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ILLINOIS INSTITUTE OF TECHNOLOGY

THE THERMAL CONDUCTIVITY OF γ -IRRADIATED KCl

CRYSTALS BETWEEN 0.4 AND 4°K

BY

RAYMOND A. GUENTHER

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy in Physics
in the Graduate School of
Illinois Institute of Technology

CHICAGO, ILLINOIS
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ABSTRACT

Thermal conductivity measurements between 0.4 and 4°K were undertaken to test a defect model proposed by Sonder and associates. This model postulates the formation of interstitial chlorine (formed in conjunction with trapped electron centers) and that these interstitials aggregate to form clusters (colloids) - the size of and number of which depend on the irradiation temperature and impurities in the crystal.

Using the low temperature thermal conductivity as a means of detecting and gauging the size of clusters, it was found that for two samples irradiated at room temperature there were aggregates of an effective radius of $70 \text{ \AA}$. A sample irradiated at liquid nitrogen temperature and warmed to room temperature before the thermal conductivity was measured showed no evidence of colloids for the radiation dose available. On the other hand, a sample irradiated at liquid nitrogen temperatures and measured without warming produced results characteristic of colloids, but from the measurements performed one could not rule out resonant scattering of phonons by point defects. For two samples of different purity, but irradiated identically, the aggregate size appeared to be the same.

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CHAPTER I INTRODUCTION

The fact that the heat flux, $\underline{F}$, in a material is the opposite direction of the temperature gradient, ∇T , and is proportional to it, leads one to define the thermal conductivity as that constant of proportionality K for which

$$\underline{F} = -K \nabla T. \quad (1)$$

In general K depends on properties of the material, the direction in which it is measured and also on the shape and size of the material specimen. In general the transport of heat in a material is very complicated in that conduction electrons, magnetic properties, purity and structure have pronounced effects on the thermal conductivity. In this work, only insulating, nonmagnetic, crystalline solids will be considered so that the properties of the lattice, including defects and crystal boundaries, are dominant.

I. Discussion of Lattice Thermal Conductivity

The thermal properties of a crystal are best studied by treating it as a dynamical system. For the perfect crystal, one sets up the Hamiltonian, H .

$$H = \sum_{\underline{l}, \underline{b}} \frac{1}{2} \frac{\underline{P}_{\underline{l}, \underline{b}} \cdot \underline{P}_{\underline{l}, \underline{b}}}{m_{\underline{b}}} + V(\underline{R}_{\underline{l}, \underline{b}}). \quad (2)$$

The vector $\underline{l}$ points from some arbitrary lattice point, chosen as origin, to a lattice point of the unit cell labeled by $\underline{l}$. The vector $\underline{b}$ goes from the tip of $\underline{l}$ to the equilibrium position of an atom, within the l th cell, labeled by $\underline{b}$. $\underline{\eta}_{\underline{l}\underline{b}}$ is the displacement of the $\underline{l}\underline{b}$ th atom from its equilibrium position $\underline{l} + \underline{b}$. $\underline{P}_{\underline{l}\underline{b}}$ is the momentum of that atom and m_b its mass. $V(\underline{R}_{\underline{l}\underline{b}})$ is the potential energy of the atom at $\underline{R}_{\underline{l}\underline{b}} = \underline{l} + \underline{b} + \underline{\eta}_{\underline{l}\underline{b}}$ due to its interaction with all other atoms of the perfect crystal.

A power series expansion of $V(\underline{R}_{\underline{l}\underline{b}})$ in $\underline{\eta}_{\underline{l}\underline{b}}$ about $\underline{\eta}_{\underline{l}\underline{b}} = 0$ yields terms quadratic in the $\underline{\eta}_{\underline{l}\underline{b}}$'s and higher order terms. The constant term $V(\underline{l} + \underline{b})$ can be dropped because the potentials are arbitrary within a constant and $\left. \frac{\partial V}{\partial \underline{\eta}_{\underline{l}\underline{b}}} \right|_{\underline{R} = \underline{l} + \underline{b}} = 0$ for all $\underline{l}\underline{b}$ because the nominal sites are considered positions of equilibrium. One can then write

$$H_0 = \frac{1}{2} \sum_{\underline{l}\underline{b}} \frac{\underline{P}_{\underline{l}\underline{b}} \cdot \underline{P}_{\underline{l}\underline{b}}}{m_b} + \frac{1}{2} \sum_{\underline{l}\underline{b}} \sum_{\underline{l}'\underline{b}'} \underline{\eta}_{\underline{l}\underline{b}} \cdot \textcircled{G} \cdot \underline{\eta}_{\underline{l}'\underline{b}'} , \quad (3)$$

where $\textcircled{G}_{\underline{l}, \underline{b}, \underline{l}', \underline{b}'}$ symbolizes the interaction between atoms at $\underline{l} + \underline{b}$ and $\underline{l}' + \underline{b}'$. H_0 is the Hamiltonian for a crystal whose atoms are connected by Hook's law forces.

The Hamiltonian for crystals with defects is then

$$H_D = H_0 + H' + H'' . \quad (4)$$

H' is the part of the Hamiltonian containing the higher order, or anharmonic, terms. H'' contains momenta and potentials for the defects and any changes that occur in the perfect crystal due to the introduction of defects and the presence of boundaries.

At this point the methods for treating the problem are numerous. The most common approaches^{1*} consider the momentum and position variables as quantum mechanical operators obeying the relationship

$$\underline{n}_{\underline{l}\underline{b}} \cdot \underline{P}_{\underline{l}'\underline{b}'} - \underline{P}_{\underline{l}'\underline{b}'} \cdot \underline{n}_{\underline{l}\underline{b}} = 2\hbar \delta_{\underline{l}\underline{l}'} \delta_{\underline{b}\underline{b}'}, \quad (5)$$

thus, turning all functions in the Hamiltonian into operators.

The translational symmetry of the perfect crystal together with its finite dimensions permits one to write the wave function of the system as a finite sum of complex traveling waves. For a crystal composed of one type of atom,

$$\Psi_{\underline{l},t} = \left(\sum_{\underline{q}\lambda} A_{\underline{q}\lambda} e^{j(\omega_{\underline{q}\lambda}t + \underline{q} \cdot \underline{l})} \right). \quad (6)$$

Here $\underline{q}$ is the wave vector, λ , the polarization and $\omega_{\underline{q}\lambda}$, the frequency. One polarization is parallel to $\underline{q}$, the other two are perpendicular to $\underline{q}$ and to each other.

The physical interpretation of this is that $A_{\underline{q}\lambda}^* A_{\underline{q}\lambda}$ is proportional to the probability of finding a quantum of energy,

^{1*} For all numbered references, see Bibliography.

$\hbar \omega_{\underline{q}\lambda}$, in a unit volume of the crystal. Such a quantum of energy is called a phonon. The polarization along $\underline{q}$ corresponds to the classical idea of longitudinal waves; the polarizations perpendicular to $\underline{q}$ correspond to shear waves.

If there are more than one species of atom in the lattice, then there are other branches of higher energy, called optic branches, to the phonon spectrum. At low temperatures these will not be excited. Phonons obey Bose statistics.

Phonons as Carriers of Heat

If one wants to describe what is happening in a small region of space, one cannot use infinite wave trains, but forms wave packets from them. These will propagate with the group velocity

$$v_{\underline{q}\lambda} = \frac{\partial \omega_{\underline{q}\lambda}}{\partial \underline{q}\lambda} \quad \text{and will be localized at position } \underline{x}, \text{ have wave}$$

vector $\underline{q}$ and polarization λ . The term phonon will be used for such packets in subsequent discussions. The symbol $N_{\underline{q}\lambda}(\underline{x})$ will mean the number of such packets per unit volume averaged over a small volume centered at $\underline{x}$. The energy $\hbar \omega_{\underline{q}\lambda}$ is associated with each packet. The heat flux is then

$$\underline{F} = \sum_{\underline{q}\lambda} v_{\underline{q}\lambda} N_{\underline{q}\lambda} \hbar \omega_{\underline{q}\lambda} \quad (7)$$

The number of phonons in a region of space can change in two ways. They can drift in and out of that region or they can be created and destroyed due to sources of such packets. Collisions can be

interpreted in terms of sources where the incident phonons disappear and new phonons, with different wave vectors, are created. The net change is then

$$\frac{dN_{\underline{q}\lambda}}{dt} = \left. \frac{\partial N_{\underline{q}\lambda}}{\partial t} \right|_{\text{drift}} + \left. \frac{\partial N_{\underline{q}\lambda}}{\partial t} \right|_{\text{sources}} . \quad (8)$$

The drift term obeys the equation of continuity and so

$$\left. \frac{\partial N_{\underline{q}\lambda}}{\partial t} \right|_{\text{drift}} = - \underline{v}_{\underline{q}\lambda} \cdot \nabla N_{\underline{q}\lambda}(\underline{x}) . \quad (9)$$

If one had a perfect crystal with the atoms connected by Hook's law forces only, phonons created in one part of the crystal would move away from there with the speed of sound. In real crystals the other terms in the Hamiltonian, H' and H'' must be considered. H' gives rise to the interaction of phonons with each other and H'' accounts for the scattering of phonons from defects and boundaries. Both mechanisms impede the propagation of phonons. For the steady state $\frac{dN_{\underline{q}\lambda}}{dt} = 0$ so that

$$\underline{v}_{\underline{q}\lambda} \cdot \nabla T \frac{\partial N_{\underline{q}\lambda}}{\partial T} = \left. \frac{\partial N_{\underline{q}\lambda}}{\partial t} \right|_{\text{sources}} . \quad (10)$$

The source term is equal to the rate at which phonons of wave vector $\underline{q}$, and polarization λ are created minus the rate at which such phonons are destroyed. In general, this depends on the

populations of all the energy states and involves the quantum mechanical concept of transition probabilities.

For small temperature gradients, $N_{\underline{q}\lambda}(T(x))$ is not very different from the Planck distribution, $N_{\underline{q}\lambda}^0(T(x))$, characteristic of local equilibrium. One can write

$$N_{\underline{q}\lambda} = N_{\underline{q}\lambda}^0 + n_{\underline{q}\lambda} \quad (11)$$

The magnitude of $n_{\underline{q}\lambda}$ is determined by the temperature gradient which causes it. As the gradient vanishes, so does $n_{\underline{q}\lambda}$.

Approximate Solution of the Linearized Boltzmann Equation

The object is to get an expression for $n_{\underline{q}\lambda}$ which can be substituted into (7) which then becomes

$$\underline{F} = \sum_{\underline{q}\lambda} \underline{v}_{\underline{q}\lambda} \hbar \omega_{\underline{q}\lambda} n_{\underline{q}\lambda} \quad (12)$$

because

$$0 = \sum_{\underline{q}\lambda} \underline{v}_{\underline{q}\lambda} \hbar \omega_{\underline{q}\lambda} N_{\underline{q}\lambda}^0 \quad (13)$$

The introduction of relaxation times $\tau_{\underline{q}\lambda}$ leads to useful results. For the case of elastic scattering by imperfections and the boundaries (processes which tend to return the perturbed distribution to the Planck distribution), it is possible to define a relaxation time such that

$$\left. \frac{\partial N_{\underline{q}\lambda}}{\partial t} \right|_{\text{sources}} = - \frac{1}{\tau_{\underline{q}\lambda}} n_{\underline{q}\lambda} \quad (14)$$

This type of scattering does not mix modes. If there are different types of such imperfections, their effects of returning $N_{\underline{q}\lambda}$ toward $N_{\underline{q}\lambda}^0$ are additive and, therefore, the inverse relaxation times for the different scatterers are also additive. From subsequent discussion, it will become clear that these are important processes at low temperatures.

From Equations (10) and (14), one can eliminate $\left. \frac{\partial N_{\underline{q}\lambda}}{\partial T} \right|_{\text{sources}}$ and using (11), one gets

$$v_{\underline{q}\lambda} \cdot \nabla T \frac{\partial N_{\underline{q}\lambda}^0}{\partial T} + v_{\underline{q}\lambda} \cdot \nabla n_{\underline{q}\lambda} = - \frac{n_{\underline{q}\lambda}}{\tau_{\underline{q}\lambda}} \quad (15)$$

It can be shown² that $v_{\underline{q}\lambda} \cdot \nabla n_{\underline{q}\lambda}$ can be neglected compared to

$$\frac{n_{\underline{q}\lambda}}{\tau_{\underline{q}\lambda}} \quad \text{provided that } \nabla T \text{ varies slowly over the distance}$$

$v_{\underline{q}\lambda} \tau_{\underline{q}\lambda}$ - the average distanced traveled by the phonons before being scattered. If the temperature gradients are fairly constant, one can then write

$$\underline{v}_{\underline{q}\lambda} \cdot \nabla_T \frac{\partial N_{\underline{q}\lambda}^0}{\partial T} = - \frac{n_{\underline{q}\lambda}}{\tau_{\underline{q}\lambda}}, \quad (16)$$

and using this result together with

$$C_{\underline{q}\lambda} = \frac{\partial \hbar \omega_{\underline{q}\lambda} N_{\underline{q}\lambda}^0}{\partial T}, \quad (17)$$

and Equation (12) one gets

$$\underline{F} = - \sum_{\underline{q}\lambda} \underline{v}_{\underline{q}\lambda} \underline{v}_{\underline{q}\lambda} \cdot \nabla_T C_{\underline{q}\lambda} \tau_{\underline{q}\lambda}. \quad (18)$$

For isotropic media,

$$\underline{F} = - \sum_{\underline{q}\lambda} v_{\underline{q}\lambda}^2 C_{\underline{q}\lambda} \tau_{\underline{q}\lambda} |\nabla_T| \cos^2 \theta, \quad (19)$$

where θ is the angle between ∇_T and $\underline{v}_{\underline{q}\lambda}$.

