THERMAL CONDUCTIVITY OF INERT GAS SOLIDS

by

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We accept this thesis as conforming to the required standard

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ABSTRACT

The thermal conductivity of perfect infinite crystals of neon, argon, krypton, and xenon has been calculated numerically. It was assumed that the crystals possessed face centred cubic structure with the atoms interacting in pairs through a Lennard-Jones $12:6$ potential energy function. The calculations considered only the effects of three-phonon interactions. It was possible to simplify the calculations by introducing "reduced" physical quantities. The thermal conductivity of each of the inert gas solids considered was obtained from the "reduced thermal conductivity" which was calculated for argon. Agreement with experimental data for neon, argon, and krypton was obtained for temperatures higher than those for which the effects of crystal size and lattice defects determine the thermal conductivity. This agreement suggests that for sufficiently high temperatures the thermal conductivity is determined by the effects of three-phonon Umklapp processes.
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CHAPTER I

INTRODUCTION

In dielectric solids all of the electrons are bound to atoms of the lattice and heat is transferred by the phonons of the solid. The thermal conductivity of dielectric solids is considered to be due to processes which interfere with the motion of the phonons. These processes are reflection at the crystal boundaries, scattering in the region of lattice imperfections, and interactions among the phonons.

As long as there are few enough phonons, as is the case at very low temperatures (see Section II.3), the phonons are able to encounter the bounding surfaces of the crystal and imperfections in the lattice many times before they encounter interactions with other phonons. Then the contributions to the thermal conductivity are dominated by the effects of the boundaries and Imperfections of the crystal. For higher temperatures the phonons become so numerous that the motion of any phonon is governed chiefly by its interactions with other phonons. For these temperatures contributions to the thermal conductivity due to interactions among the phonons will be dominant.

1. REVIEW OF PREVIOUS STUDIES

Experimental observations (de Haas and Biermasz (1937 and 1938), Berman, Simon, and Wilks (1951), White and Woods
(1956 and 1958) indicate that the thermal conductivity $\kappa(T)$ of dielectric solids has the following properties.

1. At very low temperatures (less than about 5°K)
\[ \kappa(T) \sim T^a, \]  
where $T$ is the absolute temperature of the solid and $a$ is a positive number with a value of about two or three, depending on the sample used in the experiment.

2. At slightly higher temperatures the thermal conductivity attains its maximum value and begins to decrease rapidly with increasing temperatures. Values of the thermal conductivity remain dependent on the sample being examined, but the variation in values diminishes as the temperature increases.

3. At high temperatures
\[ \kappa(T) \propto \frac{1}{T}, \]  
and experimental values of the thermal conductivity are independent of the sample used. For solid neon, argon, and krypton White and Woods (1958) found that the thermal conductivity begins to have the temperature dependence of (1.2) at about 15°K.

Theoretical considerations (See, for example, Klemens (1958).) indicate that at very low temperatures the effect of the scattering of the phonons at the crystal boundaries and near
various types of lattice imperfections is that the temperature variation (1.1) should be observed in the thermal conductivity. Since the size and detailed structure of a real crystal are characteristic of particular samples, it is to be expected that the values of the thermal conductivity should depend on the particular sample used in the experiment.

At high temperatures the effect of interactions among the phonons determines the temperature dependence of the thermal conductivity. These interactions are virtually independent of particular samples of a dielectric solid and produce the observed temperature variation (1.2) for extremely high temperatures (See Sections I.2 and II.3).

For temperatures slightly higher than that of the maximum experimental value of the thermal conductivity, the temperature dependence is quite difficult to determine theoretically. Peierls (1929 and 1956) has investigated the effects of the cubic anharmonic term of the crystal potential energy (See Section I.2) and has concluded that for these temperatures

$$\kappa(\tau) \propto \exp \left[ \gamma \Theta / \tau \right],$$

where $\Theta$ is the Debye characteristic temperature and $\gamma$ is a numerical constant of order unity. Other investigators have suggested that

$$\kappa(\tau) \propto \left( \frac{\tau}{\Theta} \right)^n \exp \left[ \Theta / \beta \tau \right],$$
but there has been little agreement on the values of the parameters \( n \) and \( \beta \). Berman, Simon, and Wilks (1951) stated that \( \beta \) is a constant with a value slightly greater than two and depending on the solid being considered. Klemens (1958) claimed that \( n=3 \) with \( (\Theta/\beta) \) as an arbitrary parameter from a theoretical point of view. Ziman (1960) expected \( n=3 \) and \( \beta=2 \). Julian (1965) has developed a formula of the form (1.4) which he claimed to be valid for the temperature range

\[
\frac{1}{2 \alpha} \leq \frac{T}{\Theta} \leq \frac{1}{8}
\]  

(1.5)

and for which \( n=8 \) and \( \beta=1.030 \). Julian also showed that a non-zero value of \( n \) is required in formula (1.4) in order that \( \beta \) be constant with temperature. However, the strong variation of the exponential factor in (1.4) makes the actual value of \( n \) not very crucial to the problem of fitting experimental data.

2. REVIEW OF LATTICE DYNAMICS

Before proceeding with this discussion of thermal conductivity and stating the problem of this thesis, it is useful to review lattice dynamics briefly to define terms and establish basic equations. The theory which is presented may be found in Maradudin, Montroll, and Weiss (1963) and Leibfried and Ludwig (1961).

In a perfect crystal lattice with one atom per unit cell and which is "generated" by the three linearly independent
vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, the equilibrium position of the atom labelled $\vec{m}$ is

$$\vec{R}_{\vec{m}} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3,$$

(1.6)

where $m_1$, $m_2$, and $m_3$ are integers. The "reciprocal lattice" corresponding to this "direct lattice" is generated by the vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$, which are defined by the relation

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}; \quad i, j = 1, 2, 3.$$

(1.7)

Points of the reciprocal lattice are labelled $K$ and are denoted by the "reciprocal lattice vectors"

$$\vec{K} = h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3,$$

(1.8)

where $h_1$, $h_2$, and $h_3$ are integers. As a result of equations (1.6)-(1.8),

$$\vec{R}_{\vec{m}} \cdot \vec{K} = 2\pi (\text{integer}).$$

(1.9)

The potential energy of the crystal lattice $\Phi$ is a function of the position of each atom in the crystal and has its minimum value $\Phi_0$ when every atom is in its equilibrium position. If the $\alpha$th component of the displacement of the atom $\vec{m}$ from its equilibrium position is $\vec{u}_{\vec{m}}^\alpha$, the crystal potential energy may be written as a Taylor series expansion in the displacements $\vec{u}_{\vec{m}}^\alpha$.

$$\Phi - \Phi_0 = \sum_{\vec{m}} \left( \frac{\partial^2 \Phi}{\partial u_{\vec{m}}^\alpha \partial u_{\vec{m}}^\beta} \right)_{u_{\vec{m}}^\alpha = 0} u_{\vec{m}}^\alpha u_{\vec{m}}^\beta +$$

$$\frac{1}{2!} \sum_{\vec{m}, \vec{m}', \vec{m}''} \left( \frac{\partial^2 \Phi}{\partial u_{\vec{m}}^\alpha \partial u_{\vec{m}'}^\beta \partial u_{\vec{m}''}^\gamma} \right)_{u_{\vec{m}}^\alpha = 0} u_{\vec{m}}^\alpha u_{\vec{m}'}^\beta u_{\vec{m}''}^\gamma + \ldots,$$

(1.10)
where the subscript "0" means that the derivatives are to be evaluated for the equilibrium position of every atom. The term linear in the displacements $u_0^\alpha$ vanishes because there are no net forces on any of the atoms when they are all in their equilibrium positions. The quadratic term is called the "harmonic term" and all subsequent terms are called "anharmonic terms" or "anharmonicities". The usual method of continuing the analysis of the motion of the lattice is to make the "harmonic approximation" by truncating the series (1.10) after the harmonic term.

In the harmonic approximation, the equations of motion for the atoms of the lattice form a system of second order linear differential equations in the displacements $u_\alpha^\gamma$. The solutions of the equations of motion have sinusoidal time dependence, the angular frequencies $\omega$ of which must satisfy the "secular equation"

$$\left| (D_{\alpha\beta}(\vec{k}) - \omega^2 \delta_{\alpha\beta}) \right| = 0 ,$$  

(1.11)

where the "wave vector" $\vec{k}$ is a vector in the space of the reciprocal lattice and the "dynamical matrix",

$$D_{\alpha\beta}(\vec{k}) = \frac{1}{M} \sum_\mathbf{h} \left( \frac{\partial^2 E}{\partial u_\alpha \partial u_\beta} \right)_0 e^{-i \vec{k} \cdot \vec{h}} ,$$  

(1.12)

may be shown to be unitary and positive definite so that its eigenvalues are positive and may be written as $\omega^2$. $M$ is the mass of each atom of the crystal and
The secular equation (1.11) is a cubic equation in the eigenvalues \( \omega^2 \). For every vector \( \vec{k} \) there are three solutions of (1.11) and each solution corresponds to an eigenvector of the dynamical matrix, \( \hat{\varepsilon} \). These three eigenvalues and corresponding eigenvectors, or "polarization vectors", are labelled by the "polarization index" \( j \):

\[
\omega^2 = \omega^2(\vec{k}_j) \quad \text{and} \quad D(\vec{k}) \vec{\varepsilon}(\vec{k}_j) = \omega^2(\vec{k}_j) \vec{\varepsilon}(\vec{k}_j). \tag{1.14}
\]

The "normal coordinates" \( \alpha(\vec{k}_j) \) of the crystal are defined so that

\[
\sum_{\vec{k}_j} \epsilon(\vec{e}_j; \alpha(\vec{k}_j) \vec{e}(\vec{k}_j)) \epsilon(\vec{e}_j; \alpha(\vec{k}_j) \vec{e}(\vec{k}_j)) = \sum_{\vec{k}_j} \epsilon(\vec{e}_j; \alpha(\vec{k}_j) \vec{e}(\vec{k}_j)) \epsilon(\vec{e}_j; \alpha(\vec{k}_j) \vec{e}(\vec{k}_j)) \quad \text{(1.15)}
\]

where the summation is over as many wave vectors \( \vec{k} \) as there are atoms in the crystal so that (1.15) defines the normal coordinates uniquely. Using (1.15), the expansion of the crystal potential energy (1.10) may be rewritten in terms of the normal coordinates. (See Leibfried and Ludwig (1961).)

\[
\Phi - \Phi_0 = \frac{1}{2} \sum_{\vec{k}_j} \omega^2(\vec{k}_j) |\alpha(\vec{k}_j)|^2 + \sum_{j, j'} c(\vec{k}_j, \vec{k}_{j'}) \alpha(\vec{k}_j) \alpha(\vec{k}_{j'}) \quad \text{(1.16)}
\]

where

\[
c(\vec{e}_j, \vec{e}_{j'}) = \sum_{\mu \nu \rho} \left( \frac{\partial^2 h}{\partial u_\mu \partial u_\nu \partial u_\rho} \right)_0 \epsilon(\vec{e}_j) \epsilon(\vec{e}_{j'}) \epsilon(\vec{e}_{j'}) \quad \text{(1.17)}
\]

and

\[
\sum_{\mu \nu \rho} \left( \frac{\partial^2 h}{\partial u_\mu \partial u_\nu \partial u_\rho} \right)_0 \epsilon(\vec{e}_j) \epsilon(\vec{e}_{j'}) \epsilon(\vec{e}_{j'})
\]

\[
X \epsilon(\vec{e}_j) \epsilon(\vec{e}_{j'}) \epsilon(\vec{e}_{j'})
\]
is called the "cubic coefficient" and may be shown to vanish unless
\[
\bar{\xi} + \bar{\xi}' + \bar{\xi}'' = \bar{\xi}^X.
\] (1.18)

The quadratic term of (1.16) is the potential energy of a collection of independent harmonic oscillators moving in the normal coordinates \(a(\bar{\xi}_j)\) with angular frequencies \(\omega(\bar{\xi}_j)\). In a transition to quantum mechanics the normal coordinates \(a(\bar{\xi}_j)\) become coordinate operators \(\hat{a}(\bar{\xi}_j)\) and the vibrations in the normal coordinates may be treated as particles called "phonons". The operators \(\hat{a}(\bar{k}_j)\) are bose operators and the phonons are bosons.

