partly specular reflection from crystal surfaces.

The effect of the separate scatterers is additive in  $1/\lambda$ , i.e.,  $1/\lambda$  is proportional to  $\eta$ . When boundary scattering is to be included as well it can also be inserted in an additive manner:

$$1/\lambda = \alpha \sigma \eta + (1/\lambda)_{\text{Boundary}}. \quad (6)$$

This rudimentary theoretical structure is all we shall need for discussing the present experiments. All of the thermal conductivities to be discussed quantitatively can be taken to have the  $T^3$  dependence, in the limit of low temperature.

A more extensive quantitative treatment might be based, for example, on the phenomenological theory first used by Callaway.<sup>22</sup> This scheme has, in fact, been used to fit the data presented in this paper.<sup>23</sup> At the very low temperatures at which the theory is valid, it produces results identical to those described here, i.e., the frequency independent mean free path or scattering rate can be found by inspection. At higher temperatures, the mean free paths required to fit the data are largely devoid of meaning, because (a) there is no good way of handling the intrinsic normal three-phonon scattering unless it is very weak, (b) there are no good estimates of the rate of intrinsic scattering, and (c) the theory neglects phonon dispersion and hence overesti-

<sup>19</sup> H. B. G. Casimir, *Physica* **5**, 495 (1938).

<sup>20</sup> J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), Chap. VII.

<sup>21</sup> V. C. Anderson, *J. Acoust. Soc. Am.* **22**, 426 (1950).

<sup>22</sup> J. Callaway, *Phys. Rev.* **113**, 1046 (1959).

<sup>23</sup> J. M. Worlock, Ph.D. thesis, Cornell University, 1962 (unpublished).

mates both energy content and group velocity for the higher frequency modes.

V. EXPERIMENTAL RESULTS AND DISCUSSION

This section contains a presentation of the thermal conductivity measurements obtained on the crystals described in Sec. III, and a discussion of their consequences.

A. Pure NaCl Crystals

Figure 3 shows the thermal conductivity of the sample of "pure" NaCl, and its relation to earlier measurements by Klein,<sup>5</sup> McCarthy and Ballard,<sup>24</sup> and Eucken.<sup>25</sup> The agreement with Klein's measurements above 10°K is very satisfactory, as is the manner in which the curves lead into the high-temperature data of Eucken, and of McCarthy and Ballard.

The three straight lines superimposed on the data represent the thermal conductivities calculated according to the simple theory outlined above, using constant phonon mean free paths  $\lambda_1=5.6$  mm,  $\lambda_2=7.3$  mm,  $\lambda_3=15.0$  mm, and a phonon velocity  $v=3.8 \times 10^5$  cm/sec.  $\lambda_1$  and  $\lambda_2$  are the Casimir mean free paths  $1.12d$  for the two samples measured and  $\lambda_3$  is a mean free path required by Klein's measurements. The agreement between line 1 and our data in the low-temperature limit indicates that the surface scattering of phonons was in fact diffuse while the disagreement between line 2 and Klein's data indicate an admixture of specular reflection.

From a study of the surface scattering of thermal phonons, Pohl concluded that sandblasting produces a

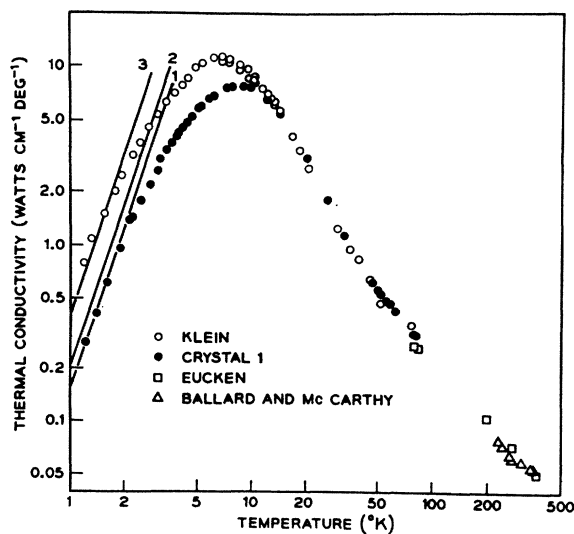


FIG. 3. Thermal conductivity of pure NaCl crystals. The straight lines represent boundary-scattering limited thermal conductivity, proportional to  $T^3$ .

<sup>24</sup> K. A. McCarthy and S. S. Ballard, J. Appl. Phys. 31, 1410 (1960).