A useful approximation is to handle the phonon spectrum the same way as Debye did. The optic modes are neglected and the velocity of sound taken as independent of frequency. For low temperatures, $T \ll \theta$, these are valid assumptions. The first Brillouin zone is taken as spherical. The thermal conductivity then is

$$K = \frac{1}{2\pi^2 v} \int_0^{\omega_D} T(\omega, T) \frac{(\hbar^2 \omega^4 / kT^2) e^{\hbar\omega/kT} d\omega}{(e^{\hbar\omega/kT} - 1)^2}.$$

The velocity, v , is an appropriate average of the longitudinal as well as transverse waves. In this work it will be computed from

$$\Theta/T = \hbar \omega_D/kT = \hbar v(6\pi^2 N)^{1/3}/kT, \quad (21)$$

where Θ is the Debye temperature as obtained from heat capacity measurements and N is the number of atoms per unit volume.

$\tau(\omega, T)$ is the relaxation time which characterizes the rate at which the equilibrium population for phonons of frequency ω is achieved.

Thermal Resistance due to Phonon-Phonon Interactions

The relaxation time can be understood in terms of the scattering of phonons. The thermal conductivity of crystalline, insulating solids increases as the temperature is lowered till a maximum is reached. (Representative approximate values are: 6°K for KCl, 10°K for NaCl, and 20°K for LiF.) As the temperature is lowered from room temperature, one might expect a decreasing thermal conductivity since there are so many high energy phonons to carry the heat at the higher temperatures. This does not happen, because the more phonons there are, the more they interact with each other (phonon-phonon scattering) and this gives rise to thermal resistance. The maximum in the thermal conductivity occurs because at the low temperatures boundary and defect scattering become more important than phonon-phonon scattering in decreasing the thermal conductivity.

The most common interactions between phonons are three phonon processes, two phonons combining to form a third and vice versa. Energy in such processes must be conserved,

$$\hbar \omega_{\underline{q}} \lambda_1 + \hbar \omega_{\underline{q}} \lambda_2 = \hbar \omega_{\underline{q}} \lambda_3, \quad (22)$$

but the momentum of the phonons, $\hbar \underline{q}$, need not be conserved.

Instead,

$$\underline{q}_1 + \underline{q}_2 = \underline{q}_3 + 2\pi \underline{g}, \quad (23)$$

where $\underline{q}_1$ and $\underline{q}_2$ are the wave vectors of the interacting phonons, $\underline{q}_3$ is the resulting phonon and $\underline{g}$ is a reciprocal lattice vector. The momentum conserving interactions, $\underline{g} = 0$, are called normal processes; those where the momentum is not conserved are called umklapp processes. As a consequence of the above conditions, all three phonons cannot have the same polarization.

Further analysis shows that the energy flux due to phonons undergoing normal processes is the same before and after interaction, but that the flux is decreased by phonons participating in umklapp processes. In general, this does not allow us to dismiss the normal processes because they tend to force the distribution of phonons toward that characteristic of a drifting gas whereas the umklapp processes, like the scattering from boundaries and defects, tend to return the system to local equilibrium. The normal processes, therefore, effect the frequency of occurrence of the other processes.

Carruthers³ and Callaway^{4, 5} have examined this question, and they have suggested corrections to Equation (20). Callaway found, that in addition to including the relaxation time for umklapp processes in (20), one had an additional term. Walker⁶ estimated this additional term to be of the order of 20% for pure KCl, KBr, and KI — presumably near the conductivity maximum above which phonon-phonon interactions determine the thermal conductivity since he was trying to fit data between 1°K and 100°K. It goes to zero as the relaxation times characterizing the normal processes become large. Klemens⁷ reviews the estimates of these relaxation times. They all increase rapidly as one goes to lower temperatures, therefore, it seems proper to neglect Callaway's additional term below 4°K for the alkali halides mentioned above. The umklapp processes have relaxation times which increase as $e(\theta / \alpha T)$ where θ is the Debye temperature and α is of order unit. This term is also negligible below 4°K.

Boundary Resistance

At low temperatures, the effect of the surface becomes important in decreasing the thermal conductivity. If the boundary were perfect, the heat flow would be unimpeded since specular reflection is a normal process. The fact that real crystal surfaces are not perfect gives rise to partially diffuse reflection. The crystal surfaces are, therefore, roughened to eliminate or greatly reduce specular reflection. The relaxation times for boundary scattering, τ_b , was worked out by Casimir⁸ as d/v for a cylinder of diameter d and as $1.12 d/v$ for a square cross section of side d .

A general equation for partially diffuse reflection was given by Ziman⁹ who finds that the relaxation time for boundary scattering is still frequency independent.

Point Defects

Defects of crystals have a pronounced effect on the thermal conductivity. Of the many types of defects, only point defects and aggregates will be considered here. Point defects are isolated imperfections of atomic dimensions. Examples are isotopes, interstitials, chemical impurities, vacancies and F centers.

Klemens⁷ predicted that for impurities substituted into the lattice

$$\tau_p^{-1} = \frac{\omega_a^4}{4\pi v^3} \sum_i f_i \left(\frac{\Delta M_i}{M} - \sqrt{2} \frac{\Delta G_i}{G} \right)^2 = X_2 \omega^4. \quad (24)$$

Here ΔM_i represents the difference between the mass of an atom of the i 'th species and an atom of the lattice. ΔG_i is the corresponding difference between the elastic constants. The fraction of sites occupied by species i is f_i . a is the effective radius of the impurity atom. The formula is valid for $\omega \ll v/a$ and because a is less than the shortest permissible wavelength, it should be good for most of the phonon spectrum.

The total inverse relaxation time is then given by

$$\tau^{-1} = X_1 + X_2 \omega^4, \quad (25)$$

where X_1 represents the boundary scattering and $X_2 \omega^4$ that of the point defects. Figure 1 shows the effect on the thermal conductivity of varying X_2 over several orders of magnitude in the range of values encountered for real crystals. X_1 is kept fixed and is characteristic of a pure KCl crystal $1/8'' \times 1/8''$ as measured.

Experiments on crystals containing varying concentrations of Li^7 in Li^6 were done by Thacher^{5,10} as well as by Berman¹¹ and Brock. Their results are shown in Figure 2. At low temperatures where phonon-phonon interactions can be neglected, a relaxation time as given in Equation (25), can be used to fit the data.

Another effort to demonstrate the effect of point defects on the thermal conductivity was to use irradiated crystals.^{6,12,13} It was not possible to fit the data between 1°K and 4°K with an ω^4 term alone but Walker⁶ had to use an additional term in the inverse relaxation time proportional to ω . Further, to fit the data above 4°K, near the conductivity maximum, a resonance term had to be included in τ^{-1} . The explanation of this term involves the concept of quasi-localized modes of the lattice.

Other investigators^{14,15,16,17,18,19,20,21,22,23,24} have added chemical impurities to alkali halide crystals, and often rather complex dips were observed in the K versus T curves. Fitting the data involves the use of resonance terms in τ^{-1} .

At temperatures below the thermal conductivity maximum, the explanations of these dips involve the assumption of motional states for the impurities. For example, the CN^- substituted into KCl has the degrees of freedom of a rotating top.^{25,26,27}

Figure 1. Calculated values of K versus T for various values of X_2 with $X_1 = 1.85 \times 10^6 \text{ sec}^{-1}$ and $X_3 = a = g = 0$.

Figure 2. The thermal conductivity of LiF with different concentrations of ${}^7\text{Li}$ as obtained by Berman and Brock compared to Thacher's data.

Dips at the higher temperatures, at the conductivity maximum or above, are ascribed to so-called quasi-localized modes.¹¹ These modes are understood from a detailed solution of the Hamiltonian including the defect term.^{28, 29, 30, 31, 32, 33, 34, 35, 36, 27} For a single substituted atom of mass and coupling constants differing from those of the lattice, there are two changes in the acoustic spectrum. One is that the energy levels of the perfect lattice are changed slightly; the other is that new modes of frequency ω_0 , localized around the defect, are predicted. The first effect does not influence the observed thermal properties. The second, on the other hand, depresses the thermal conductivity at temperatures where phonons of frequency ω_0 are the dominant carriers of heat. The expressions obtained for the relaxation times¹⁴ all have the same general form which is

$$\tau_p^{-1} = \frac{A\omega^4}{(\omega_0^2 - \omega^2)^2 + \Gamma\omega^6} \quad (26)$$

Defects which produce local modes or have motional states enhance the heat capacity at the same temperatures where the thermal conductivity is most effected.

Experiments to Study the Effects of Colloids

The effect of colloids on the thermal conductivity has been studied in some detail by Worlock, who also gives a review of such work.^{38, 39} He has measured the thermal conductivity of NaCl

with different concentrations of AgCl in solid solution in the temperature range between 1°K and 100°K. Figure 3 shows his results. The curves show a scattering characteristic of point defects with an inverse relaxation time proportional to ω^4 . Next he formed silver colloids in NaCl and found that instead of the above behavior the curves of $\log K$ versus $\log T$ are shifted parallel to each other at the low temperature end. This is shown in Figure 4. He explains this by saying that at wavelengths small compared to the size of the defect, one expects a cross section for phonon scattering which is independent of frequency (geometrical cross section). At low temperatures, a greater fraction of the thermally excited phonons have long wavelengths such that the above behavior must change. In the limit of wavelengths larger than the scatterers, Rayleigh scattering is expected. At some low temperatures, the thermal conductivity of the crystal containing colloids should approach that for the pure crystal. Walton⁴⁰ extended Worlock's measurements to 0.2°K and found that there was, indeed, a change of slope as suggested by the above arguments.

Theories to Understand the Effects of Colloids

To study how phonons are scattered by colloids, one can approach the problem by studying elastic waves in isotropic media and their scattering from spheres of different materials. This approach is outlined in numerous textbooks.⁴¹

One must solve the equation

$$\rho \frac{\partial^2 \underline{s}}{\partial t^2} = \nabla \cdot \underline{\underline{\sigma}} \quad (27)$$

Figure 3. Thermal conductivity of NaCl containing AgCl in solid solution. The solid lines were calculated using various X_2 's in Equation (24). The figure is from Warlock's thesis.

Figure 4. Thermal conductivity of NaCl containing colloidal particles of silver (Warlock).

where $\underline{S}$ is the displacement from equilibrium of a small portion of the material and $\odot$ is a diad whose components are the stresses. For isotropic elastic media, the stresses can be written in terms of the strains ϵ_{ij} as

$$\sigma_{ij} = 2\mu \epsilon_{ij} + \lambda \delta_{ij} (\epsilon_{11} + \epsilon_{22} + \epsilon_{33}). \quad (28)$$

$2\epsilon_{ij} = \left(\nabla \underline{S} \right)_{ij} + \left(\nabla \underline{S} \right)_{ji}$, μ and λ are known as Lamé's moduli. Equation (27) can then be written as

$$\left(\lambda + \mu \right) \nabla \left(\nabla \cdot \underline{S} \right) + \mu \nabla^2 \underline{S} = \rho \frac{\partial^2 \underline{S}}{\partial t^2}. \quad (29)$$

Using $\underline{S} = \underline{s} \exp j\omega t$, Equation (29) becomes

$$\frac{1}{k^2} \nabla \left(\nabla \cdot \underline{s} \right) + \frac{1}{K^2} \left[\nabla^2 \underline{s} - \nabla \left(\nabla \cdot \underline{s} \right) \right] + \underline{s} = 0 \quad (30)$$

where

$$k = \omega \left[(\lambda + 2\mu) / \rho \right]^{-1/2} \quad (31)$$

and

$$K = \omega \left[\frac{\mu}{\rho} \right]^{-1/2}. \quad (32)$$

ρ is the density of the medium.