In the absence of anharmonic terms in (1.16) the phonons are non-interacting particles. But the anharmonic terms do not separate into summations over single normal modes or phonon states. These terms represent the manner in which the phonons may interact with each other.

The number of normal coordinates which may be defined uniquely by (1.15) is \(3N'\) where \(N'\) is the number of atoms in the crystal. In the case of infinite crystals, there would be an infinite number of normal coordinates and an infinite crystal potential energy. A convenient method of normalizing the crystal potential energy and making the number of normal coordinates finite without significantly altering the distribution of the angular frequencies \(\omega(\bar{\xi}_j)\) is to impose "cyclic boundary conditions," such
where \( N_\alpha (\alpha = 1,2,3) \) are positive integers so large that \( N_\alpha \) is negligible compared with \( (N_\alpha)^2 \). The number of normal coordinates under these boundary conditions is \( 3N \) where

\[
N = N_1 N_2 N_3
\]

is the number of atoms in the "cyclic volume" and the term "crystal potential energy" means the potential energy of a cyclic volume of the crystal. If \( N \) is chosen to be equal to the number of atoms in a real crystal, then the properties of a cyclic volume of an infinite crystal are a very good approximation to the properties of a real crystal.

The normal coordinates \( a(E_j) \) belong to wave vectors \( \mathbf{k} \) which have uniformly distributed and discrete values, such that

\[
k_\alpha = (\mathbf{K}^*)_\alpha / N_\alpha , \quad \alpha = 1,2,3.
\]

The "first Brillouin zone" of a crystal lattice is that unit cell of the reciprocal lattice which is centred on the origin of the coordinate system of the reciprocal lattice. For any wave vector \( \mathbf{k} \) which ends on a point outside of the first Brillouin zone of the lattice, a vector \( \mathbf{k}' \) which ends on a point inside the first Brillouin zone may be found such that

\[
\mathbf{k} = \mathbf{k}' + \mathbf{R}^F .
\]
Because the wave vector appears in the definition of the dynamical matrix and the normal coordinates in an exponential of the form
\[ e^{\mathbf{k} \cdot \mathbf{R}} \] (1.23)
which as a result of (1.9) is equal to
\[ e^{\mathbf{k} \cdot \mathbf{R}'} \] (1.24)
the angular frequencies and normal coordinates corresponding to a wave vector \( \mathbf{k} \) are the same as those for a wave vector \( \mathbf{k}' \) if the two wave vectors satisfy (1.22). Therefore, only wave vectors which end on points inside the first Brillouin zone of the lattice need be considered.

3. STATEMENT OF THE PROBLEM

The problem to be investigated in this thesis is the calculation of the thermal conductivity of the inert gas solids by considering the interactions among the phonons of their crystals due to the cubic anharmonic term in the expansion of the crystal potential energy. The inert gases were chosen for the calculations for two reasons.

1. Except for helium the inert gases crystallize in face centred cubic lattices. These are particularly simple lattices to deal with mathematically; therefore, the inert gases neon, argon, krypton, and xenon were chosen for the calculations.

2. Experimental and theoretical studies have indicated
that the interaction among the atoms of inert gases and inert gas solids is pairwise and central. The Lennard-Jones 12:6 potential was chosen to represent the interaction among the atoms of an inert gas solid for the calculations of this study. (Whalley and Schneider (1955), Grindlay and Howard (1964).)

In the body of this thesis it is assumed that the crystals being considered have perfect infinite lattices with cyclic boundary conditions. The thermal conductivity of such crystals is due only to interactions among the phonons. Of the interactions which could occur in these crystals, only those due to the cubic anharmonic term of the crystal potential energy are considered since higher order anharmonic terms are not thought to provide significant contributions to the thermal conductivity. (Berman, Simon, and Wilks (1951).)

The results of the calculations were not expected to provide good agreement with experimental data at low temperatures. But for temperatures higher than that of the maximum experimental value of the thermal conductivity, the effects of interactions among the phonons should dominate the contributions to the thermal conductivity. Good agreement was expected for such temperatures.

4. ORGANIZATION OF THESIS

In Chapter II a general theory of thermal conductivity
of dielectric solids is presented. The theory is based on a relaxation method and most of the chapter is concerned with the derivation of a formula for the effect of the interactions among the phonons on the "relaxation time" for each phonon state. Only the interactions allowed by the cubic anharmonicities are considered.

In Chapter III the general theory of Chapter II is applied to a model of the inert gas solids. It is shown that the thermal conductivity of the inert gas solids may be written as

\[ K(T) = C \tilde{\kappa} (\Theta/T) \]  

(1.25)

where \( C \) and \( \Theta \) are constants characteristic of the solid under consideration. \( \tilde{\kappa} \) is called the "reduced thermal conductivity" and if it is calculated for any set of values of \( (\Theta/T) \), the thermal conductivity of any inert gas solid may be obtained by using equation (1.25) with appropriate values of \( C \) and \( \Theta \).

Chapter IV describes the procedure by which the thermal conductivities were calculated numerically. The temperature dependence of the reduced thermal conductivity is determined. For neon, argon, and krypton, the calculated thermal conductivities are compared with the experimental data of White and Woods (1958). For xenon the calculations are compared with calculations made by Julian (1965).

Chapter V contains a summary of the material in the
body of this thesis and comments on the problem of calculating the thermal conductivity of the inert gas solids.
CHAPTER II

THEORY OF LATTICE THERMAL CONDUCTIVITY

In this chapter the effect on the thermal conductivity of dielectric solids due to the cubic anharmonic term of the crystal potential energy is considered. The theory is taken from the review article on thermal conductivity by Klemens (1958).

1. FORMAL THEORY

A dielectric solid with a perfect infinite lattice and cyclic boundary conditions may be treated as a collection of phonons belonging to the phonon modes \((\mathbf{k}_j)\), where the wave vector \(\mathbf{k}\) has values uniformly distributed throughout the first Brillouin zone and the polarization index \(j\) has values 1, 2, and 3. If, as is true in all practical cases, the temperature gradient present in a dielectric solid is small enough that the relative change in temperature over the distance of one phonon wavelength is small, the phonons may be considered as localized wave packets moving with the group velocity

\[
\mathbf{v}^g(\mathbf{k}_j) \equiv \frac{\partial \omega(\mathbf{k}_j)}{\partial \mathbf{k}},
\]

(2.1)

where \(\omega(\mathbf{k}_j)\) is the angular frequency of the phonon mode \((\mathbf{k}_j)\).

If the number of phonons in the mode \((\mathbf{k}_j)\) is \(N(\mathbf{k}_j)\), the heat current carried by this collection of phonons is

\[
\mathbf{Q} = \sum_{\mathbf{k}_j} N(\mathbf{k}_j) \times \omega(\mathbf{k}_j) \times \mathbf{v}^g(\mathbf{k}_j),
\]

(2.2)
where ℏ is Planck's constant. Because the wave vectors are uniformly distributed throughout the first Brillouin zone, for every phonon mode \( k_j \) which contributes to the heat current there corresponds a mode \(-k_j\) with equal angular frequency which also contributes. Therefore, when the "phonon distribution" \( \mathcal{N}(k_j) \) is isotropic in the wave vector, the summation over \( k \) in (2.1) vanishes. In this case, the phonon distribution is the "equilibrium distribution" \( \mathcal{P}(k_j) \) and (2.2) becomes

\[
\bar{Q} = \sum_{k_j} \mathcal{P}(k_j) \hbar \omega(k_j) \delta(k_j) = \bar{Q}.
\] (2.3)

As mentioned in Section 1.2, in the quantum mechanical treatment the phonons may be treated as bosons, which have the equilibrium distribution

\[
\mathcal{P}(k_j) = \left\{ \exp \left[ \frac{\hbar \omega(k_j)}{kT} \right] - 1 \right\}^{-1}
\] (2.4)

where \( k \) is Boltzmann's constant. If \( n(k_j) \) is the deviation of \( \mathcal{N}(k_j) \) from \( \mathcal{P}(k_j) \) then

\[
\mathcal{N}(k_j) = \mathcal{P}(k_j) + n(k_j)
\] (2.5)

and (2.2) may be rewritten as

\[
\bar{Q} = \sum_{k_j} n(k_j) \hbar \omega(k_j) \delta(k_j).
\] (2.6)

For a phonon mode which is not in equilibrium, it is assumed that the return to equilibrium is exponential in time and that the following "relaxation law" is obeyed.
\[
\frac{dN(\varepsilon_j)}{dt} = \frac{n(\varepsilon_j) - N(\varepsilon_j)}{\tau(\varepsilon_j)} = - \frac{n(\varepsilon_j)}{\tau(\varepsilon_j)}.
\]  
(2.7)

\(\tau(\varepsilon_j)\) is called the "relaxation time" of the phonon mode \((\varepsilon_j)\) and depends on no other phonon mode nor on time.

In the presence of a temperature gradient \(\nabla T\) and no other external disruptive effects, the rate of change of the phonon distribution may be written as

\[
\frac{dN(\varepsilon_j)}{dt} + \left[ \mathbf{\nabla} \cdot (\mathbf{\nabla} T) \right] \frac{dN(\varepsilon_j)}{dT} = 0.
\]  
(2.8)

For small deviations \(n(\varepsilon_j)\), a first approximation to the deviations from equilibrium may be obtained by replacing \(N(\varepsilon_j)\) in the second term of (2.8) by \(\gamma(\varepsilon_j)\) and comparing the result with the relaxation law (2.7). It is found that

\[
n(\varepsilon_j) \approx - \left[ \mathbf{\nabla} \cdot (\mathbf{\nabla} T) \right] \tau(\varepsilon_j) \frac{k}{\varepsilon_j} \frac{\alpha(\varepsilon_j)}{\omega(\varepsilon_j)} \]  
(2.9)

where

\[
S(\varepsilon_j) = \frac{\alpha(\varepsilon_j)}{\omega(\varepsilon_j)} \frac{k}{\varepsilon_j} \frac{e^{\beta / \varepsilon_j} \left( \frac{\beta}{\varepsilon_j} \right)^{\beta / \varepsilon_j}} \left[ e^{\beta / \varepsilon_j} \left( \frac{\beta}{\varepsilon_j} \right) - 1 \right] \]  
(2.10)

is the contribution to the specific heat of a crystal due to a phonon mode \((\varepsilon_j)\). The heat current (2.6) may be rewritten

\[
\dot{Q} = - \sum_{\varepsilon_j} \left[ \mathbf{\nabla} \cdot (\mathbf{\nabla} T) \right] \tau(\varepsilon_j) S(\varepsilon_j) \dot{\mathbf{v}}(\varepsilon_j) \]  
(2.11)

and compared with the definition of the thermal conductivity tensor \(\kappa_{lm}\).
\[ Q_x = - \sum_n \kappa_{x,m} (\nabla T)_m \]  

(2.12)

to yield

\[ \kappa_{x,m} = \sum_{k_j} v_x(\varepsilon_j) v_m(\varepsilon_j) \tau(\varepsilon_j) S(\varepsilon_j). \]  

(2.13)

In this thesis, the crystals which are to be investigated have cubic symmetry. For such crystals the thermal conductivity tensor is proportional to the identity; that is

\[ \kappa_{x,m} = \kappa \delta_{x,m} \]  

(2.14)

or

\[ \kappa = \frac{1}{3} \tau (\kappa_{x,m}). \]  

(2.15)

Then, the thermal conductivity of dielectric solids with cubic lattices is

\[ \kappa = \frac{1}{3} \sum_{\varepsilon_j} v^3(\varepsilon_j) \tau(\varepsilon_j) S(\varepsilon_j). \]  

(2.16)

Equation (2.13), and its particular case (2.16), represents a complete formal solution for the thermal conductivity of dielectric solids. Since both the group velocities and specific heat contributions may be calculated from the phonon angular frequency spectrum of a crystal, all that is required for the calculation of the thermal conductivity of any particular dielectric solid is its phonon angular frequency spectrum and the relaxation time for each phonon made. The angular frequencies of the phonons may be calculated from the secular equation of the dynamical matrix (1.11). The relaxation times are calculated in the next
2. RELAXATION TIMES

In the summary of lattice dynamics in Chapter I, it was stated that interactions among the phonons of a crystal occur as a result of anharmonicities in the expansion of the crystal potential energy. The cubic anharmonic term involves a summation over triples of phonon modes and represents all possible interactions among three phonons. These interactions are called "three-phonon processes". Higher order anharmonic terms represent interactions among larger numbers of phonons. They do not contribute significantly to the thermal conductivity (Berman, Simon, and Wilks (1951).) and are ignored in the derivation of a formula for the relaxation times.

