

FOREWORD

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ABSTRACT

The lattice thermal conductivity of simple alloys can be calculated by assuming that the only effects of alloying on the thermal conductivity can be represented by point defect scattering mechanisms. The scattering of phonons by point defects has an inverse relaxation time proportional to the fourth power of the frequency. The proportionality constant depends on the particular scattering mechanism considered. In simple substitutional alloys where one chemically similar element is substituted for another there are three scattering processes to be considered besides phonon-phonon scattering. Phonons are scattered by the fluctuation in mass, the change in force constants, and the lattice distortion caused by the impurity atom. The relaxation time for all these processes acting simultaneously has been derived.

The relaxation time for phonon-phonon scattering due to cubic anharmonic terms in the expansion of the potential energy of the crystal in the displacements of the atoms comprising the crystal from equilibrium is proportional to the inverse frequency squared. When the relaxation time for point defect scattering is combined with that for phonon-phonon scattering to obtain an effective relaxation time one may calculate the lattice thermal conductivity as a function of alloy composition. We have done this for the case of Ge-Si alloys and find reasonable agreement with experiment.

The possibility of modifying the theory with the aid of ideas from nonequilibrium statistical mechanics is considered.

This technical documentary report has been reviewed and is approved.



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LIST OF SYMBOLS

A	constant in relation between frequency and relaxation time for point defect scattering of phonons
a	lattice constant
a^3	volume of a unit cell
a_k	annihilation operator for the kth mode
a_k^*	creation operator for the kth mode
B	constant in relation between frequency and relaxation time for phonon-phonon scattering by U-processes
b	magnitude of a reciprocal lattice vector
c_{ij}	the ijth elastic constant
$E(\hbar\omega(k)/KT)$	Einstein specific heat function
f	harmonic force constant
$f(k)$	density of states in k space
g	cubic anharmonic force constant
$g(\omega)$	density of states in frequency space
H	Hamiltonian for a system of oscillators
H_0	Hamiltonian for a system of harmonic oscillators
H_1	Hamiltonian for the cubic anharmonic term in V
H'	perturbation of H due to a change of mass of an oscillator
h	Planck's constant
\hbar	$h/2\pi$
i	$\sqrt{-1}$
K	Boltzmann's constant
k	magnitude of a wave propagation vector for the kth mode

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L	Wiedemann-Franz-Lorenz number
ℓ	running index which labels the atoms
M	mass of an atom in the lattice
M_i	atomic weight of the i th constituent of an alloy
\bar{M}	mean atomic weight
N	number of atoms in a lattice
N_0	Avogadro's number
n	number of particles per unit cell
$n(k)$	number of quanta in the k th mode
$ n(k)\rangle$	eigenstate of the k th mode
P_k	momentum canonically conjugate to the U_k th normal coordinate operator
P_ℓ	momentum of ℓ th atom
q	magnitude of the heat current density
\vec{q}	heat current density
r	distance between nearest neighbors in a lattice
T	absolute temperature
t	time
U-processes	phonon-phonon scattering events for which the sum of the k 's is a non zero reciprocal lattice vector
U_k	normal coordinate operator for the k th mode
u_ℓ	displacement of the ℓ th atom from its equilibrium position
$v_g(\omega) = v_g(k)$	group velocity for the k th mode
v_0	group velocity if all modes have the same velocity
X_i	position of the i th atom
x_i	concentration of the i th constituent of an alloy