$\underline{s}$ can then be broken into $\underline{s}'$ and $\underline{s}''$ such that

$$\underline{s} = \underline{s}' + \underline{s}'' , \quad (33)$$

$$\nabla \times \underline{s}' = 0 , \quad (34)$$

and

$$\nabla \cdot \underline{s}'' = 0 .$$

This splits (30) into two equations:

$$\nabla^2 \underline{s}' + k^2 \underline{s}' = 0 \quad (36)$$

and

$$\nabla^2 \underline{s}'' + K^2 \underline{s}'' = 0 . \quad (37)$$

The first, the curl free part of $\underline{s}$, represents longitudinal waves and k is the magnitude of the wave vector; the second, the divergence free part of $\underline{s}$, represents transverse waves with K the wave vector for transverse waves.

Incoming plane waves, transverse or longitudinal, are scattered to give rise to radial waves, both transverse and longitudinal.

This problem was first treated by Lord Rayleigh who studied the scattering of sound from dust particles in gases. Much subsequent work has taken place. Particularly pertinent is the work of Truell^{42, 43} and associates, and of Pao and Mao.⁴⁴ These papers deal with the calculation of cross sections for the scattering of

energy by spheres in homogeneous, isotropic, elastic media. The solutions for cavities, fluid spheres, hard spheres and elastic spheres are given. For most cases, the limiting forms of these expressions at $\left. \begin{matrix} ka \\ Ka \end{matrix} \right\} \ll 1$ (Rayleigh scattering) and for $\left. \begin{matrix} ka \\ Ka \end{matrix} \right\} \gg 1$ (geometrical scattering) are given. In general, the solutions are infinite sums of terms involving special functions.

In thermal conductivity, in order to get relaxation times, one needs the transport cross section given by

$$\sigma_T = 2\pi \int_0^\pi \sigma(\theta) [1 - \cos \theta] d\theta, \quad (38)$$

instead of the total cross section

$$\sigma = 2\pi \int_0^\pi \sigma(\theta) \sin \theta d\theta \quad (39)$$

as given by Truell^{42, 43} and associates. This is so because waves that are scattered still contribute to the heat current in proportion to the component of velocity in the direction of the thermal gradient. $\sigma(\theta)$ is the differential cross section.

Values of Cross Sections in the Rayleigh Limit

Since transport cross sections and total cross sections are identical for wavelengths much greater than the radii of the inclusions, that is, when $\left. \begin{matrix} Ka \\ ka \end{matrix} \right\} \ll 1$, the results, as obtained by Truell and associates are pertinent. The cross sections for elastic inclusions are:

A. For Longitudinal Waves⁴³

$$\sigma = \frac{4}{9} \pi k_1^4 a^6 g_e \quad (40)$$

$$g_e = \left\{ \frac{3(K_1/k_1)^2}{[3(K_2/k_2)^2 - 4] \mu_2/\mu_1 + 4} - 1 \right\}^2$$

$$+ \frac{1}{3} \left[1 + 2(K_1/k_1)^3 \right] \left[(K_2/K_1)^2 (\mu_2/\mu_1) - 1 \right]^2$$

$$+ 40 \left[2 + 3(K_1/k_1)^5 \right] \times$$

$$\left\{ \frac{\mu_2/\mu_1 - 1}{2 \left[3(K_1/k_1)^2 + 2 \right] (\mu_2/\mu_1) + 9(K_1/k_1)^2 - 4} \right\}^2$$

(41)

B. For Transverse Waves⁴²

$$\sigma = \frac{8}{3} \pi a^6 \left[1 + \frac{1}{2} \left(\frac{k_1}{K_1} \right)^3 \right] K_1^4 \quad (42)$$

$$\left[\frac{3 \left(\frac{K_1}{K_2} \right)^2 - 3 \left(\frac{K_2}{K_1} \right)^2 - 4 \frac{k_2^2 K_1^2}{K_2^4} + 10 \frac{k_2^2}{K_2^2} - 6 \frac{k_2^2}{K_1^2}}{\left[1 - 10 \frac{K_1}{k_1} + 6 \frac{k_2}{k_1} - 6 \frac{k_2}{k_1} \frac{K_2^2}{K_1^2} + 9 \frac{K_2^2}{K_1^2} \right]^2} \right]$$

The subscript 1 refers to the matrix and the subscript 2 refers to the scatterer.

Other results in the literature,⁴⁶ of a more approximate nature are:

$$\sigma = \frac{4\pi}{9} a^6 k^4 \left\{ \left| \frac{\partial G}{G} \right|^2 + \frac{1}{3} \left| \frac{\delta \rho}{\rho} \right|^2 \right\} \quad (43)$$

for longitudinal waves, and a result for the combined effects of transverse and longitudinal waves,⁴⁷ for hard spheres,

$$\sigma = \frac{4}{9} \pi a^6 k^4 \left| \frac{\delta \rho}{\rho} \right|^2. \quad (44)$$

Here, $\delta \rho = \rho_2 - \rho_1$ and $\delta G = G_2 - G_1$. G is the modulus of rigidity. In these equations a is the radius of the inclusions.

The Cross Section in General

Walton and Lee⁴⁵ have investigated transport cross sections for the scattering of longitudinal waves in order to approximate them with simpler functions. Since the differential cross section often oscillates quite wildly, one has to be particularly careful in generalizing the low and high frequency approximations for the cross sections. They consider strong and weak scattering separately. Strong scattering occurs when the properties of the inclusion are considerably different from those of the matrix; weak scattering when they are fairly similar.

A. Strong Scattering

At high frequencies, the cross section approaches πa^2 . To fit the low frequency part, one can use Ludwig's⁴⁸ expression for the total cross section — at those frequencies it is equal to the transport cross section.

$$\sigma = 2V_o \epsilon \gamma \left(\frac{\omega}{\omega_R} \right)^4 \frac{k}{\omega} (1 + F_R)^2$$

$$V_o = \frac{4}{3} \pi a^3, \quad \epsilon = \frac{\delta \rho}{\rho}, \quad \omega_R^2 = \frac{6\omega^2}{\epsilon a^2} (2K^2 + k^2)^{-1},$$

$$\gamma = \frac{2\omega}{\epsilon a} (2K^3 + k^3) (2K^2 + k^2)^{-2},$$

$$F_R = \omega^2 / \omega_R^2 - \omega^2 - j 2 \gamma \omega^3 / \omega^2.$$

(45)

This expression permits one to take into account the first resonance of the differential cross section. Walton and Lee find that this nicely reproduces the hump which they find in their total cross section.

B. Weak Scattering

For weak scattering, the hump in the transport cross section disappears. At low frequencies, Equation (40) is a good approximation. At higher frequencies, the equation

$$\sigma_T = \pi a^2 \left\{ \left| \frac{\delta \rho}{\rho} - \frac{\delta k}{k_1} \right| + \left| \frac{\delta \rho}{\rho} - \frac{\delta \mu}{\mu} \right|^2 \right\} \quad (46)$$

with

$$\delta \rho = \rho_2 - \rho_1 \quad \text{and} \quad \delta k = k_2 - k_1 ,$$

is given by Walton and Lee.⁴⁵ No expression for the total cross section for the scattering of transverse waves is available.

The effect on the thermal conductivity of spherical inclusions has also been discussed by Walker⁴⁹ and associates.

II. Discussion of the Effects of Radiation on Alkali Halides

The most striking visual effect of radiation on alkali halide crystals is the change of color it produces. Absorption spectroscopy has been widely used to study this. The absorption bands are assumed to be due to defects in the crystal called color centers. In many cases it has been possible to identify the type of defect responsible for certain bands. The growth of these bands is dependent on total dose, intensity of radiation, and temperature during irradiation and measurement. Also, the presence of some impurities enhances the growth rate, during irradiation, of bands present in the pure crystal as well as causing new bands. Illumination of colored crystals by light of selected frequencies causes profound changes in the absorption spectra. Among the physical properties effected by radiation are hardness, as studied by flow stress measurements, and the thermal conductivity.

Changes in physical properties are often considered in conjunction with changes in the absorption spectra in order to see

whether the center can be associated with such changes. The author will not attempt to give a detailed account of all the facets of this subject but will concentrate on those features which will serve as background for the understanding of this work. The best supplement to this section is Compton and Schulmann's⁵⁰ book on color centers.

A. Color Centers

Some color centers are effectively studied through their optical spectra and paramagnetic resonance. Other centers are not very well understood. The absorption peaks for KCl are given in Table I, together with the temperatures at which they were measured.

The Negative Ion Vacancies

Most researchers now agree that negative ion vacancies and interstitial halides are the chief products of irradiation. Positive ion vacancies have been pretty well ruled out. The F, F', M and R bands are attributed to centers designated as such. The F center is an electron trapped by a negative ion vacancy. The M center is two adjacent F centers and the R centers are higher aggregates of F centers. The F' center is an extra electron trapped by an F center and is not important in irradiated samples that have been kept in the dark. The K band, a hump on the short wave length side of the F band, has been studied by Luty.⁵¹ He attributes it to the F center and suggests that the F and K bands are due to transitions of the trapped electron to higher bound states and that

Table I. Color Centers in KCl.

Center	Temperature of Observation (°K)	Wavelength [m μ]
L ₃	93	251
L ₂	93	288
L ₁	93	344
K	93	457
F	300	556
F'	170	750
R ₁	300	658
R ₂	300	727
M	300	825
α	~ 90	177
β	~ 90	166
H	4	335
V ₁	77	356
V _K	77	365
V ₂	300	230
V ₃	300	212
V ₄	90	~ 254

the L bands are transitions of the F center to free unbound states.

The β band is present in alkali halide crystals containing F centers. It is observed at long wavelengths near the absorption edge of the crystal and is attributed⁵⁴ to the perturbations of the lattice by the F centers. Illuminating a colored crystal with F light at nitrogen temperatures bleaches the β as well as the F bands and the α band is formed. The α band is attributed⁵⁴ to perturbations of the lattice by negative ion vacancies. Warming to room temperature restores the β and F bands to their original intensity and the α band disappears.

All of the centers discussed can also be formed by coloring the crystal in alkali vapor.

Trapped Hole Centers

If one asks what happens to the halide ions when negative ion vacancies are formed, one has many possible answers. A trapped electron center may be formed in which case a halide ion must lose its electron, thus becoming an atom. This atom can leave the crystal, stay in an interstitial position or combine with other halides to form new entities. On the other hand, if a chlorine ion retains its electron after the vacancy is formed, the ion might remain in an interstitial position, form new entities by combining with other atoms or move to the surface of the crystal.

Depending upon the temperature of irradiation, different bands appear in the absorption spectra at wavelengths shorter than the F band. Most of these have been labeled as V bands.

The V bands were first observed by Mollwo⁵² in alkali crystals containing a stoichiometric excess of the halide. These were prepared by heating the crystals in the presence of more than 50 atmospheres of the halogen gas to slightly below the melting point and then rapidly cooling them. The bands he saw were the V_2 and V_3 bands.

These bands are also observed in crystals irradiated at room temperature or at low temperatures with subsequent measurement room temperature. Lütty⁵³ has been able to show that the V_3 bands are due to $(OH)^-$ impurities. The origin of the V_2 band is not clear but seems to grow and bleach with the F center.

The H band appears if the irradiation is performed at liquid helium temperatures and if the sample is measured at that temperature without warm up. The H center was studied by paramagnetic resonance,⁵⁵ and due to its symmetry and hyperfine structure, it could be identified as a molecular halogen ion, X_2^- , at a single halide ion site with orientation along the $\langle 110 \rangle$ direction. If the temperature is raised to 55°K this band disappears and the V_1 band is formed together with partial bleaching of the F band. Also, there is an increase of absorption near the V_2 - V_4 bands.

Irradiation at nitrogen temperatures produces the V_1 band and small unresolved absorptions attributed to V_2 and V_4 bands. In impure crystals large V_k bands are formed. Warming to room temperature destroys all but the V_2 band in KCl.

B. Some Other Properties of γ -Irradiated Alkali Halides

Hardness

Radiation hardening in eleven alkali halides was studied by Nadeau^{56, 57} through flow-stress measurements. These are made by measuring the stress necessary to compress a crystal at a steady rate. As the crystal flows, a large number of dislocations are introduced and forced through it. Lattice defects, through the strain fields associated with them, impede the motion of the dislocations through the crystal and thus increase the flow-stress needed to maintain the motion.

For γ -irradiated samples, he found that the increase in flow-stress is proportional to the square root of the F center concentration and that it does not depend on the size of the V_3 bands. From studies on additively colored KCl, he found that the flow-stress is not very dependent on the F center concentration. In both cases the concentration of F centers was varied by illuminating the sample with a sodium vapor lamp. He concluded that the hardening of irradiated crystals is not due to the F centers themselves but is due to the interstitial halides which are created with the F centers but do not manifest themselves optically or in ESR measurements.