The transport equation. In his review article Klemens (1958) gives the following transport equation for the phonon distribution $N(E_j)$, considering only three-phonon processes.

$$
t \frac{dN}{dt} = \frac{3k}{M^3} \sum_{E_j} \left| c(E_j, E'_j, E''_j) \right|^2 \frac{1 - \cos \omega t}{(\omega)^2} \frac{[(N + 3N') - NNN'']}{\omega \omega' \omega''}
$$

(2.17)

where

$$
\omega = \omega(E_j), \omega' = \omega(E'_j), \omega'' = \omega(E''_j)
N = N(E_j), N' = N(E'_j), N'' = N(E''_j)
$$

(2.18)

$$
\Delta \omega = \pm \omega \pm \omega' \pm \omega''
$$

(2.19)
and \( c(jj'j'') \) is the cubic coefficient in the expansion of the crystal potential energy in normal coordinates.

The "resonance factor" of the transport equation

\[
\frac{1 - \cos \omega t}{(\Delta \omega)^2}
\]

(2.20)
is the time dependent part of the quantum mechanical probability for the interaction of three phonons of the modes \((\tilde{X}_j), (\tilde{X}'_j),\) and \((\tilde{X}''_j)\). It ensures that the only significant contributions to the transport equation are from those interactions with \( \Delta \omega \) almost equal to zero. Later in this section it will be shown that for times \( t \) much greater than \( |\omega|^{-1} \), the resonance factor behaves like a Dirac delta function selecting only those processes for which

\[
\Delta \omega = 0.
\]

(2.21)

In the quantum mechanical treatment the operators \( \hat{a}(\tilde{X}_j) \) corresponding to the normal coordinates \( a(\tilde{X}_j) \) are coordinate operators for harmonic oscillators. They allow the number of phonons in any mode to change only by the "creation" or "destruction" of one phonon. For interactions among the three phonon modes \((\tilde{X}_j), (\tilde{X}'_j),\) and \((\tilde{X}''_j)\) with the resultant number of phonons in each mode being \( N, N' \), and \( N'' \), respectively, the probability of the creation of one phonon in each mode is proportional to

\[
\frac{N N' N''}{\omega_0' \omega''}. \]

(2.22)
and the probability for the destruction of one phonon in each mode is proportional to

\[
\frac{(N+i)(N'+i)(N''+i)}{\omega \omega' \omega''} \quad (2.23)
\]

However, the presence of the cubic coefficient in the transport equation requires that the wave vectors of the three interacting phonons be related by the condition (1.18). The result of this condition is that (2.22) really represents the annihilation of at least one of the phonons and (2.23) really represents the creation of at least one of the phonons. With the difference between (2.23) and (2.22) as a factor, the right hand side of the transport equation is the probable change in the number of phonons in the mode \( \vec{k}_j \) at time \( t \) due to three-phonon processes.

The problem with the transport equation as it stands in (2.17) is that it contains time as an explicit variable in a form which prevents its elimination by simple algebraic manipulation. Unless this explicit time dependence is eliminated from the transport equation, it is impossible to use the relaxation law (2.7) to derive time independent relaxation times.

**Elimination of the time dependence of the transport equation.** For convenience the transport equation is written

\[
\frac{\partial N}{\partial t} = \sum_{k'k''}^j A_{j'j''}^{k'k''} \frac{1 - \cos \omega t}{(\omega)^2}, \quad (2.24)
\]

where \( A_{j'j''}^{k'k''} \) includes all of the time independent factors of the
right hand side of (2.17). The condition (1.18) permits the summation over $\mathbf{K}''$ to be eliminated from (2.24) by making the substitution

$$
\mathbf{K}'' = \mathbf{K}^* - \mathbf{K} - \mathbf{K}'
$$

(2.25)

so that the transport equation may be rewritten as

$$
\frac{dN}{dt} = \sum_{j j'} \sum_{\mathbf{K}'} A_{j j'}^* \mathbf{K}^* \mathbf{K} - \mathbf{K}' \frac{1 - \cos \Delta \omega t}{(\Delta \omega)^2} .
$$

(2.26)

If a large enough cyclic volume $V$ has been chosen, then the summation over the wave vector $\mathbf{K}'$ may be satisfactorily replaced by the following integrations

$$
\sum_{\mathbf{K}'} \longrightarrow \frac{V}{(2\pi)^3} \int d^3\mathbf{k}' = \frac{V}{(2\pi)^3} \int \frac{1}{|\nabla_{\mathbf{K}} \Delta \omega|} \ dS' d(\Delta \omega)
$$

(2.27)

where $\nabla_{\mathbf{K}}$ is the gradient operator in the space of the reciprocal lattice and $S'$ is the surface $\Delta \omega = 0$. With the substitution (2.27), equation (2.26) may be rewritten

$$
\frac{dN}{dt} = \sum_{j j''} \sum_{\mathbf{K}'} \frac{V}{(2\pi)^3} \int \frac{1}{|\nabla_{\mathbf{K}} \Delta \omega|} \ dS'(\Delta \omega) A_{j j''}^* \mathbf{K}^* \mathbf{K} - \mathbf{K}' \frac{1 - \cos \Delta \omega t}{(\Delta \omega)^2} .
$$

(2.28)

For $\Delta \omega \neq 0$, the resonance factor varies with $\Delta \omega$ approximately as

$$
1/ (\Delta \omega)^2
$$

(2.29)

but in the limit as $\Delta \omega \to 0$, the resonance factor becomes equal to

$$
t^2/2 .
$$

(2.30)

Therefore, on the assumption of large enough times, $t >> |\Delta \omega|^{-1}$
which for non zero $\Delta \omega$ is on the order of $|\omega|^{-1}$, the resonance factor is considerably larger for $\Delta \omega = 0$ than for $\Delta \omega \neq 0$. The integration over $\Delta \omega$ in (2.28) may be performed by removing every factor but the resonance factor from that integral and placing the restriction $\Delta \omega = 0$ on all factors in the integration over the surface $S'$. The result is

$$ T \frac{dn}{dt} = \sum_{j'j''} \frac{V}{(2\pi)^3} \int d \Delta \omega \int \frac{1 - \cos \Delta \omega}{(\Delta \omega)^2} A_{j'j''} \Delta \omega \left\{ \int ds' \frac{\partial < k^* >}{\partial \Delta \omega} \right\}. \quad (2.31) $$

The maximum and minimum values of $\Delta \omega$ are $+3 \omega_{\text{max}}$ and $-3 \omega_{\text{max}}$, respectively, where $\omega_{\text{max}}$ is the maximum angular frequency of the phonon modes. These, then, are the limits of the $\Delta \omega$ integration, but because of the largeness of $t$, the limits may be extended to infinity without significantly altering the value of the integral but simplifying its calculation. It is easily shown that

$$ \int_{-\infty}^{\infty} \frac{1 - \cos \Delta \omega}{(\Delta \omega)^2} d\Delta \omega = \pi t. \quad (2.32) $$

If this result is substituted into (2.31), the explicit time dependence cancels and the transport equation may be written as

$$ T \frac{dn}{dt} = \pi \sum_{j'j''} \frac{V}{(2\pi)^3} \int d \Delta \omega \int ds' \frac{1}{\nabla k \Delta \omega} A_{j'j''} \Delta \omega. \quad (2.33) $$

In any crystal for which the substitution (2.27) is valid, the number of phonon modes is so great that it is practically impossible to evaluate every angular frequency. Usually some method is found to approximate the actual distribution of
angular frequencies, such as considering only a uniformly distributed sample of all of the wave vectors. But any sample with few enough wave vectors to make the calculations feasible represents too few angular frequencies for the surface $S'$ to be known well enough that an integration over it could be performed. Instead, it is desirable to transform the integration back to a summation over $\vec{k}'$.

It is well known that if $S(x)$ is the Dirac delta function and $F(x)$ is any function continuous at $x=0$, then

$$\int_{-\infty}^{\infty} F(x) \delta(x) \, dx = F(0). \quad (2.34)$$

(See Lighthill (1962).) Putting $F(x)=1$ and $x=\Delta\omega/|\omega|^1$, equation (2.34) becomes

$$\int_{-\infty}^{\infty} \delta\left(\frac{\Delta\omega}{|\omega|}\right) \delta\left(\frac{\Delta\omega}{|\omega|}\right) = 1. \quad (2.35)$$

The left hand side of (2.35) may be inserted into the right hand side of equation (2.33) without changing the equation. The delta function need not appear because the restriction $\Delta\omega=0$ has the same effect on the integrals. The substitution (2.37) may be used to rewrite the transport equation as

---

1The substitution $x=\Delta\omega/|\omega|$ is used rather than $x=\Delta\omega$, so that with $F(x)=1$, (2.34) is dimensionless and independent of the phonon modes $(\vec{k}'j')$ and $(\vec{k}''j'')$. The absolute value of $\omega$ is used to that when (2.35) is substituted into (2.33) the signs of the terms of the summations are not changed.
\[
\frac{dN}{dt} = \pi \sum_{j,j''} \sum_{k,k'} \frac{1}{\omega \omega'} A_{j,j''}^{k,k'} \delta(k' - k, \omega - \omega')
\]

or, replacing \(k' - k\) by \(\kappa''\) and writing \(A_{j,j''}^{k,k''}\) explicitly

\[
\frac{dN}{dt} = \frac{\pi T}{M^3} \sum_{k,k''} \frac{1}{\omega \omega''} \left[(N+N')(N''+1) - NN''\right].
\]

The energy of a phonon with angular frequency \(\omega\) is \(\hbar \omega\), therefore, the condition \(\Delta \omega = 0\) means that only those interactions which conserve energy contribute to the rate of change of \(N(\kappa_j)\). Before deriving relaxation times from (2.37) it is possible to simplify the equation by approximating the factor containing the phonon distributions \(N\), \(N'\), and \(N''\).