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α, β	force constants in Born model for diamond cubic lattices
Γ	volume element of phase space
ϵ	mean square fluctuation parameter for point defects
$\epsilon_{\Delta M}$	mean square mass fluctuation parameter
$\epsilon_{\Delta r, \Delta f}$	mean square fluctuation parameter for changes in r and f
π_{ℓ}	net instantaneous power transmitted from ℓ th to $(\ell + 1)$ st atom
$f_{\ell, \ell+1}$	force on ℓ th atom due to $(\ell + 1)$ st atom
θ_D	Debye temperature
K	thermal conductivity
K_u	thermal conductivity for $T \geq \theta_D$ when phonons are scattered only by U-processes
K_{ℓ}	lattice thermal conductivity
ρ	density
σ	electrical conductivity
$T(\omega) = T(k)$	relaxation time for the k th mode
$T_i(\omega)$	relaxation time for point defect scattering of phonons
$T_u(\omega)$	relaxation time for phonon-phonon scattering by U-processes for $T \geq \theta_D$
$\omega(k)$	circular frequency of the k th vibrational mode
ω_D	Debye cutoff frequency
ω_0	frequency for which a phonon is scattered with equal probability by point imperfections and U-processes
$\nabla T, dT/dx$	temperature gradient
$\langle i H_1 f \rangle$	matrix element for a transition between the initial state $ i\rangle$ and final state $ f\rangle$
$P_N(\{\text{qp}\})$	probability of finding a system of N particles in the volume element $d\Gamma$ in phase space
$d\Gamma$	volume element in phase space; $\prod_i dq_i dp_i$
$\langle \Omega(\{\text{qp}\}) \rangle$	value of a property $\Omega(\{\text{qp}\})$ averaged over $P_N(\{\text{qp}\})$

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INTRODUCTION

The flow of charge carriers in a solid due to a potential gradient constitutes an electric current. Similarly, the flow of charge carriers in a temperature gradient represents a heat current, and the proportionality constant between the heat current due to the charge carriers and the temperature gradient (in isotropic materials) is the electronic thermal conductivity.

Since the charge carriers are responsible for both the electrical and thermal currents one would expect the electrical and thermal conductivities to be intimately related. Indeed it is found that ratio of the electrical conductivity to the product of the electrical conductivity and the absolute temperature for good electrical conductors is equal to a constant independent of temperature and the scattering mechanism. The relation known as the Wiedemann-Franz Law is not obeyed in poor conductors of electricity. In semiconductors and insulators, for instance, where one might reasonably expect to find very few charge carriers the quotient of the thermal to electrical conductivity at a given temperature usually exceeds the Wiedemann-Franz ratio. The thermal conductivity evidently depends upon other mechanisms as well as on the heat transported by the free charge carriers. Among these other mechanisms are lattice thermal conduction, excitation diffusion, ambipolar diffusion, and radiation. To a first approximation the contributions of the various mechanisms to the thermal conductivity are additive. We will ignore all contributions other than lattice thermal conductivity, K_l , and the electronic contribution due to the convection of the free charge carriers, K_e , which may be equated to $L\sigma T$ where L is the Wiedemann-Franz-Lorenz number, σ is the electrical conductivity, and T is the absolute temperature. Thus,

$$K = K_l + L\sigma T \quad (1)$$

A plot of K versus σ at constant T would enable us to determine K_l and L . Since this report will be principally concerned with calculating the lattice thermal conductivity, this is the only use we will make of Equation (1).

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The lattice thermal conductivity arises from the heat current carried by the thermal vibrations of the atoms comprising the crystal. To a first approximation the atoms may be considered as a set of coupled harmonic oscillators whose normal vibrations give rise to a set of traveling waves which can transport energy (heat) from one part of the crystal to another. In the limit of long wave length the lattice waves are sound waves and in analogy with light quanta, photons, the different modes of vibration in the lattice are called phonons. The heat current due to the phonons is then the energy of a particular mode $\hbar\omega(\vec{k})$, where \hbar is Planck's constant, h , divided by 2π , and $\omega(\vec{k})$ is the circular frequency of the \vec{k} th mode, multiplied by the number of phonons, $n(\vec{k})$, in the \vec{k} th mode, and the group velocity $\vec{v}_g = \nabla_{\vec{k}} \omega(\vec{k})$ for that mode summed over all modes.