Sonder, Sibley, Rowe and Nelson⁵⁸ measured, at room temperature, the flow-stress of KCl crystals irradiated at low temperatures. Their results are shown in Figure 5. For samples irradiated at about 300°K, 196°K and 147°K, they found an F center

Figure 5. Increase in flow stress plotted versus the square root of the F center concentration for KCl irradiated at various temperatures with 1.5 MeV electrons (Sonder, Sibley, Rowe, and Nelson).

dependence much like that observed by Nadeau. Samples irradiated at 80°K showed a considerable decrease in the flow-stress for a given F center concentration.

Bleach Rates

The rate at which color centers disappear as they are illuminated with light depends on the temperatures at which the radiation damage occurred. Results by Sonder and associates⁵⁸ are shown in Figure 6. The figure shows the total area of bands between 350 and 1400 nm divided by the area of the initial F band as a function of illumination time for different irradiation temperatures. One sees that the lower the temperature of irradiation, the greater the bleach rate. The bleaching was done at room temperature with white light and in conjunction with the flow-stress measurements.

III. Motivation of Present Work

To explain some of the observations described in the preceding section, Sonder proposed that intense irradiation of alkali halides produces aggregates of interstitial halides. Because the low temperature thermal conductivity is sensitive to the presence of large defects, such experiments were undertaken by Walton⁵⁹ as well as the author. In the remainder of this chapter the model proposed by Sonder and the work of Walton will be discussed.

Sonder's Model⁵⁸

From the change in slope of the curves in Figure 6, relating flow-stress to F center concentration, it appears that crystals at

Figure 6. Decrease of total area of absorption bands between 350 and 1400 nm due to bleaching with white light for KCl irradiated at different temperatures with 1.5 MeV electrons (Sonder, Sibley, Rowe, and Nelson).

room temperature contain a different species of interstitial if they were irradiated at 80°K than if the irradiation took place at 150°K or above.

From the optical bleaching, where the recombination of vacancy and interstitial centers depends upon radiation temperature above, as well as below, 150°K it appears that there is a continuous change in the structure of the defects over the whole temperature range. This must involve the interstitials because the F centers do not change their structure.

Analysis of the absorption bands in the V_2 - V_3 region shows a systematic shift of the principal absorption peak to longer wavelengths for lower irradiation temperatures. Sonder suggests that the broadness of the bands is due to absorption by many clusters of different size. He explains the shift in the position of the absorption peak by assuming that the distribution of clusters changes toward a larger average cluster size for the samples irradiated at higher temperatures. This interpretation is consistent with the bleach rate. However, the interpretation of the flow-stress results in terms of clusters leads to the opposite result. Elasticity theory predicts that the size of the cluster is not very important in impeding the passage of dislocations and that the resistance is due mostly to strains. If this is true, then there must be more defects produced at the higher irradiation temperatures, or those produced have a larger strain field. If more clusters are produced for a given F center concentration, then they must be smaller provided that the number of halogen interstitials is the same. Sonder suggests that the theory does not adequately describe large defects.

The bleaching rate is faster for impure samples. This might be explained by the fact that impurities serve as nucleation points for clustering causing more and smaller clusters to be formed. Bleach rate and cluster size may be related by considering that the larger the clusters, the fewer there are and the greater is the average distance between them and the electron centers which are thought to be uniformly distributed. As bleaching is the combination of the electron centers and the material making up the clusters, the bleaching rate will be smaller when the distance is greater between these entities.

Walton's⁵⁹ Work on Irradiated KCl

Figure 7 shows a graph of K as a function of T for two KCl crystals as measured by Walton. One crystal was irradiated at liquid nitrogen temperature until it contained 6×10^{18} F centers/cm³. The upper curve shows its thermal conductivity. The other crystal was irradiated at room temperature to a F center concentration of 3×10^{18} F centers/cm³. The lower curve shows its thermal conductivity.

Sonder and Walton⁵⁹ conclude that the shape of the curves is characteristic of aggregates and give a size of about $70 \text{ \AA}$ for the room temperature irradiated sample. The size of the clusters in the other crystal is smaller.

Figure 7. Thermal conductivity of γ -irradiated KCl crystals as measured by Sonder and Walton.

CHAPTER II EXPERIMENTAL

In this chapter the low temperature apparatus, as well as procedures for its operation, calculation of thermal conductivities from data, methods for irradiation and handling of samples and absorption spectroscopy, are discussed.

I. The He^3 Refrigerator

In order to conduct measurements of thermodynamic properties at low temperatures, one must, of course, achieve those temperatures. Down to 80°K , liquid nitrogen is used; to get to 4.2°K , one needs liquid helium. By controlled pumping on the helium, any temperature between 4.2°K and 1°K can be reached and maintained.

To get to lower temperatures, one needs an additional coolant. Liquid He^3 is a substance which can be used for this. The gaseous He^3 is condensed into a chamber, which will be referred to as the He^3 cryostat and the He^4 bath absorbs the latent heat. By pumping on the liquid He^3 , temperatures down to 0.3°K can be reached if the system is thermally isolated from the He^4 bath. Therefore, it is necessary to provide thermal switching with the bath. This is done, as in Figure 8, by suspending the He^3 cryostat from thin-walled stainless steel tubes inside a chamber into which one can put a few torr of He^4 gas for thermal contact.

Figure 8. He³ refrigerator system.

The contact can be broken by evacuating the chamber. The gas used in this way is called exchange gas; the container is called the exchange gas can.

One more feature is needed. After the He^3 cryostat is thermally isolated, the vapor pressure of the He^4 bath can no longer be used to calibrate secondary thermometers and one has to use the vapor pressure of He^3 .⁶⁰ A small vessel, again, see Figure 8, in thermal contact with the He^3 cryostat and containing a drop of liquid He^3 serves as a vapor pressure thermometer bulb. It communicates via a long tube with a manometer at room temperature. This vapor pressure thermometer is fairly reliable down to about 0.55°K . To measure temperatures below this, large corrections have to be made. These corrections, due to the thermomolecular pressure difference,⁶¹ become exceedingly large below 0.55°K . Therefore, the vapor pressure thermometer was calibrated against the susceptibility of cerium magnesium nitrate — a paramagnetic salt. The details of this will be discussed later.

A. The Cryostat

General Description of the Cryostat

Figure 8 shows a schematic of the refrigerator. The glass dewar in the center contains the low temperature part of the apparatus. The dewar holds the liquid helium which surrounds the outer can. Inside the outer can is an inner can consisting of the He^3 cryostat, the vapor pressure bulb and the sample space.

Brass was used as much as possible. Where a high thermal conductivity is needed, copper (shown cross-hatched in Figure 9) was used.

On top of the dewar is a large tee equipped with flanges. A brass plate is fastened with screws to the top of the tee compressing an O-ring into a groove in the flange. Through the plate pass the pumping tubes which support the low temperature part of the apparatus, as well as a short tube, closed with a rubber stopper, for adding liquid helium. Above the plate the pumping tubes can be interrupted by disconnecting O-ring couplings, and electrical connections are made using vacuum feed-through multiple headers. The plate, the tubes and the cans form a unit, called the cryostat, which can be removed by lifting it.

The dewar, a combination liquid nitrogen and liquid helium vessel, is fastened to the flange at the bottom of the tee. It rests in a cradle and can be lowered into a hole in the floor making it possible to work on the cryostat without removing it.

The tubes below the top plate are of 0.010" wall thickness stainless steel. The one for pumping on the outer can has an O. D. of 0.75" and reduces to 0.25" just before entering the outer can where it terminates. Going to the He^3 cryostat, the pumping tube has an O. D. of 0.75" reducing to 0.375" above the outer can. The tube for pumping on the sample space has an O. D. of 0.5" and narrows to 0.25" above the outer can. A 0.125" tube goes to the vapor pressure thermometer. All tubes have bends in them to keep

Figure 9. Detailed drawing of cryostat for thermal conductivity measurements.

room temperature radiation from reaching the experimental chambers. Inside the outer can, the tubes going to the vapor pressure bulb and sample space are of 0.125" diameter, whereas the one going to the He³ cryostat contracts to 0.250". To minimize the heat flow along these tubes, the wall thickness is only 0.006".

Sealing the Cans

A large number of screws are used (18 for the inner and 24 for the outer) to fasten the cans to their tops and to crush a 0.033" indium wire between the special profiles of the mating parts to form a vacuum seal (see Figure 9). The can has a lip on its flange like a conventional O-ring connection. Before assembly, the wire is placed along the edge of the can's lip. The ends of the wire are permitted to cross each other before being cut off. Care must be taken not to get the ends caught in the screws when the cans are mounted.

The reliability of the seal depends on the condition of the surface of the mating flanges. Tinning these parts with indium made the seal almost 100% reliable. Cycling between room and low temperatures has little influence on the seal. A mass spectrometer leak detector did not respond when the sealed outer can was immersed in super fluid liquid He⁴.

Electrical Leads

Another difficulty when building equipment of this sort is to bring the wires needed for electrical measurements from room temperature and atmospheric pressure to the sample. At room

temperature it is easy to get leads into a vacuum system. Two 14 prong kovar seals are used to take them into the pumping tube for the outer can. Passing the wires down this tube, one ends up in the outer can.

In the pumping tube the wires are grouped into two bundles which are covered with nylon stocking material and G. E. 7031 cement. As they enter the outer can, they are wrapped around a copper post assuring contact with the He^4 bath.

From there 18 wires go into the inner can. The heat flow from outer to inner can is made small by using gauge 40 manganin wires and letting them spiral so that 3" lengths are needed to traverse the distance between the two cans.

To get the wires into the inner can, a copper sleeve is soldered into the top of this can and the wires are passed through it. A special organic substance of jelly-like consistency was used as cement. It is made by dissolving 10 gm of Estane 5702 in 50 gm of acetone together with 56 gm of methylene chloride. Estane 5702 is a thermal plastic urethane commercially available from B. F. Goodrich Chemical Company. The recipe for the sealant and initial samples were given to the author by J. Hughes.⁶² After twenty-four hours, the cement sets into a tough rubbery material with a vapor pressure low enough so that a good vacuum, order of 10^{-5} torr, can be pumped at room temperature. The seal is helium leak tight and has been in operation for two years without repairs, having withstood at least fifty cyclings to nitrogen temperatures and

and over twenty to liquid He^4 temperatures. As the sealing compound is soluble in acetone, it is easy to make repairs or alterations.

B. Vacuum Components at Room Temperature

Figure 8 shows a schematic of the vacuum system. The valves are numbered and identified as to type and make by the code explained on the drawing. The tubing is all of copper with frequent O-ring flanges to facilitate cleaning and alterations. According to function, the system can be divided into three interconnecting parts. The figure is drawn to show this.

Vacuum and Exchange Gas System

The components on the right of the cryostat are for evacuating any part of the system, except the dewar, by means of a diffusion pump backed by a forepump. Pumping tubes leading to the inner and the outer can each have a Pirani, as well as a cold cathode gauge in them before they enter the cryostat. One can thus read pressure from 10^{-7} to 200 torr in these two systems. He^4 gas can be supplied to the inner and outer can as exchange gas and for leak checking.

The He^3 System

The left side of Figure 8 shows the He^3 system. The valving makes it possible to charge the He^3 cryostat and to pump on it when needed, to fill the vapor pressure bulb and to connect it to the high pressure side of a gauge for vapor pressure measurements.

For pumping on the He^3 cryostat, there is a diffusion pump backed by a forepump (Welch 1402 K) which is sealed at the output end so that the He^3 is returned to its reservoir. The three valves in parallel, KG-13, HN-11, and VN-12 serve to regulate the pumping.

For vapor pressure measurements, a capacitance manometer was used in the first few experiments. It was replaced with a Texas Instrument Precision Pressure Gauge Model 145 containing a Bourdon tube which is coupled optically to a servo mechanism giving a digital readout of the pressure. Pressures from 0.001 torr to 760 torr can be read with a precision of 0.001 torr. During operation the vacuum pumps on the right are used to back the gauge.

To connect the He^3 system with the vacuum and exchange gas system or the leak detector, valves VS-42 and VIC-41 have to be opened. These two valves are in series so that if one of them leaks slightly, the He^3 would still be contained and contaminants on the other side are not permitted to pass. The wiring to the solenoid valve VS-42 is arranged in such a way that it cannot be opened without VS-21 being closed. This is to ensure that one cannot pump off the He^3 in the reservoir by accident.

The dial gauge near the reservoir helps to monitor the pressure there. It is useful in determining how much He^3 remains condensed in the cryostat and for observing the possibility of large leaks in the system due to some possible malfunctioning of the seals in the mechanical pump.

2

To check the condition of the vacuum in the vapor pressure bulb and the He^3 cryostat, the lines leading to them each have a Pirani gauge.