**Approximation of the phonon distribution factor.** The factor of (2.57) which contains the phonon distributions is

\[
\left[(N+1)(N'+1)(N''+1) - NN'N''\right]
\]

which may be expanded in terms of the deviations \(n\), \(n'\), and \(n''\).

\[
(n'n + nn'' + n'n') + (n + n' + n'' + 1) + n(n' + n'' + 1) + n'(n + n'' + 1) + n''(n + n' + 1)
\]

The term in (2.39) which is independent of the deviations from equilibrium may be shown to be zero because of the condition \(\Delta \omega = 0\) and the algebraic form of the equilibrium distributions.
In Section II.1 it was assumed that the deviations from equilibrium were small. Therefore, the term of (2.39) which is quadratic in the \( n \)'s may be neglected compared with the linear terms. To first order, (2.38) is

\[ n(n' + n'' + 1) + n'(n + n'' + 1) + n''(n + n') \tag{2.40} \]

Klemens (1958) gives the following alternative to equation (2.9) for the deviations

\[ n = \frac{\lambda}{\kappa T} \frac{\partial \eta}{\partial x} \tag{2.41} \]

where

\[ \chi = \frac{\lambda \omega}{\kappa T} \tag{2.42} \]
\[ \lambda \frac{\nabla T}{T} \sim \kappa \nu^2 \tau \tag{2.43} \]

It will be shown later in this section that the only important feature of the vector \( \lambda \) is that it is parallel to the temperature gradient \( \nabla T \). If the deviations from equilibrium given by (2.41) are substituted into (2.40), use may be made of the fact that for \( \Delta \omega = 0 \)

\[ \frac{3n}{\partial x} (n' + n'' + 1) = \frac{3n'}{\partial x} (n + n'' + 1) = \frac{3n''}{\partial x} (n + n') = -\eta n' \eta'' \tag{2.44} \]

to show that (2.40) is equal to

\[ -\frac{\lambda}{\kappa T} \frac{\partial \lambda}{\partial x} \eta n' \eta'' = \frac{\lambda}{\kappa T} \frac{\partial \lambda}{\partial x} n(n' + n'' + 1) \tag{2.45} \]
A formula for the relaxation times. In terms of the first order approximation to the phonon distribution factor (2.38), the transport equation is

$$\frac{dN}{dt} = n \frac{2 \pi k}{M^2} \sum_{j,j''} \left| c_{j,j',j''} \right|^2 \frac{\hat{\alpha} \cdot \hat{K}}{\hat{\alpha} \cdot \hat{K}} (\eta' + \eta'' + 1). \quad (2.46)$$

A formula for the relaxation times follows directly from (2.46) and the relaxation law (2.7).

$$\frac{1}{\tau} = -\frac{1}{n} \frac{dN}{dt} = -\frac{2 \pi k}{M^2} \sum_{j,j''} \left| c_{j,j',j''} \right|^2 \frac{\hat{\alpha} \cdot \hat{K}}{\hat{\alpha} \cdot \hat{K}} (\eta' + \eta'' + 1). \quad (2.47)$$

The factor of (2.47) which contains the vector \( \hat{\alpha} \) is

$$\frac{\hat{\alpha} \cdot \hat{K}}{\hat{\alpha} \cdot \hat{K}}. \quad (2.48)$$

Since \( \hat{\alpha} \) appears in both the numerator and denominator of (2.48), only its direction (parallel to the temperature gradient) affects the evaluation of the relaxation times. In the calculation of the thermal conductivity of cubic crystals using (2.16), the summation over the wave vector \( \hat{K} \) includes wave vectors uniformly distributed throughout the first Brillouin zone, so that any choice for the direction of \( \hat{\alpha} \) is equivalent to any other choice.

The presence of the reciprocal lattice vector \( \hat{K} \) in (2.48) allows two types of interaction to be distinguished. In "normal processes" or "N-processes"

$$\hat{K} + \hat{K} + \hat{K}'' = 0. \quad (2.49)$$
These processes do not contribute to the relaxation times or the thermal conductivity because they cause the factor (2.48) to vanish. Therefore, N-processes do not allow the phonon modes to return to equilibrium. However, they may be useful in rearranging the contents of the phonon modes so that the second type of interaction may occur. "Umklapp processes" or "U-processes" are those for which

$$\bar{k} + \bar{k}' + \bar{k}'' = \bar{k} \neq 0.$$  \hfill (2.50)

Those are the only three-phonon processes which contribute to the thermal conductivity of dielectric solids.

3. HIGH AND LOW TEMPERATURES

For very high temperatures,

$$\tau \gg \hbar \omega_{\text{max}} / k,$$  \hfill (2.51)

the temperature dependence of the relaxation times and the thermal conductivity assumes a very simple form. The temperature dependence of equation (2.47) for the relaxation times is through the factor containing the phonon equilibrium distributions which for temperatures satisfying (2.51) has the form

$$\eta' + \eta'' + 1 \approx -\frac{e}{\omega^2} \kappa \tau.$$  \hfill (2.52)

Each term in (2.47) has this temperature dependence. The result is that

$$\tau \propto \frac{1}{T}.$$  \hfill (2.53)
The thermal conductivity depends on the temperature through the relaxation times and the specific heat contributions. But for high temperatures the specific heat contributions are almost constant,

\[ S(E_j) \propto \kappa, \quad (2.54) \]

so that the thermal conductivities have the same temperature dependence at high temperatures as the relaxation times,

\[ \kappa(T) \propto \frac{1}{T}. \quad (2.55) \]

Therefore, in the limit of very high temperatures the effect of the cubic anharmonicities on the thermal conductivity agrees with that found experimentally. However, temperatures satisfying (2.51) are much higher than the temperature at which the behavior (2.55) is found experimentally. Therefore, the prediction (2.55) is not relevant to the experimental situation.

In order to examine low temperatures it is tempting to write, in analogy with (2.51)

\[ T \ll \hbar \omega_{\text{min}} / \kappa. \quad (2.56) \]

Unfortunately there is no non-zero minimum value for the angular frequencies and since the equations for the relaxation times and the thermal conductivity contain summations over all phonon modes, the expression (2.56) has no meaning. What may be written though, is that for

\[ T \ll \hbar \omega(E_j) / \kappa \quad (2.57) \]
the equilibrium number of phonons in the mode $\langle \vec{k}^j \rangle$ is

$$\mathcal{N}(\vec{k}^j) \approx \exp \left[ -\frac{\kappa \omega(\vec{k}^j)}{\kappa T} \right]$$

which for low temperatures is very small. For $T = \theta K$, there are no phonons in any mode, the specific heat contribution of every mode vanishes, and the relaxation times given by (2.47) have finite non-zero values. Therefore, the thermal conductivity due to three-phonon processes vanishes, as it must if there are no phonons to carry heat in the crystal.
CHAPTER III

THERMAL CONDUCTIVITY OF INERT GAS SOLIDS

In this chapter, the theory of the previous two chapters is applied to a model for the inert gas solids. It is shown that the problem of calculating the thermal conductivity of all of the inert gas solids for which the model is valid may be reduced to the problem of calculating the thermal conductivity of one of the solids and a set of constants for the other solids.

1. THE MODEL

The theory of Chapters I and II is sufficient for the calculation of the thermal conductivity due to three phonon processes for any dielectric solid about which enough is known that the crystal potential energy may be written as a Taylor series expansion in the displacements of the atoms of the crystal from their equilibrium positions. This may be accomplished by defining the form of the interaction among the atoms and the structure of the crystal lattice.

Interatomic interaction. Whalley and Schneider (1955) have shown that experimental data for gaseous neon, argon, and krypton may be satisfactorily calculated if the interaction among the atoms is pairwise and of the form

$$\varphi (r) = 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^2 - \left( \frac{\sigma}{r} \right)^6 \right].$$

(3.1)
\( \varphi(\gamma) \) is the Lennard-Jones 12:6 potential energy function for a pair of atoms whose centres are separated by a distance \( \gamma \). The parameters \( \varepsilon \) and \( \sigma \) have values characteristic of the gas to which they apply. In terms of the formula (3.1), \( \sigma \) is the value of \( \gamma \) for which the potential energy is zero and \(-\varepsilon\) is the minimum value of the potential energy.

The attractive part of the 12:6 potential energy, the inverse sixth power term, may be derived by considering the interaction between the instantaneous dipole moments of a pair of interacting, electrically neutral, chemically inert atoms. The inverse twelfth power term in the 12:6 potential energy has no physical significance. It represents a short range repulsive force which prevents the gas from collapsing, but the particular form of this term was chosen for ease of mathematical manipulation.

Grindlay and Howard (1964) have used the 12:6 potential energy to calculate the lattice energy at \( 0^\circ K \) and the Debye function of solid argon and krypton. From their calculations they obtained values for \( \varepsilon \) and \( \sigma \) which agreed well with the experimentally determined values for gaseous argon and krypton. On the basis of this success, it is assumed that the potential energy of a crystal of the inert gas solids is

\[
\Phi = \frac{1}{2} \sum_{i,j} \varphi(\gamma_{ij}),
\]

(3.2)
where \( \varphi(r_{ij}) \) is the 12:6 potential energy of the atoms labelled \( i \) and \( j \). The prime on the summation means that \( i \) and \( j \) vary over every atom in the crystal except \( i \neq j \). The numerical values of \( \sigma \) and \( \alpha \) used in subsequent calculations are those of the gaseous state of the inert gases. These values are listed in TABLE I.

The lattice. Except for helium the inert gases crystallize in face centred cubic lattices. Since this is a particularly simple type of lattice with which to work, in what follows it is assumed that the inert gas solids being considered are neon, argon, krypton, and xenon.

For a face centred cubic lattice with lattice spacing \( a \), the vectors which generate the lattice are

\[
\begin{align*}
\vec{a}_1 &= \frac{a}{\sqrt{2}} (0,1,1) \\
\vec{a}_2 &= \frac{a}{\sqrt{2}} (1,0,1) \\
\vec{a}_3 &= \frac{a}{\sqrt{2}} (1,1,0).
\end{align*}
\] (3.3)

The corresponding reciprocal lattice is body centred cubic and is generated by the vectors

\[
\begin{align*}
\vec{b}_1 &= \frac{2\pi}{a} (-1,1,1) \\
\vec{b}_2 &= \frac{2\pi}{a} (1,-1,1) \\
\vec{b}_3 &= \frac{2\pi}{a} (1,1,-1).
\end{align*}
\] (3.4)

There are two ways in which the atoms may be labelled. The first method uses the lattice vectors (3.3). For any integers \( m, m_1, \) and \( m_2 \), the atom labelled \( \vec{m} \) has the equilibrium position
<table>
<thead>
<tr>
<th></th>
<th>( M^a ) (amu)</th>
<th>( E^b ) ((10^3) joule)</th>
<th>( a_0^{bc} ) ((10^9) m)</th>
<th>( \alpha^c ) (°K)</th>
<th>( \alpha \tilde{v}_{\text{max}}^d ) (°K)</th>
<th>( \Theta^e ) (°K)</th>
<th>( \lambda = KT ) (10^-4 erg/cm·sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>20.18</td>
<td>0.492</td>
<td>4.35</td>
<td>12.035</td>
<td>92.32</td>
<td>64 e</td>
<td>75 e</td>
</tr>
<tr>
<td>Argon</td>
<td>39.94</td>
<td>1.69</td>
<td>5.31</td>
<td>12.831</td>
<td>98.42</td>
<td>80 e</td>
<td>250 e</td>
</tr>
<tr>
<td>Krypton</td>
<td>83.80</td>
<td>2.30</td>
<td>5.68</td>
<td>9.7854</td>
<td>75.06</td>
<td>63 e</td>
<td>270 e</td>
</tr>
<tr>
<td>Xenon</td>
<td>131.30</td>
<td>3.11</td>
<td>6.1</td>
<td>8.450</td>
<td>64.82</td>
<td>76.1 f</td>
<td>732 f</td>
</tr>
</tbody>
</table>

- \(1\text{amu} = 1.6604 \times 10^{-27}\) kg
- Dobbs and Jones (1957)
- \(\alpha = \frac{k}{R} \left( \frac{2}{a_0} \right) \sqrt{\frac{8e}{m}}\), \(a_0 = 1.542\sigma\)
- \(\tilde{v}_{\text{max}} = 7.6706\)
- White and Woods (1958)
- Julian (1965)
In the second method the atom labelled $\vec{m}$ has the equilibrium position

$$\vec{R}^{\vec{m}} = \frac{a}{2} (m_1, m_2, m_3) = \frac{a}{2} \vec{m}$$

(3.6)

where $m_1$, $m_2$, and $m_3$ are any integers such that

$$m_1 + m_2 + m_3 = \text{even integer.}$$

(3.7)

In the following analysis, it is convenient to use the second method of denoting the equilibrium positions of the atoms.

Points of the reciprocal lattice are given by

$$\vec{K} = h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3$$

(3.8)

where $h_1$, $h_2$, and $h_3$ are integers.

2. PHONON FREQUENCIES

The angular frequencies for the phonon modes of the inert gas solids may be obtained by solving the secular equation of the dynamical matrix. For the model of the inert gas solids presented in Section III.1 the dynamical matrix is

$$D_{\alpha \beta}(\vec{K}) = \frac{8 \varepsilon}{M} \sum_{\vec{R}} \left\{ \left( \frac{\sigma^2}{|\vec{R}|^2} - \frac{12 \sigma^2}{|\vec{R}|^4} \right) \delta_{\alpha \beta} 
- \left( \frac{\gamma \sigma^2}{|\vec{R}|^2} - \frac{16 \sigma^2}{|\vec{R}|^4} \right) \delta_{\alpha \beta} \right\} \sin \left( \frac{\vec{K} \cdot \vec{R}}{2} \right)$$

(3.9)

The summation extends over all lattice sites in the crystal.
As it stands in (3.9), the dynamical matrix must be evaluated separately for every solid to be considered. However, it is possible to write the dynamical matrix as a product of a constant characteristic of the solid being examined and a matrix independent of the specific properties of the inert gas solids.