<sup>25</sup> A. Eucken, Ann. Physik 34, 185 (1911).

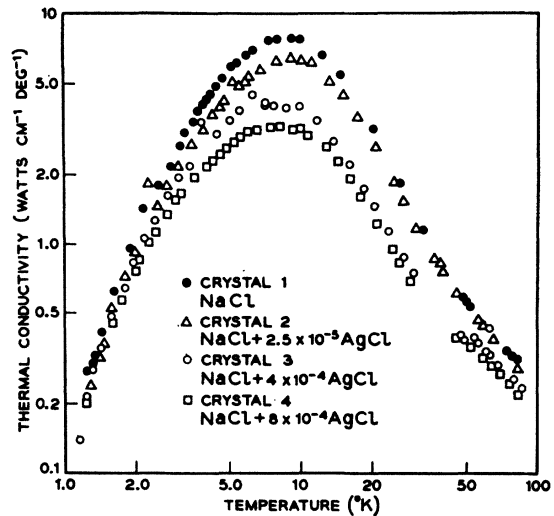


FIG. 4. Thermal conductivity of NaCl containing AgCl in solid solution.

surface which scatters diffusely.<sup>26</sup> His mean free path was, however,  $2.0d$ , rather than the Casimir value  $1.1d$ . Klein's crystals were also sandblasted, as were those in the present study. However, both Pohl and Klein annealed their crystals after the sandblasting, whereas the order of annealing and sandblasting was reversed in this work. One is led to suggest that it is not surface roughness which is responsible for diffuse scattering, but the tangle of dislocation loops produced beneath the surface by the impact of abrasive particles. An anneal will remove most of the dislocations and reduce the diffuseness of phonon reflection.

A simple set of experiments would test this hypothesis, involving a series of thermal conductivity measurements on samples with several types of surfaces: (a) cleaved and annealed (b) cleaved, annealed, and sandblasted, (c) cleaved, sandblasted, and annealed, (d) cleaved, annealed, sandblasted, and chemically polished to leave a smooth surface with subsurface damage. Recent experiments by Thacher, on the boundary scattering in LiF samples, have produced results consistent with the foregoing suggestion.<sup>27</sup>

B. NaCl Crystals Containing Dissolved AgCl

Figure 4 shows the thermal conductivity of the three crystals containing dissolved AgCl, along with the "pure" NaCl sample. The figure shows the features that have come to be expected in point defect thermal resistivity: a more or less symmetrical reduction in thermal conductivity on both sides of the maximum, which reduction disappears at both low and high temperatures. There is an indication of a depression in thermal conductivity between 20 and 50°K, which may possibly have some connection with the type of resonant

<sup>27</sup> P. D. Thacher (private communication).

<sup>26</sup> R. O. Pohl, Phys. Rev. 118, 1499 (1960).

phonon scattering discussed by Wagner<sup>28</sup> and by Walker and Pohl.<sup>29</sup>

Further experiments on this effect would be interesting; in particular, extending the range of defect concentration. AgCl is soluble in NaCl up to at least 10%, which would allow 20 times the concentration studied here.

These measurements will not be discussed quantitatively, and are included primarily to show the contrast between the effects of dissolved and precipitated silver.

### C. NaCl Crystals Containing Colloidal Ag

Figure 5 shows the thermal conductivity of NaCl containing colloidal particles of silver. Also shown is the conductivity of the pure sample. The five straight lines represent calculated thermal conductivities, using phonon mean free paths:  $\lambda_1 = 5.6$  mm,  $\lambda_2 = 0.55$ ,  $\lambda_3 = 0.38$ ,  $\lambda_4 = 0.065$ ,  $\lambda_5 = 0.040$  mm. From the additivity of inverse mean free paths and the identity in size of the five samples, we can compute a quantity  $\lambda_c$  or mean free path against colloid scattering:

$$\frac{1}{\lambda_c} = \frac{1}{\lambda_{\text{measured}}} + \frac{1}{\lambda_{\text{boundary}}} \quad (7)$$