Since the modes are distributed symmetrically in k space, that is, $\omega(k) = \omega(-k)$, the zero point energy carries no heat current nor is there any heat current if the distribution of phonons is isotropic or if the $n(k)$'s have their thermal equilibrium values. Net heat flow arises from an anisotropy of the phonon distribution. However, this is not enough to limit the thermal conductivity to a finite value since in the absence of processes tending to restore equilibrium a small asymmetry in the distribution and the associated thermal current persists indefinitely, even in the absence of a temperature gradient. Thermal resistance is the result of processes that allow the lattice waves to interchange energy. For a large ideally perfect crystal at moderate or high temperatures the only possible interaction mechanism is phonon-phonon scattering which must arise from anharmonic terms in the potential energy of the lattice since normal modes cannot interact. One, therefore, sets up a Boltzmann equation for the steady state in the presence of a temperature gradient and calculates the phonon-phonon scattering due to the anharmonic terms in the potential by perturbation theory.

It is often convenient to assume that the return to equilibrium follows an exponential law. This is equivalent to defining a relaxation time, $\tau(k)$, for each mode and requires that the occupation numbers for all modes but the one in question have their equilibrium values. When more than one scattering mechanism is operative the effective relaxation time for all processes acting simultaneously

is determined in the same way as the resultant resistance of resistors in parallel. That is,

$$\frac{1}{\tau_{\text{eff}}(k)} = \sum_i \frac{1}{\tau_i(k)} \quad (2)$$

In general the relaxation times will be found to be a function of the frequency of the mode and of the temperature. In particular for the three phonon-phonon interactions and for the scattering of phonons by any type of point defect we find that $1/\tau$ varies as ω^2 and ω^4 , respectively. In simple alloys the effects of alloying on the thermal conductivity can be characterized by various point defect scattering mechanisms, namely, scattering due to mass fluctuations, changes in the force constants and lattice distortion due to the incorporation of foreign atoms in the lattice. The lattice thermal conductivity for certain types of alloys can be quite accurately predicted by a combination of τ 's due to phonon-phonon interactions and phonon-point defect scattering. These calculations as well as some attempts to extend the theory of lattice thermal conductivity are discussed in this report.

EXPRESSION FOR K_l

In a one-dimensional lattice the heat current, q , due to the phonons is the energy of a particular mode $\hbar\omega(k)$, where \hbar is Planck's constant divided by 2π and $\omega(k)$ is the circular frequency of the k th mode multiplied by the number of phonons, $n(k)$, in the k th mode, and the group velocity of the lattice wave, $v_g = \partial\omega(k)/\partial k$ for that mode with $k = (2\pi/a) \times \text{integer}$, the wave propagation vector summed over all modes. That is, q is given by

$$q = \sum_k \hbar\omega(k)n(k)v_g(k) \quad (3)$$

Since the modes are distributed symmetrically in k space, i.e., $\omega(k) = \omega(-k)$ and $v_g(k) = -v_g(-k)$, the heat current will vanish if the distribution of phonons is isotropic. In particular $q = 0$ if $n(k)$ has its thermal equilibrium value. Net heat flow arises from an anisotropy of the phonon distribution. If one

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assumes that any departure of $n(k)$ from its equilibrium value $\bar{n}(k)$ decays exponentially one can write

$$\left. \frac{dn(k)}{dt} \right|_{\text{scatt}} = \frac{\bar{n} - n}{\tau} \quad (4)$$

The left hand side denotes the average rate of change due to interaction and $\tau(k)$ is a relaxation time. The heat current can, therefore, be expressed in the form

$$q = - \sum_k \hbar \omega(k) \tau(k) \left. \frac{dn(k)}{dt} \right|_{\text{scatt}} v_g(k) \quad (5)$$

since the heat current due to $\bar{n}(k)$ vanishes. A Boltzmann equation can be set up for the steady state in the presence of a temperature gradient which in one dimension becomes

$$\left. \frac{dn(k)}{dt} \right|_{\text{scatt}} = v_g(k) \frac{dT}{dx} \frac{dn(k)}{dT} \quad (6)$$

The heat current may, therefore, be expressed in the form

$$q = - \left\{ \sum_k \tau(k) v_g^2(k) \hbar \omega(k) \frac{dn(k)}{dT} \right\} \frac{dT}{dx} \quad (7)$$