Pumping on the He^4 Bath

Pumping on the He^4 bath is done by a Stokes mechanical pump, capable of $140 \text{ ft}^3/\text{min.}$ displacement, via a 3" pumping line. Figure 10 shows the He^4 system. The He^4 pressure is measured with an aneroid manometer and a McLeod gauge which are connected at the tee above the dewar. A large gate valve and two smaller valves in parallel with it control the pumping. For automatic control⁶³ a manostat is used. In this device one pumps through a cylindrical, flexible rubber membrane 1-1/2" in diameter and 2-1/2" long. It expands or collapses depending on the pressure difference between the inside and the outside of the membrane. The space on the outside of the membrane is connected to a volume (100 lt) which is large compared to the volume of the space inside the membrane. The pressure on the outside of the membrane is set at a desired value and is called the reference pressure. The pumping then adjusts itself so that the pressure inside the membrane is slightly less than the reference pressure. The pressure equilibrium is reached in a few minutes above the λ -point and the pressure can be held steady within a torr for an hour. Below the λ -point the pressure of the bath settles at a few torr below the set reference pressure. An aneroid manometer as well as a McLeod gauge are used to measure the vapor pressure of the liquid He^4 .

Figure 10. He⁴ pumping system showing schematic of manostat.

Mounting of the Components

Certain precautions were taken to eliminate vibrations. All vacuum components except the mechanical pumps and the 3" pumping line were mounted on a wooden frame made of two-by-fours. The legs of this frame protrude into wells in concrete blocks lined on the sides and bottoms with styrofoam. The small mechanical pumps were bolted to the concrete blocks and isolated from the rest of the equipment by two bellows in the pumping lines on the He^3 side and with two pieces of rubber vacuum hose on the vacuum side. The large Stokes mechanical pump is bolted to the concrete floor and the pumping line is isolated via a series of bellows. Also, the pumping line is fastened to the concrete ceiling of the laboratory. The fact that the room is in the basement is considered an advantage.

C. Operation of the Refrigerator

Initial Cooling

The strip silvered pyrex dewar was manufactured by H. S. Martin to specification. There are a number of coaxial spaces. The outermost is evacuated and is permanently sealed, the next is for liquid nitrogen and has two ports for filling, the third space contains about .150 torr of air at room temperature and communicates to the outside via a stopcock. Then comes the innermost space for the liquid He^4 .

Before cooling, about 1 torr of helium exchange gas is put into the liquid helium space and into the outer can. All other spaces

are evacuated. One then cools to liquid nitrogen temperatures overnight. Leak checking is done at room temperature as well as at liquid nitrogen temperature. After the pressure in the helium space is brought to one atmosphere by admitting additional helium gas and the exchange gas in the outer can is brought to about 1 torr, the liquid He^4 can be transferred from its storage container. The air in the space between the nitrogen jacket and the helium vessel solidifies eliminating thermal contact between the two spaces. The dewar has been in use for nearly two years without the need for re-evacuation. One expects that the air gets contaminated by helium gas which diffuses through the glass thus spoiling the heat switch. This has not occurred. The initial cool down usually requires 12 liters of liquid helium. One shipment of about 22 liters gives two good transfers.

Usually one has to wait about 3 hours before the temperature of the crystal is the same as the bath. Klein⁶⁴ had a similar difficulty with his apparatus. This is very undesirable and the reason is not understood.

Operation Below 4.2°K

Pumping on the He^4 as previously described permits one to reach temperatures between 4.2 and 1.1°K. If one wants to go to lower temperatures, the procedures are as follows.

At about 1.45°K, the He^3 cryostat is filled by letting the gas pass into the cryostat through valves GP-22, VS-21 and GP-14 with valves GP-16, VN-12, HH-11 and KG-13 closed. After the pressure as read on the dial gauge is static, one fills the He^3 bulb.

As the volume of the bulb is only 0.17 cm^3 , care must be taken not to overfill the bulb. Also, one must realize that as the temperature is lowered more and more of the He^3 gas trapped in the bulb and the fill line volumes connected to the bulb, will condense because the vapor pressure of He^3 decreases rapidly with temperature. If the liquid rises into the fill line above the liquid He^3 chamber, a higher temperature than that existing in the chamber may be indicated. The following procedure assures that the minimum amount of He^3 needed is introduced into the vapor pressure thermometer.

With valve GP-15 closed, one connects the He^3 cryostat to the Texas Instrument Gauge through valve GP-16. The sequence of closing valve GP-14, opening and closing GP-15 and opening GP-14 until the pressure in the bulb is about the same as the He^3 cryostat. Then GP-16 is closed, leaving the bulb only in communication with the Texas Instrument Gauge. The exchange gas in the outer can is then pumped off until the cold cathode gauge reads 10^{-6} torr. This may take up to 45 minutes. During this time one also pumps on the He^4 bath as hard as one can, lowering the temperature to about 1.1°K .

To achieve temperatures below 1.1°K , one has to pump on the He^3 cryostat. The pumping is regulated by adjusting the three valves KG-13, HH-1 and VN-12 until there is a slow cooling near the desired temperature. Adding heat to the cryostat heater then conveniently stabilizes the temperature.

The vapor pressure bulb is used to calibrate the secondary thermometers in this range.

II. Cryostat for Thermal Conductivity Measurements

The refrigerator described in the previous section can be turned into an instrument for measuring thermal conductivities by fastening one end of the sample to be measured beneath the He^3 cryostat, as in Figure 9. This sample should be long compared to its other dimensions. Mounted on it are a heater at the free end and resistance thermometers at two points along the sample. As will be explained later, provisions for adding power to the heater at a steady, measurable rate must be made. Also, it must be possible to measure the resistance of the thermometers on the sample, as well as the difference in their resistance.

A. Details of the Apparatus

Mounting the Sample

The sample, usually $1/8''$ by $1/8''$ by $1''$ to $1-1/2''$ long, is fastened below the He^3 cryostat in a vertical position. It is pressed against the side of a step in the bottom of this vessel by a rectangular piece of $0.020''$ phosphor bronze which is held by two screws. The parts of the step and clamp touching the crystal are tinned with indium to make the surface softer. To get good thermal contact, a small amount of stopcock grease is placed on the end of the sample before it is butted against the bottom of the He^3 cryostat.

The Thermodes and Crystal Heater

To mount the resistance thermometers and heaters to the crystal, two identical pieces of phosphor bronze, $1/2'' \times 0.125'' \times 0.020''$, with a hole drilled near either end are made.

These two pieces go on opposite sides of the crystal and can be connected by passing 0-80 bolts through the holes. Putting on the nuts allows one to clamp onto the crystal. The thermometers or heaters are soft soldered to the clamps. Next the sides of the clamps touching the crystal are covered with a layer of indium about 10^{-3} " thick and the indium is then pressed in a vice using lead as a backing on the side where the components are connected. The resistors themselves protrude from the vice. The indium assures uniform thermal contact and a soft surface so that the crystal is not damaged.

The two clamps carrying thermometers are called thermodes. Each carries a 68 ohm and a 12 ohm nominal value resistor of the Ohmite brand. The resistors of the same nominal value have been matched in resistance to within 0.5% at liquid nitrogen and room temperatures.

The heater is a homemade 10 K ohm wire wound resistor with 0.001" diameter, formvar insulated, manganin wire wound on a copper spool $1/2" \times 1/16"$. The ends of this wire are soldered to gauge 40 manganin wires and several more turns are taken around the spool before the entire assembly is drenched with G.E. 7031 resin. The heater is connected to the clamps with a $1/16"$ copper wire.

The leads from the resistors as well as the heaters are all 3" long and of gauge 40 manganin, so that most of the heat generated by the heater must flow through the crystal and a negligible amount through the leads. These wires all terminate at a terminal strip for ease of handling.

The Heater Circuit

The crystal heater is fed by a D. C. power supply. An attenuator cuts the current from this source by powers of ten. The current then passes through a reference resistor and then through the heater. The voltage across these two components is measured with a millivolt potentiometer to four significant figures. The voltage across the heater includes about 16 ohms of lead resistance as a result of the wires going from the heater to a terminal strip. This is negligible compared to the 10 K ohm resistance of the heater.

The Measurement of Resistance Thermometers

Figure 11 shows a schematic of a Wheatstone bridge designed to measure the resistance or the difference of resistance between a pair of resistors. To power the bridge and to determine the balance point, a Princeton Applied Research lock-in detector was used. The bridge was operated at 22 Hz, and it was found that no additional components were needed to balance the bridge. Presumably, the complex impedances are small and are the same in each arm of the bridge. The power input into a resistor was kept below $10^{-2} \mu$ watts. The value of R could generally be measured to within .1% and ΔR to within 1%. There are a few cases though, in which ΔR is less than 10, causing the error in ΔR to be greater than 1%.

The Cryostat Heater

To aid in controlling the temperature of the He^3 cryostat, a heater made of gauge 40, formvar insulated manganin wire is wound

Figure 11. A.C. Wheatstone bridge circuit.

around it. The sides of the He^3 cryostat were first covered with a layer of lens tissue soaked with G. E. 7031 to eliminate the possibility of electrical contact between wire and cryostat because of cracks in the insulation.

Current from a D. C. power supply can be varied, with fine control, over three decades by an attenuator circuit and a helipot.

B. Thermal Conductivity Measurements Between 4.2 and 1°K

After the crystal reaches the temperature of the bath, one of the 68 ohm nominal value resistors on the upper thermode is calibrated against the vapor pressure of the He^4 bath.⁶⁵ This resistor is labeled R_3 and its mate on the lower thermode is called R_4 . The difference between R_4 and R_3 , $\Delta R_{43 \text{ off}} = R_4 - R_3$, is also measured. $\Delta R_{43 \text{ off}}$ represents the difference in resistance due to mismatch when both are at the same temperature.

Next, one pumps to a lower temperature, about 3.8°K, regulates with the manostat, waits for thermal equilibrium and again measures $\Delta R_{43 \text{ off}}$ and R_3 together with the vapor pressure. Then current is passed through the crystal heater and after the resistors reach a steady value, one measures R_3 and $\Delta R_{43 \text{ on}} = R_4 - R_3$. Also, one measures the quantities needed to compute the power input into the heater, namely the voltage across the heater and across a known resistor in series with the heater.

For thermal conductivity points at higher temperatures, more heat is added while the bath is kept at the same temperature. As the resistors are not calibrated above 4.2°K, it is of no use to

go above that temperature. Power inputs of as much as 3000 μ watts were used. The minimum amount of power in this temperature range is the power needed to give a certain predetermined minimum percent error in $\Delta R_{43 \text{ net}}$.

$$\Delta R_{43 \text{ net}} = \Delta R_{43 \text{ on}} - \Delta R_{43 \text{ off}} \quad (47)$$

The measurements then consist of going to ever lower base temperatures, calibrating R_3 and $\Delta R_{43 \text{ off}}$ and measuring a number of thermal conductivity points with different power inputs. It is to be noted that as one passes the λ -point about 1/3 of the liquid in the He^4 dewar is used to supply the heat of transformation.

At about 1.4°K, the 12 ohm nominal value resistors become sensitive and calibration points for these can be taken. The one on the upper thermode will be referred to as R_1 , and that on the lower thermode will be called R_2 . The measurements in the temperature range where He^3 is used as a refrigerant are the same as in the He^4 region except that R_1 is calibrated against the vapor pressure of He^3 60, 61 and the temperature is stabilized as discussed under "Operation of the Refrigerator." R_3 and R_4 become too large at about 1.1°K to be useful. At the lowest temperatures about 0.3°K, the power inputs which give good thermal conductivity points is about 2 μ watts.

III. Calculation of Thermal Conductivities from Data

For the case of crystals with a constant cross sectional area A , steady power input Q , average distance between thermodes, l , and a temperature difference ΔT between the two thermodes the average thermal conductivity is

$$\bar{K} = \frac{Q l}{A \Delta T} \quad (48)$$

The problem is to express ΔT in terms of the measured quantities. As the following discussion applies to the pairs R_1, R_2 and R_3, R_4 the subscripts 1, 2 and 3, 4 will be dropped. Resistors on the upper thermode will be referred to as R_{up} .