Neglecting the zero point energy of the inert gas solids, it is possible to calculate the lattice spacing at \( 0^\circ K \), \( a_o \), in terms of the parameter \( \sigma \). Grindlay and Howard (1964) have performed this calculation and found that for all solids for which the model is valid

\[
a_o = 1.542 \sigma.
\]

In what follows thermal expansion is neglected and the relation (3.10) is assumed to be valid at all temperatures with \( a_o \) replaced by \( a \).

If the form of \( \vec{R} \vec{m} \) given by (3.6) is substituted into (3.9), the dynamical matrix may be rewritten as

\[
D_{\alpha\beta}(\vec{k}) = \frac{2\pi}{\lambda a^2} \tilde{D}_{\alpha\beta}(\vec{q}),
\]

where

\[
\tilde{D}_{\alpha\beta}(\vec{q}) = \sum_{\gamma} \left\{ \left( \frac{6b^6}{m\delta} - \frac{12b^2}{m\gamma} \right) D_{\alpha\beta} - \left( \frac{48b^6}{m\alpha} - \frac{16b^2}{m\kappa} \right) m_{\alpha} m_{\kappa} \right\} \sin^2 \left( \frac{\pi}{2} \frac{q}{\lambda} \right).
\]

(3.12)
is the "reduced dynamical matrix"\(^1\),
\[
\mathbf{\tilde{q}} = \frac{a}{2\pi} \mathbf{k}
\]  
(3.13)
is the "reduced wave vector", and
\[
b \equiv 2\sigma/a = 1.297.
\]  
(3.14)
The reduced dynamical matrix is not dependent on the particular properties of the solid being considered. It has the same eigenvectors \(\mathbf{e}\) as does \(D_{\alpha\beta}(k)\), but its eigenvalues are \(\tilde{\omega}\) where
\[
\tilde{\omega} = \frac{a}{2\sqrt{\frac{M}{8\varepsilon}}} \omega
\]  
(3.15)
is the "reduced frequency". As with the eigenvalues of \(D_{\alpha\beta}(k)\), the eigenvalues of \(\tilde{C}_{\alpha\beta}(\mathbf{q})\) are labelled by the polarization index \(j\), which is assigned so that
\[
\tilde{\omega}^2(\mathbf{q},1) \leq \tilde{\omega}^2(\mathbf{q},2) \leq \tilde{\omega}^2(\mathbf{q},3).
\]  
(3.16)The phonon modes with \(j = 3\) are called "longitudinal" modes and the modes with \(j = 1\) or \(2\) are called "transverse" modes. These names do not necessarily describe the manner in which the phonons are propagated. They have been assigned only for the purpose of distinguishing the phonon mode with the highest phase velocity \((\omega/|k| \ll \tilde{\omega}/|q|)\) for a given reduced wave vector from the other two modes (Klemens (1958)).

---

\(^1\)Throughout this chapter several "reduced" quantities are introduced. In most cases they are denoted by a tilde above the symbol for that quantity.
The form of the reduced dynamical matrix as a summation over the lattice sites of a face centred cubic crystal in equation (3.12) is too complicated to allow its evaluation in a closed form. For any reduced wave vector $\vec{q}$ the elements $\xi_{\omega\rho}(q)$ must be evaluated numerically and the reduced frequencies obtained by solving the secular equation of the reduced dynamical matrix. However, this need not be done for every reduced wave vector, because the symmetry of the crystal lattice causes many reduced wave vectors to be equivalent.

Both the direct and reciprocal lattices of crystals of the inert gas solids have the symmetry of the cubic point group $\bar{O}_h$. For any element $R$ of the group $\bar{O}_h$ the symmetry operator $O_R$ is such that if $\vec{q}$ is any reduced wave vector then so is

$$\vec{q}' = O_R \vec{q}.$$  \hspace{1cm} (3.17)

The symmetry operators $O_R$ represent combinations of rotations, reflections, and inversions and their application to a reduced wave vector changes the corresponding reduced dynamical matrix by an orthogonal transformation, which does not change the reduced frequencies. For any $\vec{q}'$ satisfying (3.17)

$$\Xi^\times(\vec{q}',j) = \Xi^\times(\vec{q},j)$$ \hspace{1cm} (3.18)

$$\Xi(\vec{q}',j) = O_R^{-1} \Xi(\vec{q},j).$$ \hspace{1cm} (3.19)

The group $\bar{O}_h$ represents forty eight symmetry operations which
divide the first Brillouin zone into forty eight different but equivalent "irreducible regions". One such irreducible region contains all reduced wave vectors for which

\[
\begin{align*}
0 \leq y_3 \leq y_2 \leq y_1 & \leq 1, \\
0 \leq y_1 + y_2 + y_3 & \leq \frac{3}{2}.
\end{align*}
\]  

(3.20)

Calculations of the reduced frequencies and polarization vectors need be performed only for those phonon modes whose reduced wave vectors lie in the irreducible region defined by (3.20). The reduced frequencies and polarization vectors of every other phonon mode may be obtained from these calculations by means of equations (3.18) and (3.19).

For cyclic volumes of macroscopic size the number of phonon modes is on the order of \(10^{23}\). Even the reduction in the amount of calculation provided by the symmetry of the lattice is not enough to make the calculation of \(\tilde{\omega}\) and \(\tilde{e}\) for every phonon mode practically possible. An approximation to the actual distribution of reduced frequencies may be obtained by performing the calculations for a network of uniformly distributed, sample reduced wave vectors. This method of sampling the phonon modes of a crystal with macroscopic cyclic volume is equivalent to the solution for \(\tilde{\omega}\) and \(\tilde{e}\) of every phonon mode in a crystal with a very much smaller cyclic volume.
3. CUBIC TERM OF THE CRYSTAL POTENTIAL ENERGY

The contribution of the cubic anharmonicities to the crystal potential energy is

\[ \sum_{i,j} c(i,j,j') a(k_i) a(k'_j) a(k''_j), \]  

(3.21)

where

\[ c(i,j,j') = \frac{1}{3!} \sum_{\rho \neq \sigma} \left( \frac{\partial^3 \Phi}{\partial \rho_i \partial \rho_j \partial \rho'_j} \right) e_\rho e'_\rho e'' \]  

(3.22)

is the cubic coefficient defined by (1.17). The result of applying the model for inert gas solids to equation (3.22) is

\[ c(i,j,j') = \frac{N}{3!} \sum_{\rho} \sum_{\tilde{R}} \chi^{\tilde{R}} \Delta(\tilde{R} + \tilde{R} + \tilde{R}''). \]  

(3.23)

\( N \) is the number of atoms in the cyclic volume. The function

\[ \Delta(\tilde{R}) = \begin{cases} 1, & \text{if } \tilde{R} = \tilde{R}^r \\ 0, & \text{otherwise} \end{cases} \]  

(3.24)

is responsible for the condition (1.18) which allows only N-processes and U-processes. The other symbols in (3.23) are defined as

\[ \chi^{\tilde{R}} = 2 \left\{ \varphi''(R^2) (\tilde{R} \cdot \tilde{R}'') (\tilde{R} \cdot \tilde{R}') + \varphi''''(R^2) \tilde{R} \cdot \left[ \tilde{R}' \cdot (\tilde{R}' \cdot \tilde{R}'') + \tilde{R}'' \cdot (\tilde{R} \cdot \tilde{R}'') \right] \right\} \]  

(3.26)

The derivatives which appear in (3.26) are

\[ \varphi''(R^2) = \left( \frac{2}{(2R^2)^2} \varphi(R) = 24 \varepsilon \left[ \frac{2 \sigma^2}{R^{12}} - \frac{2 \sigma^6}{R^6} \right] \right) \]  

(3.27)

\[ \varphi'''(R^2) = \left( \frac{2}{(2R^2)^3} \varphi(R) = -48 \varepsilon \left[ \frac{4 \sigma^2}{R^{18}} - \frac{4 \sigma^6}{R^{12}} \right] \right) \]  

(3.28)
If the form of $\tilde{R}^*=\tilde{R}^*\equiv -8i\sin(\frac{\pi}{2}\tilde{g}^*\tilde{m})\sin(\frac{\pi}{2}\tilde{q}^*\tilde{m})\sin(\frac{\pi}{2}\tilde{y}^*\tilde{m})\epsilon_{\tilde{m}}^2[\tilde{s}^*\tilde{g}^*\tilde{q}^*\tilde{y}^*\tilde{m}]$ (3.29)

$\tilde{\chi}^*\equiv \frac{1}{\epsilon}(\frac{a}{2})^3 \tilde{\chi}^* = 2\left\{ \tilde{\varphi}'''(m^2)(\tilde{m}^2\tilde{e}^*\tilde{m}^2\tilde{e}^*) + \tilde{\varphi}'''(m^2)\tilde{m}^2[(\tilde{e}^*\tilde{e}^*)(\tilde{e}^*\tilde{e}^*\tilde{e}^*) + (\tilde{e}^*\tilde{e}^*)(\tilde{e}^*) + (\tilde{e}^*)^2]\right\}$ (3.30)

with

$\varphi''(m^2)\equiv \frac{1}{\epsilon}(\frac{a}{2})^4 \varphi''(\tilde{m}^2) = 24\left[ \frac{7b^2}{m^4} - \frac{3b^2}{m^6}\right]$ (3.31)

$\tilde{\varphi}''(m^2)\equiv \frac{1}{\epsilon}(\frac{a}{2})^6 \varphi''(\tilde{m}^2) = -48\left[ \frac{2b^2}{m^8} - \frac{b^2}{m^{10}}\right]$ (3.32)

so that

$\mathcal{E}^*_{(\tilde{j}\tilde{j}'\tilde{j}'')}\equiv \frac{3!}{\epsilon N}(\frac{a}{2})^3 \sum_{\tilde{m}^2} \tilde{R}^* \tilde{R}^* \tilde{R}^*$ (3.33)

4. RELAXATION TIMES

If the angular frequencies, the wave vectors, and the cubic coefficient in equation (2.47) for the relaxation times are replaced by the corresponding reduced quantities, it is possible to define a reduced relaxation time $\tilde{\tau}$ such that

$$\frac{1}{\tau(\tilde{R})} = -\frac{2\pi^2}{m} \left( \frac{N}{2\pi a} \right)^2 \frac{1}{\mathcal{E}(\tilde{k})}$$ (3.34)

where, from (2.47)

$$\frac{1}{\mathcal{E}(\tilde{k})} = \sum_{\tilde{j}\tilde{j}'\tilde{j}''} \frac{|c(\tilde{j}\tilde{j}'\tilde{j}'')|^2}{\tilde{E}(\tilde{j})^2} (\tilde{\eta}^* \tilde{\eta}^* \tilde{\eta}^* \tilde{\eta}^* \tilde{\eta}^* \tilde{\eta}^*) \frac{\tilde{R}^* \tilde{R}^* \tilde{R}^*}{\tilde{R}^* \tilde{R}^* \tilde{R}^*}$$ (3.35)
and
\[ \overline{B}^R \equiv \frac{a}{2\pi c} \overline{L}^R. \] (3.36)

The reduced relaxation times have the temperature dependence for
the factor containing the phonon equilibrium distributions \( \mathcal{N} \) and \( \mathcal{N}'' \) which are of the form
\[ \mathcal{N} = \mathcal{N} \left( \frac{\alpha}{\pi} \right) = \left[ \exp \left( \frac{\alpha^2}{\pi} \right) - 1 \right]^{-1} \] (3.37)
\[ \alpha \equiv \frac{n}{k} \left( \frac{2}{a} \right) \sqrt{\frac{M}{\varepsilon}}. \] (3.38)

Therefore
\[ \tilde{\tau}(\overline{q}, \overline{\alpha}) = \tilde{\tau}(\overline{q}, \overline{\alpha}). \] (3.39)

The reduced relaxation time at the temperature \( T \), of
a solid with \( \alpha = \alpha_j \), is equal to that of the solid with \( \alpha = \alpha_2 \) at
the temperature
\[ T_2 = \frac{\alpha_2}{\alpha_1} T_1. \] (3.40)

Therefore, the reduced relaxation times of any inert gas solid
may be obtained from those of any other inert gas solid by means
of the equality
\[ \tilde{\tau}(\overline{q}, \overline{\alpha_1}) = \tilde{\tau}(\overline{q}, \frac{\alpha_1}{\alpha_2}) \] (3.41)
with \( T_2 \) given by (3.40).