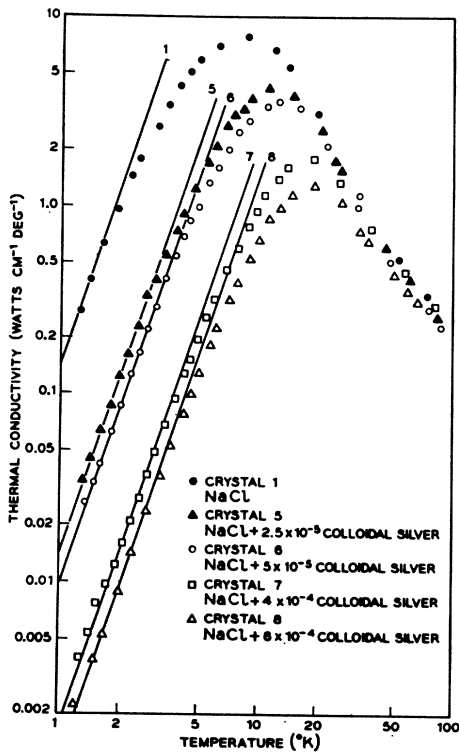


FIG. 5. Thermal conductivity of NaCl containing silver colloids. The straight lines represent the boundary-and-colloid-scattering-limited conductivity, proportional to  $T^3$ .

<sup>28</sup> M. Wagner, Phys. Rev. **131**, 1443 (1963).

<sup>29</sup> C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).

TABLE II. Values of  $\lambda_{\text{meas}}$  and  $1/\lambda_c$ .

Crystal	$\lambda_{\text{meas}}$ (cm)	$\lambda_{\text{meas}}^{-1}$ (cm <sup>-1</sup> )	$\lambda_c^{-1}$ (cm <sup>-1</sup> )
1	0.55	1.82	0
5	0.055	18.2	16.4
6	0.038	26.3	25
7	0.0065	154	150
8	0.0040	250	250

Values of  $\lambda_{\text{meas}}$  and  $1/\lambda_c$  are tabulated for the 5 crystals in Table II.  $1/\lambda_c$  is related to the size and concentration of the colloids according to Eq. (5)

$$1/\lambda_c = \alpha\sigma\eta, \quad (8)$$

where  $\alpha\sigma$  must denote some average of these parameters over the distribution of colloids.

A useful relation is that between colloid concentration  $\eta$ , mean volume  $V$ , and the fractional volume occupied by colloid<sup>31</sup> material  $F$ :

$$F = V\eta. \quad (9)$$

The simultaneous solutions of Eqs. (8) and (9) can provide two pieces of information: (1) a mean linear dimension  $l$  of the colloids, and (2) the concentration  $\eta$ .

(1) Assume that the scattering cross section  $\sigma$ , is proportional to the area, or the projected area, of a colloid. This is reasonable if the colloids are large in comparison to characteristic phonon wavelengths. Then the dimension  $l$ , can be obtained from the product  $F\lambda_c$ :

$$F\lambda_c = V\eta/\alpha\sigma\eta = V/\alpha\sigma \equiv l. \quad (10)$$

Values of  $F$ ,  $\lambda_c$ , and  $l$  are shown in Table III for the four crystals.  $F$  is calculated from the known silver concentration.

(2) A number  $\eta'$  closely related to the colloid concentration  $\eta$  is obtained by dividing  $F$  by the cube of the linear dimension  $l$ . These values are given also in Table III.

Notice that the colloid concentration  $\eta'$  is substantially independent of the silver concentration  $F$ . This allows us to conclude that the colloids are nucleated heterogeneously: homogeneous nucleation would produce a concentration varying as  $F^n$  where  $n$  is the number of silver atoms in a stable nucleus. The precipitation sites occur in concentrations of about  $5 \times 10^{13}$  per cm<sup>3</sup> in crystals 5 and 6 and of  $15 \times 10^{13}$  per cm<sup>3</sup> in crystals 7 and 8. It is noteworthy that crystals 5 and 6 came from the same boule, and crystals 7 and 8 from another. It is reasonable to conclude simply that the second boule contained three times the site concentration of the first. It seems hopeless to attempt to identify the nature of the nucleation site, since its concentration is much lower than chemical detectability, and much too high to be associated with dislocations.

It is clear from these figures that the colloids could not have been observed by optical microscopy. Their

mean separation is on the order of 2000 Å, which is well outside the theoretical resolving power, with visible light.

The more novel and more interesting result of the analysis, however, is the experimentally determined colloid dimension  $l$ . These measured colloid sizes are reasonably consistent with all previous estimates from optical scattering and absorption measurements. The discrepancy of a factor of 2 to 4 is quite acceptable in view of the stated difficulties in interpreting the optical experiments and the lack of detailed understanding of the relationship between colloid size and phonon scattering cross section.