Using log-log paper, one can construct graphs by plotting ΔR_{off} as a function of the corresponding resistor, R_{up} . A smooth curve is drawn through the data points from which values of ΔR_{off} corresponding to any value of R_{up} can be read. Then ΔR_{net} can be calculated from

$$\Delta R_{net} = \Delta R_{on} - \Delta R_{off} \quad (49)$$

For small ΔR_{net} , compared to R_{up} , one may write

$$\Delta T = R \frac{\partial \ln R}{\partial T} \Delta R_{net} \quad (50)$$

and using equation

$$\bar{K} = \frac{Q_1}{AR} \left(\left. \frac{\partial \ln R}{\partial T} \right|_T \Delta R_{\text{net}} \right)^{-1} \quad (51)$$

where T is the temperature corresponding to

$$R = R_{\text{up}} - \frac{|\Delta R_{\text{net}}|}{2}, \quad (52)$$

or roughly, the mean temperature between upper and lower thermodes. Computer analysis is used to find T and $\frac{\partial \ln R}{\partial T}$ from the calibration of R_{up} by determining the constants A, B, C, D, E , and F in the empirical formula

$$\ln R = A + B/T + C/T^2 + D/T^3 + E/T^4 + F \ln(1/T), \quad (53)$$

by a least squares fit. For a given R , the computer searches for a corresponding T and evaluates the derivative of $\ln R$ with respect to T .

IV. Calibration of the Carbon and Vapor Pressure Thermometers Using the Susceptibility of Cerium Magnesium Nitrate

Below 0.6°K the thermomolecular pressure difference between the gas at room temperature and that at the low temperature

end of the system becomes significant. Sizable corrections⁶¹ must be applied to the pressure and measured at room temperature to obtain the true vapor pressure in the bulb. This correction is of the order of 500% at about 0.3°K (for the particular system being described).

Rather than relying on these corrections, it was decided to calibrate the pressure as measured at room temperature against the susceptibility of cerium magnesium nitrate. At the same time the resistance thermometers were calibrated. As it turned out, the resistance thermometers needed to be calibrated only once as they did not change from experiment to experiment.

Figure 12 shows the cryostat adapted for susceptibility measurements. A schematic of the electronics is shown in Figure 13. Techniques for operating the apparatus in this mode are similar to the operation while making thermal conductivity experiments. For details about the design and construction, the reader is referred to R. Koch's M. S. Dissertation.⁶⁶

V. Measurement of F Center Concentration

To determine the F center concentrations, a Cary dual beam spectrophotometer was used. In this instrument a beam of light of variable frequency is split into two equal beams. One of these, the reference beam, passes through a piece of unirradiated crystal and the other through the sample. Let the intensity of the reference beam after it leaves the clear crystal be I_0 and that of the other beam, after it passes through the sample be I . The optical density of the sample due to the color centers is defined as

Figure 12. Cross sectional view of cryostat containing apparatus for magnetic susceptibility measurements.

Figure 13. Mutual inductance bridge circuit.

$$\text{O. D.} = \log \frac{I_0}{I} \quad (54)$$

The output from the spectrophotometer is a graph of this quantity as a function of frequency as the instrument scans a predetermined range of frequencies. Note that if $I = I_0$, then the $\text{OD} = 0$; as I becomes smaller, the optical density becomes large. The largest optical density that the spectrophotometer can conveniently measure without cutting down I_0 is 2.0. To measure larger optical densities, one decreases the reference beam by using filters of known optical density. The number stamped on the filter is the power of ten by which the intensity of the reference beam is decreased. Optical densities as high as 5.0 can then be measured.

The absorption constant α is related to the optical density of the crystal by $\text{OD} = \alpha x$. Values for α corresponding to F center concentrations of $10^{18}/\text{cm}^3$ are of the order of 160/cm so that the crystal must be cleaved very thin in order not to exceed the limitations of the instrument.

The F center concentration is then calculated from Smakula's⁶⁷ equation

$$Nf = 1.29(10)^{17} \frac{n}{(n^2 + 2)^2} \alpha_{\text{max}} w^{1/2}, \quad (55)$$

where N is the number of F centers per cm^3 , f is the oscillator strength and n is the refractive index of the crystal for the wavelength at the peak of the absorption band. Different workers have

used various values for f . A mean value for KCl, as given by Doyle,⁶⁸ is 0.90. In the present work f will be taken as 1. For the half-width of the absorption bands, 0.36 eV was used.

Even though the crystal had to be cleaved to about 0.27 mm, its thickness could still be measured to about 5%. The biggest source of error for the heavily irradiated crystals was the uncertainty in the height of the F band peak. Nf certainly is not known to better than 10%.

VI. Irradiation and Handling of Crystals

Three of the crystals were irradiated at IIT Research Institute in a "cave" using remote handling devices for two 1,000 Curie, Co^{60} sources. For the high intensity irradiation at liquid nitrogen temperatures, a dewar holding ten liters of liquid nitrogen narrowing to a 1.7 cm OD finger for the sample was used, so that the distance of closest approach to the sample was about 2 cm. During these irradiations the samples were wrapped in aluminum foil and were handled in the dark or in the presence of very low intensity red light.

In an experiment in which the thermal conductivity was measured without warming to room temperature, the cryostat was within a styrofoam vessel which fitted into the experimental dewar, as well as into a nitrogen dewar which could be irradiated. The styrofoam container was kept full of liquid nitrogen so that the cryostat could be kept at liquid nitrogen temperatures as it was moved from the experimental dewar to the nitrogen dewar and back

again after the irradiation was complete. As the nitrogen dewar had an OD of 14 cm, the total dosage was very small even over a time period of 4 days.

Two crystals were irradiated at Oak Ridge National Laboratory to take advantage of the greater intensities available there.

CHAPTER III

EXPERIMENTAL RESULTS AND CONCLUSIONS

All thermal conductivity measurements reported here have been carried out on KCl crystals, all but one of which were purchased from Harshaw Chemical Company and originated from the same boule. The one exception is a crystal grown by C. T. Butler⁶⁹ of Oak Ridge National Laboratory and is known to be of ultra-high purity.

Analysis of Data

As was discussed in Chapter I under "Motivation of Present Work," Page 33, the results of the thermal conductivity measurements will be interpreted in terms of scattering by the boundary, point defects and aggregates. The total relaxation time is

$$\tau(\omega, T) = [X_1 + X_2 \omega^4 + X_3 f(\omega, a, g)]^{-1} \quad (56)$$

where the interpretation of the individual terms is that X_1 represents boundary scattering, X_2 point defects and $X_3 f(\omega, a, g)$ possible large scatterers. The data will be interpreted by fitting it to the expression

$$K_{\text{calc}} = \frac{1}{2\pi^2 v} \int_0^{\omega_0} \tau(\omega, T) \frac{(\hbar^2 \omega^4 / kT^2) e^{\hbar \omega / kT} d\omega}{(e^{\hbar \omega / kT} - 1)^2} \quad (57)$$

$f(\omega, a, g)$ is

$$\begin{aligned} v \pi a^2 & \quad \text{for } \omega \geq \left(\frac{v}{a} \right) \left(\frac{9}{4} \frac{1}{g} \right)^{1/4} \text{ and} \\ g \frac{4\pi}{9} \frac{a^6}{v^3} \omega^4 & \quad \text{for } \omega < \left(\frac{v}{a} \right) \left(\frac{9}{4} \frac{1}{g} \right)^{1/4}. \end{aligned}$$

(58)

Physically, X_3 is proportional to the concentration of the colloids. The constant of proportionality is of the order of unity and will be discussed in the following section. The factor $(9/4g)^{1/4}$ multiplying v/a is chosen so as to avoid jump discontinuities in $f(\omega, a, g)$. It seems that this is the thing to do if one wants to approximate the actual transport cross sections as calculated by Walton and Lee even though these authors do not specifically say so. The effect on the results is negligible for $g \simeq 1$.

In all calculations, $\theta = 233^\circ\text{K}$ ¹⁹ and $v = 2.46 \times 10^5$ cm/sec was used.

To study the effects of $X_3 f(\omega, a, g)$ a number of curves were generated with $X_2 = 0$ and $X_1 = 1.85 \times 10^6$ /sec. Figure 14 shows the case where $g = 1$, $a = 50 \text{ \AA}$ and X_3 varies from 0 to $10^{15}/\text{cm}^3$. This covers the range of possible concentrations of colloids considering the number of F centers which can be created by irradiation. One notices that at low temperatures the curves approach that of the pure crystal and at higher temperatures they are almost parallel to that for the pure crystal. This behavior is

Figure 14. Calculated K versus T for various values of X_3 with $a = 50 \text{ \AA}$, $g = 1$, $X_2 = 0$, and $X_1 = 1.85 \times 10^6 \text{ sec}^{-1}$.

expected from the discussion in Chapter I. Figure 15 shows a similar set of curves for $g = 1$, $a = 70 \text{ \AA}$ and X_3 varying from 0 to $10^{14}/\text{cm}^3$. The larger radius gives a greater depression of the thermal conductivity for equal values of X_3 , X_1 and g .

In Figure 16 the radius is varied from 0 to $100 \text{ \AA}$ keeping X_3 at $1.4 \times 10^{13}/\text{cm}^3$ and g equal to 1. Note that as the radius increases, the temperature at which the thermal conductivity of the sample and that of the pure crystal approach each other becomes lower. Figure 17 illustrates the same thing for $X_3 = 10^{14}/\text{cm}^3$.

The effect of varying g is shown in Figure 18. The other parameters are kept fixed at the following representative values: X_3 at 2.4×10^{13} , a at $70 \text{ \AA}$, X_1 at 1.85×10^6 and X_2 at 0. The values of g are 0.5, 1.0 and 2.0, as indicated on the graph. The effect is greatest at the low temperatures. One would expect this because g influences the relaxation time for low frequency phonons.

To see the effect of changing a by a small amount, say $5 \text{ \AA}$ out of $70 \text{ \AA}$, one may refer to Figure 19. The two curves of interest in this figure were generated with $X_1 = 1.85 \times 10^6$, $X_2 = 0$ and $g = 1$ and varying X_3 , so that both curves join at about 0.3°K . The divergence of the curves is greatest at the higher temperatures. The changes in X_3 required for the 0.3°K fit were rather large.

From the last two paragraphs, one can conclude that the value of g is not very important but that the fit is very sensitive to the value of a .

Figure 15. Calculated K versus T for various values of X_3 with $a = 70 \text{ \AA}$, $g = 1$, $X_2 = 0$, and $X_1 = 1.85 \times 10^6 \text{ sec}^{-1}$.

Figure 16. Calculated K versus T for various values of a with $g=1$, $X_1=1.85 \times 10^6 \text{ sec}^{-1}$, $X_2=0$, and $X_3=1.4 \times 10^{13}/\text{cm}^3$.

Figure 17. Calculated K versus T for various values of a with $g = 1$, $X_1 = 1.85 \times 10^6 \text{ sec}^{-1}$, $X_2 = 0$, and $X_3 = 10^{14}/\text{cm}^3$.

Figure 18. Calculated K versus T for various values of g with $a = 70 \text{ A}$, $X_1 = 1.85 \times 10^6 \text{ sec}^{-1}$, $X_2 = 0$, and $X_3 = 2.4 \times 10^{13}$.

Figure 19. Calculated K versus T for two similar values of a with X_3 chosen so that the curves meet at 0.3°K .

Interpretation of g and X_3

Equations (40) and (46) in Chapter I can be rewritten as

$$\sigma_T = g_R \frac{4}{9} \pi \frac{a^6}{v} \omega^4 \quad \text{for } \omega < \frac{v}{a} \quad \text{and} \quad (59)$$

$$\sigma_T = g_G (\pi a^2) \quad \text{for } \omega > \frac{v}{a} . \quad (60)$$

From these the inverse relaxation times for n spherical scatterers per unit volume can be written as

$$n g_R \frac{4}{9} \pi \frac{a^6}{v} \omega^4 \quad \text{for } \omega < \frac{v}{a} \quad \text{and} \quad (61)$$

$$n g_G \pi a^2 v \quad \text{for } \omega > \frac{v}{a} . \quad (62)$$

g_R and g_G are functions of the densities and elastic constants and can be calculated by making some reasonable assumptions about the inclusions. Comparing Equations (56) and (58) with (61) and (62), one finds that

$$g = g_R / g_G \quad \text{and} \quad (63)$$

$$X_3 = n g_G . \quad (64)$$

If the scattering is due to aggregates of interstitial Cl atoms or Cl_2 molecules, one can calculate the density of the inclusions for

these two cases. If one then assumes that the fractional change in the elastic constants is small compared to that of the densities and that the transverse wave vector, K , is related to the longitudinal wave vector, k , as $K/k = \sqrt{3}$, one can estimate g_R and g_G .

For the case of Cl atoms, $\Delta \rho / \rho_1 = 0.48$ and $\rho_2 = 110/V$ where V is $\sqrt{2}/4$ times the volume of the unit cell. This yields $g_R = 0.87$ and $g_G = 0.47$ so that $g = 1.8$. If one has Cl_2 molecules as interstitials, then $\Delta \rho / \rho_1 = 0.951$ and $\rho_2 = 145.5/V$ so that $g_R = 3.5$ and $g_G = 1.5$ and $g = 2.5$.