5. THERMAL CONDUCTIVITY

If the phonon group velocity (2.1) is written in terms
of the reduced frequency and reduced wave vector, the reduced
group velocity is defined as
With the reduced quantities defined so far, equation (2.16) for the thermal conductivity $\kappa$ may be written to define the "reduced thermal conductivity",

$$\tilde{\kappa} = \frac{4\pi^3 k}{\hbar^2} \frac{(N/2)^2}{\bar{\epsilon}} \kappa = \sum_{j,j'} \bar{\epsilon}^2(j,j') \tilde{\epsilon}(j,j',\bar{\epsilon}) S(j,j',\bar{\epsilon}). \tag{3.43}$$

Both the reduced relaxation times and the specific heat contributions depend on temperature through the variable

$$\left( \frac{\alpha}{\tau} \right) \tag{3.44}$$

As a result, so does the reduced thermal conductivity.

If $\tilde{\gamma}_{\text{max}}$ is the maximum value of the reduced frequency for all phonon modes, the characteristic temperature $\Theta$ is defined to be

$$\Theta = \alpha \tilde{\gamma}_{\text{max}}, \tag{3.45}$$

which is the high temperature limit of the Debye $\Theta$-function. In the following analysis the variation of $\Theta$ with temperature is ignored because $\Theta(\tau)$ deviates from its high temperature limit by less than eight per cent (Grindlay and Howard (1964).) and because the results of this study are expected to give good agreement with experimental data only for high temperatures.

The reduced thermal conductivity of two different inert gas solids with $\Theta_1 = \Theta_2$ and $\Theta = \Theta_2$ are related by the equation
In this chapter a model for the inert gas solids has been presented and applied to the general theory of lattice thermal conductivity developed in Chapter II. It has been shown that every quantity which must be calculated in order to evaluate the thermal conductivities, need not be calculated separately for each inert gas solid. Once the calculation of the reduced thermal conductivity has been performed for any particular inert gas solid, the thermal conductivity of any inert gas solid may be obtained from equations (3.46) and (3.43).
CHAPTER IV

CALCULATIONS

In this chapter the calculation of the thermal conductivities of the inert gas solids is outlined.

1. PRELIMINARY REMARKS

All of the data required for the calculation of the reduced quantities introduced in Chapter III were generated from the model of the inert gas solids by an electronic computer. Not until the thermal conductivities were calculated from the reduced thermal conductivity was any experimental data required. Although the value of \( Q \) for argon given in TABLE I was used in the calculations, any other value could have been chosen.

Lattice points. In order to perform the lattice sums from which the reduced dynamical matrix and the reduced cubic coefficients are calculated, the vectors \( \hat{\mathbf{r}} \) which label the atoms of the face centred cubic lattice were generated and grouped into shells of atoms with the same value of \( |\hat{\mathbf{r}}| \). In the calculations the contributions of the atoms were considered one shell at a time for successively larger values of \( |\hat{\mathbf{r}}| \), until every single remaining shell would contribute a relative amount of less than \( 10^{-4} \) to the lattice sums. In all cases not more than the forty seven shells with \( |\hat{\mathbf{r}}| \leq 100 \) were required
for the calculations.

**Sampling points in the reciprocal lattice.** In order to approximate the reduced frequency spectrum, a network of sample reduced wave vectors was set up by dividing each of the coordinate axes of the space of the reciprocal lattice into \( N_0 \) equal intervals and writing

\[
\vec{y} \equiv \left( \frac{n_1, n_2, n_3}{N_0} \right) = \frac{n}{N_0} \quad (4.1)
\]

where \( n_1, n_2, \) and \( n_3 \) are integers such that \( \vec{y} \) corresponds to an allowed wave vector (See Sections I.2 and III.2). The vectors \( \vec{v} \) which correspond to reduced wave vectors lying in the irreducible region (3.20) are restricted by the relations

\[
0 \leq n_1 \leq n_2 \leq n_3 \leq N_0 \\
0 \leq n_1 + n_2 + n_3 \leq \frac{3}{2} N_0 \quad (4.2)
\]

The second of the restrictions (4.2) requires that \( N_0 \) be even if \( \vec{v} \) is to represent points on the boundaries of the first Brillouin zone.

For this study the value of \( N_0 \) was chosen to be six, giving forty-six points in the irreducible region defined by (4.2) and 1046 wave vectors in the whole first Brillouin zone. A larger value of \( N_0 \) would have given a better approximation to the reduced frequency spectrum, but with \( N_0 = 6 \) the total amount of data generated in later phases of the calculations was great enough to cause problems because of limited storage space in the computer.
2. CALCULATION OF THE REDUCED THERMAL CONDUCTIVITY

**Reduced frequency spectrum.** The reduced dynamical matrix was calculated from equation (3.12) for each of the reduced wave vectors defined by (4.1) and (4.2) with \( N_0 = 6 \). As a result of the truncation of the lattice sum mentioned in Section IV.1, it was assumed that the relative error in each element of the reduced dynamical matrix was \( \pm 10^{-4} \). The reduced frequencies were calculated from the secular equation of the reduced dynamical matrix and the polarization vectors were obtained by solving the equation

\[
\tilde{\varepsilon}(\vec{q}) \equiv \langle \vec{q}_j \rangle = \tilde{\varepsilon}^2(\varepsilon_j) \tilde{\varepsilon}(\varepsilon_j); \ j = 1, 2, 3 \tag{4.3}
\]

for the three mutually perpendicular unit vectors \( \{\tilde{\varepsilon}(\varepsilon_j)\}_{j=1}^3 \).

Figure 1 is a histogram of the reduced frequency spectrum based on the sample of 1046 wave vectors obtained from the forty-six vectors \( \vec{n} \) found from (4.2) with \( N_0 = 6 \). The maximum value of the reduced frequency for this sample of wave vectors was

\[
\tilde{\nu}_{\max} = 7.6706. \tag{4.4}
\]

**Reduced group velocities.** The reduced group velocities were calculated from the reduced frequencies by a method of numerical differentiation. If the reduced group velocity of the phonon mode \( \left( \frac{2\pi}{N_0} \vec{n}, j \right) \) is to be calculated and if \( \tilde{\nu}\left( \frac{\vec{n}}{N_0}, j \right) \) is denoted by

\[
\tilde{\nu}_{l m p} \text{ where } \vec{n}' = (n_1+1, n_2+m, n_3+p) \tag{4.5}
\]
Figure 1. Histogram of the reduced frequency spectrum.
then

\[ \hat{\mathbf{u}} \left( \frac{\mathbf{F}}{N_0}, j \right) = N_0 \left( \hat{\mathbf{u}}_{000} / \partial \mathbf{F} \right) \]

\[ \approx \frac{N_0}{\pi} \left[ \hat{\mathbf{u}}_{000} - \hat{\mathbf{u}}_{000} \right], \left[ \hat{\mathbf{u}}_{000} - \hat{\mathbf{u}}_{000} \right], \left[ \hat{\mathbf{u}}_{000} - \hat{\mathbf{u}}_{000} \right]. \]

Each component of \( \hat{\mathbf{u}} \) in (4.6) is a three point differentiation formula derived from a three point Lagrangian interpolation formula. The fact that the point at which the derivatives are to be evaluated is a point used to obtain the interpolation formulas causes (4.6) to appear to be three two point formulas. (See, for example, Handbook of Mathematical Functions, National Bureau of Standards (1965).)

The error caused by the approximation of the reduced group velocity by the numerical formula (4.6) involves derivatives of the reduced frequencies and is much too difficult to evaluate in terms of the standard error formula. However, detailed consideration of the calculation of \( \hat{\mathbf{u}} \) for a few phonon modes indicated that the error in each component of the reduced group velocity was about one per cent.

In cases when the vectors \( \mathbf{F} \) used in formula (4.6) lay outside of the irreducible region (4.2), the values of the reduced frequency used in (4.6) were those corresponding to \( \mathbf{F}'' \) such that, for some symmetry operator \( O_\mathbf{F} \) of the group \( O_\mathbf{F} \) and some \( \mathbf{F}'' \) defined by (3.36),

\[ \mathbf{F}'' = O_\mathbf{F} (\mathbf{F}' + N_0 \mathbf{F}'' ) \]
did lay in the irreducible region (4.2).

**Contributing phonon processes.** The only three phonon processes which contribute to the reduced thermal conductivity are U-processes which conserve energy, that is

$$\Delta \vec{\nu} = \vec{\nu} + \vec{\nu} + \vec{\nu} = 0 \quad (4.8)$$

$$\vec{\nu} + \vec{\nu} + \vec{\nu} = \vec{k} \neq \vec{0} \quad (4.9)$$

Because of the fact that only a sparse sample of all of the reduced wave vectors was considered in the calculation of the reduced frequency spectrum, it seemed unlikely that (4.8) could be satisfied exactly for any triple of reduced frequencies. Instead, triples were sought such that

$$|\Delta \vec{\nu}| \leq \delta; \quad \delta > 0 \quad (4.10)$$

Since the phonon modes corresponding to $\vec{k} = \vec{0}$ have $\vec{\nu} = \vec{0}$, when they take part in a three phonon process, the interaction is just a two phonon process. Therefore the reduced frequencies which were considered for finding triples satisfying (4.10) had a non-zero lower bound, the minimum value of the reduced frequency spectrum in Figure 1. The value of $\delta$ was chosen to be much smaller than this minimum value which was 1.187.

For $\delta < 10^{-3}$ no triples of reduced frequencies satisfying (4.10) and (4.9) were found and for $\delta = 10^{-3}$ two such triples representing 192 U-processes were found. For $\delta = 3 \times 10^{-3}$ nineteen triples satisfying (4.10) and (4.9) were found. They represented
the 1080 U-processes which were chosen for the following calculation of the reduced thermal conductivity.

Actually, only three phonon processes satisfying (4.8) contribute to the reduced thermal conductivity. However, because the reduced frequencies are continuous functions of the discrete reduced wave vectors, it should be possible to find three allowed reduced wave vectors almost the same as \( \vec{q}' \), \( \vec{q}'' \), and \( \vec{q}''' \) such that (4.9) remains satisfied and for which (4.8) is satisfied. The 1080 U-processes used for the calculations in this thesis may be regarded as convenient approximations to processes which actually contribute to the reduced thermal conductivity.

**Reduced cubic coefficients.** The reduced cubic coefficients \( \mathcal{Z}(\vec{q}, \vec{q}', \vec{q}'') \) were calculated from (3.33) for each of the 1080 U-processes satisfying (4.10) with \( \mathcal{S} = 3x/\sigma^3 \). The lattice sums were performed by treating the atoms as parts of shells (See Section IV.1). The relative error in each reduced cubic coefficient was assumed to be \( \pm 10^{-4} \) because of the truncation of the lattice sum. The values of \( |\mathcal{Z}(\vec{q}, \vec{q}', \vec{q}'')|^2 \), which appear in the formula for the reduced relaxation times, ranged from about \( 10^{-4} \) to \( 10^6 \), but almost all were in the range \( 10^{-4} \) to \( 10^6 \).

**Reduced thermal conductivity.** The reduced relaxation
times ξ were not calculated explicitly. Instead, the reduced thermal conductivity was calculated in two steps.

In the first step the temperature dependent factors appearing in the formulas for the reduced relaxation times (3.35) and the reduced thermal conductivity (3.43) were calculated. In the second step the specific heat contributions and the factors

$$\eta' + \eta'' + 1$$  (4.11)

were calculated for each of the 1080 U-processes considered as contributing to the reduced thermal conductivity. These temperature dependent factors and the calculations of the first step were multiplied and added together according to the requirements of equations (3.35) and (3.43) to give the reduced thermal conductivity.