In obtaining these figures, we have assumed that the scattering cross section is independent of the phonon wavelength, and proportional to the geometrical area of the colloid. At moderate temperatures, these assumptions are justifiable because short wavelength phonons dominate the phonon distribution and for short wavelengths, the geometrical optics analogy is valid. The experimental results indicate that the assumptions hold right down to the lowest temperature of measurement. Any deviation would show up in a departure of the conductivity from strict  $T^3$  dependence at low temperatures. It is interesting to examine the result for self-consistency, to determine whether the measured colloid size is large enough to justify geometrical optics at the lowest temperature. The quantity of interest is the product of phonon wave vector  $q$ , and colloid dimension  $l$ . Geometrical scattering is expected for  $ql \gg 1$ , and Rayleigh scattering for  $ql \ll 1$ .

If we take the scattering rate to be independent of the wave vector, then phonons of wave vector  $q$  contribute to heat flow in proportion to their contribution to the specific heat integral:

$$J_4 = \int_0^{\Theta/T} \frac{x^4 e^x dx}{(e^x - 1)^2},$$

where  $x = \hbar v q / kT$ . The maximum value of the integral occurs at  $x = 3.8$ , and the integral reaches  $\frac{1}{10}$  its final value at  $x = 2.1$ . This means that the dominant phonons at temperature  $T$  are those for which  $\hbar v q = 3.8kT$  and that 9/10 of the heat is carried by phonons for which  $\hbar v q > 2kT$ . Denote by  $q_0(T)$  the wave vector for which  $\hbar v q = 2kT$ , and consider any  $q > q_0$  to be irrelevant to the problem. For NaCl, using  $v = 3.8 \times 10^5$  cm/sec, we find

$$q_0(T) = 7 \times 10^5 \times T \text{ (cm}^{-1}\text{)}.$$

TABLE III. Values of  $F$ ,  $\lambda_c$ , and  $l$ .

Crystal	$\lambda_c$ (cm)	$F (\times 10^6)$	$F\lambda_c \equiv l$ (Å)	$\eta' \equiv F/l^3$ (cm <sup>-3</sup> )
5	0.061	9	55	$5.4 \times 10^{13}$
6	0.040	18	72	$4.8 \times 10^{13}$
7	0.0067	150	100	$1.5 \times 10^{14}$
8	0.0040	300	120	$1.6 \times 10^{14}$

At 1.2°K,  $q_0 l$  for the various samples is between about  $\frac{1}{2}$  and 1. These values are in the transition region where neither short-wavelength nor long-wavelength approximations are valid. Although it would be quite reasonable to expect the cross section to be somewhat less than geometrical for  $q_0 l \sim 1$ , there is no hint of this in the experimental curves. It would be most interesting to carry the conductivity measurements to lower temperatures, to see where the deviation from constancy sets in. This would aid substantially in the interpretation of the size parameter  $l$ , or equivalently, the effective cross section  $\alpha\sigma$ .

## VI. CONCLUSIONS

The primary importance of this work is in the demonstration that extremely small amounts of foreign matter, in colloidal form, can have a remarkable effect on the thermal conductivity at temperatures below the peak. Since almost any crystal will be impure to at least a few parts per million, this amounts to a warning that the possibility of phonon scattering by colloids can never be entirely disregarded. The chemical and physical state of an impurity are seen to be extremely important in determining the phonon scattering to be expected from that impurity. The contrast between the thermal conductivities in crystals of NaCl containing dissolved and coagulated silver has been shown in Figs. 4 and 5.

The thermal-conductivity measurements together with the knowledge of silver concentration have enabled the calculation of colloid sizes. The sizes found are consistent with estimates obtained from optical-transmission and scattering studies. More solid confirmation of the conclusions of this work will be obtained, however from (1) studies of transmission electron microscopy in which the colloids can be most directly observed, and (2) studies of thermal conductivity at even lower temperature, where the dominant phonons will have wavelengths much larger than the particle size. These studies are, in fact, currently in progress.<sup>30</sup>

In addition, measurements in pure crystals and their comparison with earlier published work indicate that surface scattering of phonons is generally not diffuse, even on artificially roughened surfaces. A series of experiments to test this conclusion has been suggested.

## ACKNOWLEDGMENTS

I wish to thank R. L. Sproull for his encouragement and guidance throughout the course of this work, Marvin Moss for his patient tutoring and his friendship, M. V. Klein and R. O. Pohl for many formative discussions, and Derek Walton for his continuing interest in the work. I am grateful to the Corning Glass Works Foundation for fellowship support during part of this work.

<sup>30</sup> Derek Walton, Bull. Am. Phys. Soc. **10**, 259 (1965).