To avoid putting undue emphasis on these values for g , the theoretical foundations of this calculation will be examined. First, there exist no calculations of the transport cross section for transverse waves (analogous to those of Walton and Lee⁴⁵ for longitudinal waves). If one wanted to use the formula, 42, given by Einspruch, Witterholt, and Truell⁴² for the total cross section in the Rayleigh limit, one could not because it gives negative answers when numbers are substituted into it. There is something wrong with this result and the originators⁷⁰ are checking their work. Using Equation (44) from Chapter I gives values for g different from those given above, but of the same magnitude. Secondly, the fact that the theory of elasticity, as presented in Chapter I, applies to polycrystalline materials and not to single crystals. That is to say, isotropic polycrystalline materials can be characterized by two elastic constants, but cubic single crystals need three independent parameters to describe their elastic

properties correctly.⁷¹ A fourth problem is the fact that the correct average velocities are not those gotten from the Debye theta.⁷² A better answer could be gotten from the measured elastic constants using Houston's⁷³ method.

Experimental Results

The results of the thermal conductivity measurements are presented in tabular form in the Appendix and as graphs of K versus T on log-log plots in Figures 20 through 23. In addition, Table II summarizes the parameters discussed in this section. The thermal conductivity of the pure crystal is labeled A and is shown, for comparison with the irradiated crystals, in all those figures except in Figure 22. The theoretical curve for the pure crystal is generated using $X_1 = 1.85 \times 10^6/\text{sec}$ and $X_2 = 2.55 \times 10^{-43} \text{ sec}^3$.

The curves labeled D and E in Figure 20 represent the thermal conductivity of crystals irradiated at room temperature. The total dosage for D was 1.4×10^8 rads at 1.6×10^5 rads/hr and for E it was 9.4×10^8 rads at 3.4×10^6 rads/hr. The F center concentrations are $2.4 \times 10^{17}/\text{cm}^3$ and $8.9 \times 10^{17}/\text{cm}^3$, respectively. The theoretical curves were generated using the same X_1 as for curve A . For curve D , $X_2 = 6.7 \times 10^{-43} \text{ sec}^3$ and $X_3 = 3 \times 10^{12}/\text{cm}^3$; for curve E , $X_2 = 2.1 \times 10^{-42} \text{ sec}^3$ and $X_3 = 2.4 \times 10^{13}/\text{cm}^3$. For both D and E , a is $70 \text{ \AA}$ and g was taken as 1.

Figure 20. Thermal conductivity versus temperature. Runs A, D, E.

Figure 21. Thermal conductivity versus temperature. Runs A, F, E.

Figure 22. Thermal conductivity versus temperature. Runs E, G.

Figure 23. Thermal conductivity versus temperature. Runs A, B, C.

Table II. Summary of Data.

Curve	Origin	Dose rads	Concentration of F centers cm^{-3}	Irrad. temp.	$a \left[\overset{\circ}{\text{A}} \right]$	X_1 $\left[\text{sec}^{-1} \right]$	X_2 $\left[\text{sec}^3 \right]$	X_3 $\left[\text{cm}^{-3} \right]$
A	Harshaw	0	0		0	1.85×10^6	2.55×10^{-43}	0
B	Harshaw	1.5×10^7	3.1×10^{16}	Liq. nitrogen*		NOT ANALYZED		
C	Harshaw	1.5×10^7	3.1×10^{16}	Liq. nitrogen**				
D	Harshaw	1.4×10^8	2.4×10^{17}	Room temp.	70	1.85×10^6	6.7×10^{-43}	3×10^{12}
E	Harshaw	9.4×10^8	8.9×10^{17}	Room temp.	70	1.85×10^6	2.1×10^{-42}	2.4×10^{13}
F	Harshaw	2.7×10^8	1.1×10^{17}	Liq. nitrogen**	0	1.85×10^6	7.5×10^{-43}	0
G	Oak Ridge	9.4×10^8	1.3×10^{18}	Room temp.		NOT ANALYZED		

* Thermal conductivity was measured without warm-up to room temperature.

** After warm-up.

Figure 21 shows curves labeled A, F and E. A and E are the same as in the previous figure and are shown for comparison. Curve F represents the thermal conductivity of a crystal irradiated at liquid nitrogen temperatures and warmed to room temperature before measuring its thermal conductivity and F center concentration. The total dose was 2.7×10^8 rads at 1.6×10^6 rads/hr. The F center concentration was $1.1 \times 10^{17}/\text{cm}^3$. The broken line was generated using $X_2 = 7.5 \times 10^{-43} \text{ sec}^3$ and $X_3 = 0$.

Curve E is again shown in Figure 22 together with curve G. Curve G represents a crystal grown at Oak Ridge National Laboratory to very high purity. It was irradiated together with the crystal from curve E so that the irradiation dose would be the same for both. The F center concentration for curve G was $1.3 \times 10^{18}/\text{cm}^3$. The theoretical fit was not attempted because the thermal conductivity of the unirradiated crystal was unknown.

Figure 23 shows the curves labeled A, B and C. Again, A represents the thermal conductivity of the pure crystal, B was obtained by irradiating this crystal at liquid nitrogen temperatures, and measuring its thermal conductivity without warming to room temperature. The total dosage was 1.5×10^7 rads at 1.6×10^5 rads/hr. Curve C was obtained by warming to room temperature, remaining there for three days and again measuring the thermal conductivity. The F center concentration after these experiments was $3.1 \times 10^{16}/\text{cm}^3$.

Discussion of Errors in the Thermal Conductivity

The scatter of the thermal conductivity points is generally less than 3 percent. Figures 20, 21, and 22 tend to amplify the discrepancies because of the way the temperature scale is expanded to emphasize the features of interest. The possible sources of scatter are: uncertainties in the ΔR_{net} 's, power input, temperatures and lack of steady state.

The maximum errors due to balancing the bridge in the measurement of ΔR_{net} occur at 4.2°K for the 68 ohm nominal value resistors and at 1.2°K for the 12 ohm nominal value resistors. At these temperatures, the smallest ΔR_{net} 's which were used were about 10 ohms. The errors in these ΔR_{net} 's is about 4 percent, but for each set of resistors the errors decrease rapidly to about 1 percent as the temperature is lowered.

The measured power input should not be a factor above 0.6°K, since the voltages involved can certainly be determined to within 0.2 percent. At the lowest temperatures, where the power input into the heater becomes small (2 μ watts), the errors in the measured voltages become significant. Also, the power input into the resistance thermometers is of the order of 1 percent of the heater power. The errors from these sources is about 2 percent.

The errors in the calibration of R should be negligible except at the lowest temperatures. Here, due to the relative insensitivity of the magnetic measurements, the error in T may be as much as 5 millidegrees. This would introduce a 1 percent error in the temperature scale and an unknown error in the slope of the

R versus T curve. Errors introduced in computer calculations of the slope are negligible as the same answers are obtained if the calculation is done by graphical methods.

Scatter due to lack of steady state can be excluded because of the care taken to achieve constant temperatures. The temperature was regulated so that the changes in resistance of R_1 and R_3 were barely detectable over a period of minutes (1 minute near 0.4°K , 5 minutes near 4.2°K) before the R 's and ΔR 's were measured.

The error from the above sources is estimated at about 3 percent over most of the temperature range. A larger error, 4 or 5 percent, is likely near 4.2°K and for data taken with the 12 ohm nominal value resistors above 1.2°K . The latter data usually was deleted because measurements made with the 68 ohm nominal value resistors extended to 1.1°K . The scatter of the data is thus pretty consistent with the above estimates.

An additional constant error of 2 percent comes from uncertainties in the cross sectional area of the crystal and the spacing of the thermodes. The error in the thermal conductivity points is, therefore, less than 5 percent except near 4.2°K . For curves A, B and C, the same crystal was used and the thermodes were not moved so that all three curves have the same constant error. This should be considered as one compares the three curves.

Interpretation and Discussion of Results

The uncolored crystal, curve A, gives a value of $X_1 = 1.85 \times 10^6/\text{sec}$. If X_1 is calculated from Casimir's expression for diffuse scattering of phonons at the boundary ($\tau_b^{-1} = v/1.12d$), one obtains $0.69 \times 10^6/\text{sec}$, which would yield considerably higher thermal conductivities. Actually, one would expect lower calculated conductivities because all surfaces have at least some specular reflection. Other experimenters have found similar problems with KCl. One possible explanation⁷⁴ is that loop dislocations are formed when the surfaces are roughened. The interpretation of X_2 is complicated by the fact that at 4.2°K phonon-phonon scattering becomes important. Thus, it is best to consider X_2 , for the unirradiated crystal, as a parameter to fit the data.

As mentioned earlier, one can account for the depression of the thermal conductivity of the irradiated samples below 1°K by postulating scatterers which can absorb and re-emit phonons. One would use the relaxation time in Equation (26) to fit the data, but this would predict that the maximum depressions in the thermal conductivities occur at the same temperatures for different concentrations of the scatterers. This is certainly not the case for curve E and D of Figure 20, the room temperature irradiated samples.

Because no such common temperature can be assigned to D and E, one would have to postulate that depending on the irradiation dose, different scatterers, with different energy levels,

are formed. Though this is not inconceivable, it is improbable. The issue can be fully decided by heat capacity measurements because the internal degrees of freedom of these scatterers would show up as anomalies in the heat capacity. These measurements are now being undertaken at this laboratory. For the present, the analysis will be made in terms of large elastic inclusions.

In general, $g = 1$ was used to fit the data because other values of g gave a slightly worse fit (even if the value of X_3 is altered). The value of a is not very sensitive to g so that the effective radius of the inclusions of curves E and D can be given as $70 \pm 5 \text{ \AA}$. The interpretation of X_3 is very sensitive to the value of g . The best one can say is that it should be of the same order of magnitude as the concentration of aggregates. To see if this is reasonable, one can calculate the number of interstitial positions in a sphere of $70 \text{ \AA}$ radius and multiply this by X_3 . For E one gets 3.9×10^{17} compared to an F center concentration of 8.9×10^{17} and for D one gets 4.9×10^{16} to be compared with an F center concentration of 2.4×10^{17} . They are of the same order of magnitude lending support to the idea that the clusters could be aggregates of interstitial halides.

In the subsequent discussion the letter subscripts refer to the curves labeled by these letters. The relationships

$$\frac{X_{2E} - X_{2A}}{X_{2D} - X_{2A}} = 4.45 \quad (65)$$

and

$$\frac{\text{F centers}_E}{\text{F centers}_D} = 3.7 \quad (66)$$

show that the increase in the number of point defects due to irradiation is proportional to the increase in the numbers of F centers; the fact that

$$\frac{\text{Dose}_E}{\text{Dose}_D} = 6.7 \quad (67)$$

and that

$$\frac{X_{3E}}{X_{3D}} = 8 \quad (68)$$

suggests that the number of aggregates is related to the dose. That the effective radii of colloids in the room temperature irradiated samples are the same seems to imply that there is a maximum size to the aggregates, which is reached at doses lower than administered to the crystal used for run D.

Considering curve F, the first thing one observes is that there is no noticeable deviation from curve A below 1°K so that there is no scattering by aggregates. The scattering appears to be due mostly to point defects. Even though the F center concentration is lower for curve F than that of curve D,

$$\frac{F \text{ centers}_F}{F \text{ centers}_D} = 0.46 , \quad (69)$$

the scattering due to point defects,

$$\frac{X_{2F} - X_{2A}}{X_{2D} - X_{2A}} = 1.2 , \quad (70)$$

is about the same. This discrepancy might be explained by assuming that for sample F there is scattering due to the F centers as well as due to the interstitial halides. These interstitial halides might be in the process of aggregating into small clusters of two or three, a size to which the method is not sensitive. The results of curve F should be compared with the low temperature irradiated sample of Sonder and Walton, keeping in mind that they used a crystal of different purity so that one can not use the X_1 as obtained from curve A to analyze the data. The shape of the curve suggests that there are significant numbers of aggregates present, their radii being considerably smaller than those in the room temperature irradiated samples.

The experiment in which the crystal was irradiated at liquid nitrogen temperatures and the thermal conductivity was measured before warming to room temperature yielded curve B in Figure 23. It is interesting that this curve is very much like curve D in Figure 20. This suggests large defects, even though the dosage and the resulting F center concentration is very much

smaller. Warming to room temperature and again measuring the thermal conductivity gives curve C. It shows the behavior expected of F centers and their associated interstitials if they are point defects. A scatterer, which is formed by moderate doses of radiation at nitrogen temperatures, disappears when warming to room temperature. Again, measurements of the heat capacity are badly needed before the topic can be pursued. If these scatterers are point defects with internal degrees of freedom, they might be due to the V_1 , V_4 or other centers which are formed under the conditions of irradiation and then go away as the sample is warmed to room temperature. If the scattering is due to aggregates, on the other hand, it would not be due to defects created complementary to the F centers because there are so few F centers. More likely, the scattering is due to clusters of negative ion vacancies or to the interstitials created with them. A similar result was observed by Pohl¹³ for LiF.