The calculations were performed for argon for which $\Theta = 98.42^\circ K$ (See TABLE I and Section III.5) for temperatures from $5^\circ K$ to $500^\circ K$. The lowest temperatures considered were lower than the temperature at which the maximum value of the experimental thermal conductivity occurs, and, therefore, in the region in which this analysis should not be expected to give good agreement with experimental data. Such temperatures were considered, in order that the temperature dependence of the contributions to the thermal conductivity due to three phonon processes could be determined in the temperature region.
for which the effects of crystal size and lattice defects become insignificant. The highest temperatures considered were far beyond the temperatures for which any of the inert gases remain solid, but at these temperatures the $T^{-1}$ dependence of the thermal conductivity should be more apparent than for lower temperatures.

Three directions for the vector $\vec{\lambda}$ (See Section II.2) were used in the calculations

$$\vec{\lambda} = \left\{ (1,0,0), (1,1,0), (1,1,1) \right\}$$

(4.12)

The values of the reduced thermal conductivity for these three directions did not differ from each other by more than one part in one hundred at low temperatures and one part in one thousand at high temperatures. TABLE II gives the average of these three values of the reduced thermal conductivity. The values have been normalized so that for $T = 10 \text{°C}$, $\tilde{\kappa} = 1.000 \text{ erg/°K}$. The temperatures for which the other inert gas solids have the same reduced thermal as argon have also been tabulated. These temperatures were calculated from the equation

$$T = \frac{\Theta}{\Theta_{\text{ARGON}}} T_{\text{ARGON}}$$

(4.13)

where $\Theta$ is one of the characteristic temperatures calculated from the parameters $\alpha$ and $\tilde{S}_{\text{max}}$. (See TABLE I).
TABLE II
REDUCED THERMAL CONDUCTIVITY FOR INERT GAS SOLIDS

<table>
<thead>
<tr>
<th>$\frac{T}{\Theta}$</th>
<th>$T_{argon}$ (°K)</th>
<th>$T_{neon}$ (°K)</th>
<th>$T_{krypton}$ (°K)</th>
<th>$T_{xenon}$ (°K)</th>
<th>$\tilde{K}(\frac{T}{\Theta})^a$</th>
</tr>
</thead>
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<tr>
<td>0.0508</td>
<td>5</td>
<td>4.69</td>
<td>3.81</td>
<td>3.29</td>
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<td>5.08</td>
<td>500</td>
<td>469</td>
<td>381</td>
<td>329</td>
<td>0.2076</td>
</tr>
</tbody>
</table>

$^a$Values normalized so that for $T_{argon} = 100°K$, $\tilde{K} = 1.000$. The value actually calculated was $1.375 \times 10^{-8}$ erg/°K.
3. TEMPERATURE DEPENDENCE OF THE REDUCED THERMAL CONDUCTIVITY

In examining the temperature dependence of the reduced thermal conductivity $\tilde{\kappa}$, two temperature regions are important. For temperatures just higher than the temperature at which the maximum value of the experimental thermal conductivity occurs, it is thought that the most important contributions are those due to interactions among the phonons. These interactions have been shown to be Umklapp processes, and this temperature region is called the "Umklapp region." The other important temperature range is the "high temperature region" for which the experimental thermal conductivity varies as $T^{-\gamma}$.

**Umklapp region.** In the Umklapp region,

$$\frac{1}{20} \leq \frac{T}{\Theta} \leq \frac{1}{8}$$

(4.14)

(Julian (1965).), it is expected that the temperature dependence of both $\kappa$ and $\tilde{\kappa}$ should be of the form

$$\tilde{\kappa} \propto \left( \frac{T}{\Theta} \right)^{\eta} e^{\frac{\Theta}{\beta T}}$$

(4.15)

(See Section I.1). An attempt was made to fit $\tilde{\kappa}$ with the curve (4.K) by a method of least squares with the "best" values of $A$, $\eta$, and $\beta$ to be calculated. However, the method was numerically unstable. Therefore, the value of $\eta$ was chosen arbitrarily and the points

$$\{ \ln \tilde{\kappa}_i + \eta \ln (\Theta_i), [\Theta_i] \}$$

(4.16)
were fitted with the line

\[ y = \ln A + \frac{1}{\beta} \left( \frac{\Theta}{T} \right) \]  

(4.17)

by the usual method of least squares fitting. For each value of \( \eta \) the parameters \( A, \beta \), and the mean square deviation

\[ S \equiv \frac{1}{N} \sum_{i=1}^{N} \left\{ \ln \bar{y}_i + \eta \ln \left( \frac{\Theta}{T} \right)_i - \left[ \ln A + \frac{1}{\beta} \left( \frac{\Theta}{T} \right)_i \right] \right\}^2 \]  

(4.18)

were calculated. The "best" value of \( \eta \) was assumed to be that value for which \( S \) had its minimum value.

This fitting procedure was applied to several temperature intervals, none of which contained temperatures higher than \( \Theta/2 \). For all of the temperature intervals considered the best integer value of \( \eta \) was one. Intervals containing temperatures greater than about \( \Theta/6 \) had best values of \( \eta \) which were slightly less than one. When none of the temperatures in an interval exceeded \( \Theta/6 \), the best value of \( \eta \) was slightly greater than one. The results of fitting \( \bar{y} \) for the temperature range

\[ 0.0508 \leq \frac{T}{\Theta} \leq 0.152 \]  

(4.19)

are given in Table III. The best value of \( \eta \) was found by estimating from a graph the value of \( \eta \) for which \( S \) was minimized. This value was \( 1.175 \pm 0.003 \). The best integer value was \( \eta = 1 \).

The cases \( \eta = 3 \) and \( \eta = 8 \) are of interest because these were the values predicted by Ziman (1960) and Julian (1965), respectively. For \( \eta = 3 \) Ziman expected that \( \beta = 2 \), while the
TABLE III
COMPARISON OF PARAMETERS CALCULATED TO FIT THE REDUCED THERMAL CONDUCTIVITY IN THE UMKLAPP REGION

<table>
<thead>
<tr>
<th>$n$</th>
<th>$A$</th>
<th>$\beta$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5112</td>
<td>3.020</td>
<td>4.96x10^{-3}</td>
</tr>
<tr>
<td>1.00</td>
<td>2.185</td>
<td>3.423</td>
<td>1.08x10^{-4}</td>
</tr>
<tr>
<td>1.05</td>
<td>2.349</td>
<td>2.399</td>
<td>5.75x10^{-5}</td>
</tr>
<tr>
<td>1.07</td>
<td>2.419</td>
<td>2.390</td>
<td>4.24x10^{-5}</td>
</tr>
<tr>
<td>1.09</td>
<td>2.490</td>
<td>2.381</td>
<td>3.02x10^{-5}</td>
</tr>
<tr>
<td>1.10</td>
<td>2.526</td>
<td>2.376</td>
<td>2.52x10^{-5}</td>
</tr>
<tr>
<td>1.11</td>
<td>2.563</td>
<td>2.371</td>
<td>2.10x10^{-5}</td>
</tr>
<tr>
<td>1.12</td>
<td>2.601</td>
<td>2.367</td>
<td>1.74x10^{-5}</td>
</tr>
<tr>
<td>1.15</td>
<td>2.717</td>
<td>2.353</td>
<td>1.12x10^{-5}</td>
</tr>
<tr>
<td>1.17$^b$</td>
<td>2.81$^b$</td>
<td>2.34$^b$</td>
<td>&lt;10^{-5}</td>
</tr>
<tr>
<td>1.20</td>
<td>2.921</td>
<td>2.331</td>
<td>1.55x10^{-5}</td>
</tr>
<tr>
<td>1.30</td>
<td>3.378</td>
<td>2.287</td>
<td>7.89x10^{-5}</td>
</tr>
<tr>
<td>2.00</td>
<td>9.338</td>
<td>2.023</td>
<td>2.57x10^{-3}</td>
</tr>
<tr>
<td>3.00$^c$</td>
<td>39.91</td>
<td>1.737$^c$</td>
<td>1.23x10^{-2}</td>
</tr>
<tr>
<td>8.00$^d$</td>
<td>5692</td>
<td>1.017$^d$</td>
<td>1.71x10^{-2}</td>
</tr>
</tbody>
</table>

$^a$A curve of the form $A(\frac{\Theta}{\Theta_0})^n exp(\Theta/\beta T)$ was fit to the reduced thermal conductivity for the temperature region $0.0508 \leq \frac{T}{\Theta} \leq 0.152$.

$^b$Interpolated values. By interpolation the value of $n$ with minimum $S$ is $1.175 \pm 0.003$.

$^c$Ziman (1960) expected $n=3, \beta=2$.

$^d$Julian (1965) expected for this temperature range $n=8, \beta=1.030$. 

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value calculated from $\tilde{\kappa}$ was 1.737. Ziman's prediction was based on studies which considered temperatures lower than $\Theta/2\alpha$. Since the best value of $\eta$ seems to increase as the temperatures for which $\tilde{\kappa}$ is fitted decrease, it is not unlikely that a temperature interval could be found such that the best value of $\eta$ would be three.

For $\kappa = 8$ Julian predicted that $\beta = 1.030$ which is remarkably close to the value of 1.017 calculated from $\tilde{\kappa}$. Julian, however, used smaller values of $\Theta$ for argon. This fact would result in lowering the temperatures in the interval (4.19). Such intervals have temperatures lower than the lowest temperatures for which $\tilde{\kappa}$ was calculated. Therefore, it was not possible to find the best value of $\eta$ for the interval (4.19) with the lower values of $\Theta$.

**High temperature region.** White and Woods (1958) have found that for temperatures higher than about 15°K, the thermal conductivities of neon, argon, and krypton vary as $T^{-1}$. In Section II.3 it was shown that such behavior would occur for temperatures

$$T \gg \Theta,$$

but the values of $\Theta$ for the inert gas solids are all much greater than 15°K. (See TABLE I.). The predictions of Section II.3 have little relevance to the experimental situation because temperatures satisfying (4.20) would exceed the melting points of
the inert gas solids.

In order to determine the temperature region for which the reduced thermal conductivity varies as $T^{-\nu}$, values of

$$\tilde{T}_{\text{argon}} \ 	ilde{\kappa} \left( \frac{\Theta}{T} \right)$$

with

$$\frac{T_{\text{argon}}}{\Theta_{\text{argon}}} = \frac{T}{\Theta} \geq 0.152$$

were calculated and listed in Table IV. These values increase for $T > 0.203 \Theta$ and seem to approach a constant value of about 104 ergs for $T > \Theta$. Although the values of (4.21) vary too much to establish an exact $T^{-\nu}$ relationship, an error of less than ten per cent would be incurred if, for $T \geq 0.508 \Theta$, the values of (4.21) were replaced by their average value 99.2, and for $T \geq 0.152 \Theta$ the values deviate by less than twenty six per cent from their average value of 92.7. For $T < 0.152 \Theta$, $\tilde{\kappa}$ varies so strongly with temperature that the assumption of a $T^{-\nu}$ dependence would be absurd. These temperatures definitely do not belong to the high temperature region, but to the Umklapp region.