The experiment on the Oak Ridge crystal (irradiated along side the Harshaw crystal which produced curve E) gave curve G in Figure 22. It was undertaken to see if impurities significantly affect the growth of colloids. Inspection of the figure shows that curve G is a parallel displacement of curve E. The simplest explanation for this is that because the crystals are from different sources, the unirradiated specimens have different boundary scattering. This, together with the assumption that there are roughly the same number of colloids with the same mean radius in both samples, would explain the curves. If this is so, one can

conclude that whatever the differences in impurity between the Harshaw and Oak Ridge crystals, they do not significantly affect cluster size and concentration.

Suggested Experiments

Aside from the fact that heat capacity measurements should be done on crystals irradiated under the various conditions discussed to make sure that the interpretation of the thermal conductivities is correct, there are modifications of the experiments performed which seem particularly attractive.

In the case of crystals irradiated at nitrogen temperatures one could measure the thermal conductivity without warmup, as was done to get curve B in Figure 23. Then, warming to a slightly higher temperature, permitting the sample to remain at that temperature for a few days, and again measuring the thermal conductivity and repeating this process with successively higher temperatures, one can discover the temperature range in which the defects of interest anneal out. This could be correlated with absorption spectroscopy done under similar conditions in the hope that the defect might be identified.

Experiments which could determine if the growth of colloids is related to impurity content of the crystal in the same way as rate of coloring and bleaching would involve doping very pure crystals with chemicals known to affect the stability of the F centers (Pb and Ag, for instance). The thermal conductivity of the doped samples would be measured before as well as after irradiation. The samples could all be irradiated together to ensure equal doses.

Summary of Results

The purpose of this work was to test the model proposed by Sonder et al.⁵⁸ These authors suggest that the chlorine ions, after they are evicted from their lattice sites and give up an electron, remain in interstitial positions and aggregate to form clusters. In addition, they predict that these clusters will be larger for the room temperature irradiation occurs at lower temperatures, and that the presence of impurities decreases the cluster size in any given situation. The low temperature thermal conductivity is particularly sensitive to defects. For large defects ($a > 10 \text{ \AA}$), one can get an estimate of their average radius using methods analogous to those developed by Walton and Lee. The thermal conductivity can be used to test the above model.

With this in mind a series of measurements in the temperature range from 0.4 to 4.0°K, on KCl crystals subjected to varying doses of γ -irradiation, were undertaken. All but one of the crystals were grown by the Harshaw Chemical Company. An unirradiated crystal was measured so that the effect of the boundaries and of defects already present would be known. Two crystals were irradiated at room temperature with different doses. For these there is ample evidence for colloids having an average radius of 70 Å. The number of aggregates is proportional to the total dose. A calculation shows that the number of interstitials which can be accommodated in the volume occupied by the aggregates is of the same order of magnitude as the number of F centers for both crystals. Thus, it seems plausible that the colloids are made up of interstitial chlorine, in agreement with Sonder's model.

Another crystal was irradiated at liquid nitrogen temperatures and warmed to room temperature. Then the thermal conductivity was measured. It showed scattering characteristic of point defects with an inverse relaxation time proportional to ω^4 . This is probably due to F centers and isolated interstitial chlorines. There was no evidence of colloids although a crystal irradiated at room temperature, with comparable dose, showed colloids. On the other hand, Sonder and Walton did find evidence of colloids in their liquid nitrogen temperature irradiated sample. Their overall dose was higher. The average radius was smaller than that found in the room temperature irradiated samples. Their work lends support to the model under consideration. Considering their results, together with the work reported here, one can conclude that it is harder to produce aggregates (which survive the warmup to room temperature) by irradiating at liquid nitrogen temperature.

A very pure crystal from Oak Ridge National Laboratory was irradiated, together with the room temperature irradiated Harshaw Chemical Company crystal to produce a large number of F centers ($\sim 10^{18}$) in each. The purer crystal did not appear to contain colloids of a larger average radius as was expected from the model. Apparently, the impurities present in the Harshaw crystal do not markedly affect the average size of the colloids.

An unexpected result was found when a crystal was irradiated at liquid nitrogen temperature and its low temperature thermal conductivity was measured without first warming. The thermal conductivity curve is very much like that of a crystal irradiated at

room temperature with a dose of 1.4×10^8 rads — almost ten times as great as was used in this low temperature irradiation. If one interprets the results in terms of clusters, one concludes that such aggregates are not made up of interstitial chlorines produced in the forming of the F centers. There simply were not that many F centers ($\sim 10^{16}/\text{cm}^3$). After this experiment, the crystal was warmed to room temperature and again its thermal conductivity was measured. This time there was no evidence of large defects. It may be that the aggregates were clusters of negative ion vacancies or of chlorine ions produced with them. At present, these ions cannot be resolved. It seems wiser to do heat capacity measurements on these crystals than to speculate further.

APPENDIX

APPENDIX

Table I. Curve A.

Temperature (°K)	Thermal Conductivity (watts/cm °K)
0.378	0.00561
0.415	0.00636
0.469	0.00824
0.474	0.00868
0.481	0.00887
0.483	0.00947
0.486	0.00958
0.596	0.0188
0.624	0.0213
0.625	0.0209
0.633	0.0223
0.635	0.0228
0.643	0.0236
0.647	0.0237
0.662	0.0256
0.664	0.0249
0.690	0.0294
0.695	0.0301
0.708	0.0329
0.798	0.0468
0.804	0.0492
0.837	0.0561
0.840	0.0577
0.882	0.0672
0.970	0.0922

Table I. (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm °K)
1.114	0.1146
1.140	0.1222
1.159	0.1326
1.185	0.1336
1.192	0.1378
1.219	0.1449
1.244	0.1478
1.256	0.1588
1.273	0.1665
1.518	0.2545
1.542	0.2625
1.632	0.298
1.954	0.450
2.036	0.5069
2.048	0.499
2.101	0.549
2.179	0.579
2.271	0.664
2.327	0.684
2.575	0.874
2.859	1.08
2.951	1.13
2.955	1.17
3.078	1.26

Table II. Curve B.

Temperature (°K)	Thermal Conductivity (watts/cm °K)
0.467	0.00732
0.481	0.00832
0.497	0.00872
0.811	0.0355
0.856	0.0418
0.861	0.0422
0.874	0.0445
0.908	0.0500
0.940	0.0549
0.980	0.0614
1.000	0.0666
1.178	0.0858
1.196	0.0887
1.220	0.0928
1.285	0.1059
1.300	0.1090
1.466	0.1448
1.512	0.1552
1.651	0.1908
1.704	0.2064
1.821	0.2367
1.870	0.2506
2.022	0.296
2.109	0.321
2.261	0.363
2.364	0.400
2.633	0.487
2.863	0.561
2.918	0.578

Table II. (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm °K)
3.139	0.673
3.388	0.762
3.493	0.798
3.758	0.928
3.890	0.980
4.116	1.08
4.248	1.14

Table III. Curve C.

Temperature (°K)	Thermal Conductivity (watts/cm °K)
0.371	0.00560
0.379	0.00578
0.394	0.00626
0.407	0.00622
0.422	0.00694
0.437	0.00772
0.454	0.00852
0.478	0.00995
0.494	0.0110
0.538	0.0144
0.555	0.0159
0.575	0.0177
0.601	0.0204
0.620	0.0223
0.636	0.0247
0.691	0.0318
0.737	0.0396
0.749	0.0417
0.786	0.0490
0.824	0.0570
0.866	0.0670
0.903	0.0768
0.922	0.0818
1.173	0.118
1.208	0.128
1.240	0.138
1.292	0.155
1.480	0.2103
1.527	0.2276

Table III. (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm °K)
1.656	0.2730
1.683	0.2863
1.844	0.3530
1.880	0.3670
2.049	0.4341
2.110	0.4738
2.345	0.5718
2.416	0.6029
2.555	0.7268
2.650	0.768
2.758	0.837
3.005	0.989
3.293	1.07
3.435	1.20
3.652	1.43
3.725	1.50
3.960	1.73
4.264	2.13

Table IV. Curve D.

Temperature (°K)	Thermal Conductivity (watts/cm °K)
0.395	0.00485
0.448	0.00613
0.456	0.00645
0.462	0.00674
0.527	0.00964
0.538	0.0104
0.576	0.0121
0.581	0.0125
0.630	0.0166
0.645	0.0178
0.658	0.0190
0.679	0.0199
0.684	0.0203
0.757	0.0292
0.854	0.0430
0.884	0.0469
0.970	0.0633
1.002	0.0681
1.131	0.9280
1.259	0.1196
1.282	0.125
1.484	0.177
1.518	0.185
1.813	0.262
1.869	0.284

Table IV. (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm °K)
2.042	0.331
2.089	0.352
2.439	0.433
2.587	0.490
2.633	0.513
2.936	0.592
2.985	0.622
3.410	0.746
3.483	0.781
3.635	0.853
3.962	0.993

Table V. Curve E.

Temperature (°K)	Thermal Conductivity (watts/cm °K)
0.405	0.00386
0.434	0.00450
0.466	0.00502
0.471	0.00522
0.506	0.00574
0.537	0.00624
0.540	0.00633
0.584	0.00703
0.616	0.00763
0.640	0.00839
0.675	0.00965
0.761	0.0125
0.789	0.0132
0.812	0.0146
0.867	0.0165
0.918	0.0197
1.047	0.0274
1.056	0.0267
1.217	0.0354
1.312	0.0408
1.364	0.0440
1.394	0.0471
1.423	0.0480
1.473	0.0521
1.591	0.0593
1.596	0.0619
1.613	0.0631
1.653	0.0666
1.852	0.0784

Table V. (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm °K)
1.937	0.0847
2.006	0.0878
2.019	0.0914
2.119	0.0968
2.156	0.1020
2.210	0.1028
2.215	0.1067
2.273	0.1084
2.378	0.1161
2.405	0.1204
2.539	0.1340
2.602	0.1387
2.634	0.1389
2.817	0.154
2.906	0.161
2.833	0.156
2.995	0.168
3.050	0.176
3.143	0.184
3.177	0.190
3.225	0.205
3.297	0.207
3.347	0.225
3.549	0.230
3.629	0.236
3.718	0.243
3.902	0.273

Table VI. Curve F.

Temperature (°K)	Thermal Conductivity (watts/cm °K)
0.417	0.00639
0.424	0.00668
0.439	0.00753
0.456	0.00815
0.466	0.00877
0.476	0.00938
0.517	0.0117
0.530	0.0127
0.580	0.0168
0.591	0.0177
0.644	0.0229
0.655	0.0243
0.662	0.0248
0.731	0.0342
0.739	0.0357
0.748	0.0369
0.839	0.0531
0.844	0.0547
0.946	0.0774
0.960	0.0799
0.996	0.0899
1.197	0.120
1.243	0.126
1.307	0.139
1.455	0.191
1.483	0.196
1.670	0.252
1.698	0.267
1.730	0.276

Table VI. (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm °K)
1.859	0.3149
1.888	0.3261
1.930	0.3504
2.251	0.4472
2.307	0.4769
2.378	0.5280
2.618	0.5980
2.672	0.6221
2.887	0.710
3.229	0.833
3.546	1.065
3.727	1.14
3.900	1.24
4.119	1.36

Table VII. Curve G.

Temperature (°K)	Thermal Conductivity (watts/cm °K)
0.405	0.00612
0.420	0.00620
0.484	0.00737
0.495	0.00778
0.508	0.00795
0.531	0.00874
0.526	0.00838
0.535	0.00882
0.545	0.00885
0.582	0.00997
0.620	0.0113
0.643	0.0120
0.664	0.0127
0.669	0.0132
0.675	0.0133
0.719	0.0150
0.750	0.0167
0.817	0.0202
0.828	0.0205
0.854	0.0224
1.002	0.0329
1.061	0.0384
1.242	0.0526
1.337	0.0615
1.510	0.0780
1.551	0.0816
1.614	0.0883
1.634	0.0907
1.694	0.0936

Table VII. (Cont.)

Temperature (°K)	Thermal Conductivity (watts/cm °K)
1.967	0.1262
2.008	0.1312
2.070	0.1379
2.209	0.1520
2.244	0.1563
2.289	0.1605
2.394	0.1734
2.459	0.1798
2.554	0.1830
2.586	0.1936
2.623	0.1970
2.683	0.2025
2.788	0.2167
2.846	0.2231
2.885	0.2268
3.138	0.2580
3.159	0.2607
3.202	0.2695
3.275	0.2736
3.346	0.283
3.664	0.328
3.739	0.333
3.857	0.359
3.968	0.376
4.048	0.390

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