4. CALCULATION OF THE THERMAL CONDUCTIVITIES

As the final stage of the calculations, the reduced thermal conductivity was used to obtain the thermal conductivities of the inert gas solids. Equation (3.43) could not be used for this purpose because the thermal conductivity $\kappa$ defined in Sec-
TABLE IV

PRODUCTS OF THE REDUCED THERMAL CONDUCTIVITY
AND TEMPERATURE IN THE HIGH TEMPERATURE
REGION FOR ARGONA

<table>
<thead>
<tr>
<th>$\frac{T}{\Theta}$</th>
<th>$T_{\text{argon}}$ (°K)</th>
<th>$T_{\text{argon}} \frac{R(\Theta)}{\Theta}$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.152</td>
<td>15</td>
<td>75.38</td>
</tr>
<tr>
<td>0.203</td>
<td>20</td>
<td>69.29</td>
</tr>
<tr>
<td>0.305</td>
<td>30</td>
<td>76.80</td>
</tr>
<tr>
<td>0.406</td>
<td>40</td>
<td>84.92</td>
</tr>
<tr>
<td>0.508</td>
<td>50</td>
<td>90.38</td>
</tr>
<tr>
<td>0.610</td>
<td>60</td>
<td>93.94</td>
</tr>
<tr>
<td>0.711</td>
<td>70</td>
<td>96.31</td>
</tr>
<tr>
<td>0.813</td>
<td>80</td>
<td>97.96</td>
</tr>
<tr>
<td>0.914</td>
<td>90</td>
<td>99.13</td>
</tr>
<tr>
<td>1.02</td>
<td>100</td>
<td>100.0</td>
</tr>
<tr>
<td>2.03</td>
<td>200</td>
<td>102.9</td>
</tr>
<tr>
<td>3.05</td>
<td>300</td>
<td>103.5</td>
</tr>
<tr>
<td>4.06</td>
<td>400</td>
<td>103.7</td>
</tr>
<tr>
<td>5.08</td>
<td>500</td>
<td>103.8</td>
</tr>
</tbody>
</table>

For other inert gas solids the values of $T$ and $T_{\text{argon}} \frac{R(\Theta)}{\Theta}$ are proportional to the values given in the table for argon ($T/T_{\text{argon}} = \Theta / 98.42$).
tion II.1 differ from the experimental thermal conductivity $\kappa_{\text{exp}}$ by a factor with the units of volume. If

$$\kappa_{\text{exp}} = V \kappa$$  \hfill (4.23)

then two cases may be considered.

1. For some temperature in the high temperature region the value of $\kappa_{\text{exp}}$ (White and Woods (1958).) may be compared with the value of $\kappa$ calculated from (3.43) to find the value of $V$. It was found that

$$V \sim 10^{-4} N^2 \text{ (cm)}^3.$$  \hfill (4.24)

For macroscopic crystals, $N \sim 10^{23}$ and $V$ is much larger than the volume of a sphere just containing the orbit of Pluto.

2. If it were the case that $V$ were the volume of the crystal, then for macroscopic crystals ($V \sim 1 \text{ cm}^3$) a comparison of $\kappa_{\text{exp}}$ and $\kappa$ calculated from (3.43) indicates that $\kappa$ is too large by a factor of order $10^{-1}$. Such an overestimation may have been due to the fact that in summations over reduced wave vectors only a small fraction (about $10^{-20}$) were included in the calculations. This would result in an underestimation in the actual value of the summation and since the reciprocals of the reduced relaxation times are calculated from such a summa-
tion, the values of $\tilde{\kappa}$ would be overestimated. In any case, it is apparent that no sensible agreement with experimental data may be obtained by using (3.43) to calculate $\kappa$.

In Section IV.3 it was found that $\tilde{\kappa}$ has approximately the sort of temperature dependence that has been predicted theoretically and found experimentally for the thermal conductivity. Therefore, the thermal conductivities of neon, argon, and krypton were calculated by finding a value of the constant $B$ such that

$$B \tilde{\kappa}(\Theta)$$

agrees exactly with the experimental data of White and Woods (1958) for one temperature in the high temperature region. Although no experimental data exist for the thermal conductivity of xenon, Julian (1965) has calculated that for high temperatures

$$\kappa_{\text{xenon}} \approx \frac{732}{T} \left(10^4 \text{ erg./}^\circ\text{K/ sec./cm.}\right).$$

The thermal conductivity of xenon was calculated by forcing (4.25) and (4.26) to agree exactly for one temperature in the high temperature region. The results of the calculations are compared with the curves to which $\tilde{\kappa}$ was fit in Figures 2-5.

In Figures 2-4, the solid curves are the experimental results of White and Woods (1958), the dashed lines are high temperature extrapolations of the experimental data, and the dots are the values calculated from $\tilde{\kappa}$. For neon (Figure 2) and argon (Figure 3), there is order of magnitude agreement be-
Figure 2. Comparison of experimental and calculated values for the thermal conductivity of neon. The curve represents the experimental data of White and Woods (1958). The dots represent the calculations made for this study.
Figure 3. Comparison of experimental and calculated values for the thermal conductivity of argon. The curve represents the experimental data of White and Woods (1958). The dots represent the calculations made for this study.
Figure 4. Comparison of experimental and calculated values for the thermal conductivity of krypton. The curve represents the experimental data of White and Woods (1958). The dots represent the calculations made for this study.
Figure 5. Comparison of two sets of calculated values for the thermal conductivity of xenon. The curve represents the calculations of Julian (1965). The dots represent the calculations made for this study.
tween calculated and experimental values of $\kappa$ for $T \geq 10^\circ K$ and quite good agreement for $T \geq 50^\circ K$. For krypton (Figure 4), the calculated values fit the experimental curve very well for $T \geq 15^\circ K$. For low temperatures, the calculated values of $\kappa$ do not agree with the experimental values at all. This is the region where crystal size and lattice defects control the value and behavior of $\kappa$.

In Figure 5 the solid curve represents the values of $\kappa$ calculated by Julian (1965) for xenon, the dashed line is the line (4.26) and the dots are the values of $\kappa$ calculated from $\tilde{\kappa}$. For $T \geq 30^\circ K$ the values of $\kappa$ calculated in this analysis lie quite close to the curve calculated by Julian. In the Umklapp region, there is order of magnitude agreement, with the values of $\kappa$ calculated in this study lying below Julian's curve and causing the disagreement between the best value of $\eta$ found in Section IV.3 and the value $\eta = 8$ predicted by Julian.

5. ERRORS

Except for the gross over estimation of $\tilde{\kappa}$ suggested in Section IV.4, the error in the calculated values of $\kappa$ arose from three approximations.

1. Quantities calculated from lattice sums were computed with a relative error of $\pm 10^{-4}$. This approximation introduced a relative error of less than about $\pm 10^{-4}$ in the reduced frequencies and
equal to $\pm 10^{-4}$ in the reduced cubic coefficients. The relative error introduced into temperature dependent quantities was estimated by noting that the relative error in

$$\varepsilon \frac{\kappa \tilde{\nu}}{\tau} \quad (4.27)$$

was about

$$\pm \frac{\kappa \tilde{\nu}}{\tau} \times 10^{-4} \quad (4.28)$$

but because of the range of values of $\tau$ and $\tilde{\nu}$ used in the calculations,

$$10^{-5} \leq \frac{\kappa \tilde{\nu}}{\tau} \leq 10^{-3} \quad (4.29)$$

so that the relative error in the exponentials (4.27) is less than about $\pm 10^{-3}$.

2. The reduced group velocities were defined in terms of a derivative which was approximated by a numerical differentiation formula. This approximation introduced a relative error of about one per cent in the reduced group velocities.

3. The condition for conservation of energy in a three phonon process was replaced by the condition

$$|\Delta \tilde{\nu}| \leq 3 \times 10^{-3} \quad (4.30)$$

The only quantity affected by this approximation was the factor

$$\eta^{'\prime} + \eta'' + 1 \quad (4.31)$$
for which the relative error introduced by (4.30) was about 0.4 per cent.

The error introduced into the calculation of $\tilde{\kappa}$ by the three approximations was less than three per cent. Therefore, if enough reduced wave vectors were included in the calculations to determine the correct temperature dependence, if not the correct values, of $\tilde{\kappa}$, then the thermal conductivities calculated in Section IV.4 would have had about three per cent error; except for the low temperatures where the error is very large because of the neglect of the effects of crystal size and lattice defects. The closeness of the fits between experimental and calculated values of $\tilde{\kappa}$ for high enough temperatures (See Figures 2-5) suggests that enough reduced wave vectors were considered to obtain the correct temperature dependence.

Throughout this chapter emphasis has been placed on the reduced quantities introduced in Chapter III. None of the qualitative statements made concerning any of the reduced quantities would have to be changed in order to apply them to the corresponding physical quantities. However, these statements would not necessarily have any application to the experimentally measured quantities. For example, for low temperatures the reduced thermal conductivity for three phonon processes has very little to do with the experimental thermal conductivity which is dominated by the effects of crystal size and lattice defects.
CHAPTER V

CONCLUSION

The previous chapters of this thesis have presented the theory and outlined the calculation of the thermal conductivities of solid neon, argon, krypton and xenon.

The theory of the thermal conductivity of dielectric solids which was presented in Chapter II was based on the assumption of a relaxation law with the relaxation times evaluated in terms of the cubic anharmonic term of the crystal potential energy. Although higher order anharmonicities could have been treated analogously, their effects were ignored as negligible compared with the effects of the cubic anharmonicities. The thermal conductivities calculated from this theory could be expected to give good agreement with experimental data only for temperatures high enough that the effects of interactions among the phonons are more important than the effects of scattering of the phonons at crystal boundaries and near lattice imperfections.

As a model it was assumed that crystals of the inert gas solids possessed perfect, face centred cubic lattices and atoms which interacted in pairs through the 12:6 potential energy function. The additional assumption that thermal expansion of the crystals could be neglected permitted the introduction of a set of "reduced" quantities. This fact meant that the
problem of calculating the thermal conductivities of four inert gas solids could be reduced to the problem of calculating four sets of constants and the "reduced thermal conductivity" $\tilde{\kappa}$ of any one of the inert gas solids.

The total number of phonon modes in a macroscopic crystal is so great that even with the use of a computer, it is possible to consider only a very small fraction of them in any calculations. In this thesis this fraction was so small (about $10^{-20}$) that the reduced thermal conductivity appeared to be too large by a factor of order $10^2$. However, the temperature dependence of $\tilde{\kappa}$ was shown to be approximately that which has been predicted and measured. For $T \gtrsim 0.5\beta_0$, $\tilde{\kappa}$ varies approximately as $T^{-1}$ and for $0.05\beta_0 \lesssim T \lesssim 0.15\beta_0$, $\tilde{\kappa}$ has the form

$$A \left(\frac{T}{T_0}\right)^n \exp \left[ \frac{\Omega}{\beta T} \right].$$

(5.1)

The best value found for the parameter $n$ was shown to be $1.175 \pm 0.003$, the best integer value being 1. (See Section IV.3).

The thermal conductivities of solid neon, argon, and krypton were obtained by multiplying the values calculated for $\tilde{\kappa}$ by a factor which produced exact agreement with the experimental data of White and Woods (1958) for one temperature in the high temperature region. Figures 2-4 show the results of these calculations. Fair agreement between calculated and experimental values of the thermal conductivities begins near the temperatures
at which the maximum value of the experimental thermal conductivities occur. For higher temperatures the agreement improves, becoming very good at very high temperatures.

The thermal conductivity of xenon was obtained by adjusting the values of $\tilde{K}$ so that for one temperature in the high temperature region, the adjusted value of $\tilde{K}$ agreed exactly with the calculations for xenon by Julian (1965). The agreement between the two sets of calculated thermal conductivities is quite good for all temperatures for which $\tilde{K}$ was calculated, but for the lowest temperatures shown in Figure 5, the values calculated in this study lay below the curve of values computed by Julian. It was in this region that (5.1) was fitted to $\tilde{K}$ and for which Julian predicted that $\gamma = 8$.

The basic assumption of this thesis has been that for sufficiently high temperatures, the thermal conductivity of real dielectric crystals is determined chiefly by interactions among the phonons. The agreement of the calculations of this study with experimental data for the thermal conductivity of inert gas solids seems to verify the theory of Chapter II and to justify this assumption.

The limitations of this study suggest a number of problems for future investigation.

1. If these calculations were repeated for a larger fraction of the phonon modes, it would be possible
to decide whether or not enough cases were considered in this thesis to obtain the correct temperature dependence of the reduced thermal conductivity.

2. If the reduced thermal conductivity were calculated for lower temperatures than have been considered in these calculations, it would be possible to determine whether or not a low enough temperature interval exists for which the best value of \( n \) in formula (5.1) would be 3 or 8.

3. It would be interesting to determine the relative significance of the effects of higher order anharmonicities on the thermal conductivity.

4. Accurate calculation of summations over phonon modes is practically impossible for three dimensional lattices. It would be valuable to find a method for considering a very large fraction of all of the phonon modes in the calculation of such summations. Perhaps, though, the concept of interacting phonons does not provide the best way of handling the problem of calculating the thermal conductivity and some entirely different approach should be sought.
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