The thermal conductivity is given by

$$q = - \kappa_l \frac{dT}{dx} \quad (8)$$

From these two equations we see that the thermal conductivity is given by

$$\kappa_l = \sum_k \tau(k) v_g^2(k) \hbar \omega(k) \frac{dn(k)}{dT} \quad (9)$$

To a first approximation $n(k)$ may be replaced by its equilibrium value in this expression to give

$$\kappa_l = \sum_k \tau(k) v_g^2(k) E \left(\frac{\hbar \omega(k)}{KT} \right) \quad (10)$$

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where K is Boltzmann's constant and $E \left(\frac{\hbar\omega(k)}{KT} \right)$ is the Einstein specific heat function for an oscillator of frequency $\omega(k)$

$$E \left(\frac{\hbar\omega(k)}{KT} \right) = K \left(\frac{\hbar\omega}{KT} \right)^2 \frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT} - 1)^2} \quad (11)$$

In the high temperature limit the Einstein function reduces to K so that

$$K_{\ell} = K \sum_k T(k) v_g^2(k) = K \int T(k) v_g^2(k) g(k) dk \quad (12)$$

where $g(k)$ is the density of states in k space. This may be transformed to an integral over the frequencies by noting that number of states included between k and $k + dk$ must equal the number of states in the corresponding frequency range, that is, ω to $\omega + d\omega$. Thus,

$$g(k) dk = g(\omega) d\omega = g(\omega) \frac{\partial \omega}{\partial k} dk \quad (13)$$

or

$$g(\omega) = g(k) / v_g(k) \quad (14)$$

The density of states in k space whether in one or three dimensions is uniform and equal to interval between successive values of k . For a one-dimensional crystal of N atoms with lattice constant a

$$k = \frac{2\pi}{L} n \quad n = 0, 1, \dots, N - 1 \quad (15)$$

With $L = Na$ so that $g(k) = \frac{1}{\Delta k} = \frac{L}{2\pi}$. Therefore, K_{ℓ} can be expressed as an integral over ω by

$$K_{\ell} = \frac{KL}{2\pi} \int_0^{\omega_{\max}} T(\omega) v_g^2(\omega) d\omega \quad (16)$$

In a three-dimensional isotropic solid at the high temperature limit this becomes

$$\begin{aligned} K_{\ell} &= \frac{K}{3} \int_0^{\omega_{\max}} v_g^2(\omega) T(\omega) g(\omega) d\omega \\ &= \frac{K}{3} \int_0^{\omega_{\max}} v_g(\omega) T(\omega) g(k) d\omega \end{aligned} \quad (17)$$

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where

$$g(\omega) = g(k)/v_g(\omega) \quad (18)$$

It now remains to discuss the form of $g(k)$ in a three-dimensional isotropic solid. We apply the method of periodic boundary conditions requiring that the vibrational wave $e^{i\vec{k} \cdot \vec{r}}$ be periodic at the boundaries of a cube of side L . Then $k_x L$, $k_y L$, $k_z L$ must be multiples of 2π , so the allowed values of k may be represented by the points of a simple cubic lattice in k space, with lattice constant $2\pi/L$. The number of modes with wave number less than k is then given closely by the volume, measured in units $2\pi/L$, of the sphere of radius K , which is

$$(4\pi/3)k^3 / (2\pi/L)^3 \quad (19)$$

for each of the three possible polarizations - one longitudinal and two transverse; thus the total number of modes with magnitude of the wave vector less than k is $k^3/2\pi^2$, per unit volume of sample. The number of modes with wave vector in dk at k is

$$g(k)dk = d(k^3/2\pi^2) = (3k^2/2\pi^2)dk$$

or

$$g(k) = 3k^2/2\pi^2 \quad (20)$$

Since we have assumed $\omega = v_0 k$ we finally have for $g(\omega)$

$$g(\omega) = 3\omega^2/2\pi^2 v_0^3 \quad (21)$$

The expression for K_ℓ in the high temperature limit then becomes

$$K_\ell = \frac{K}{2\pi^2 v_0} \int_0^{\omega_{\max}} \omega^2 T(\omega) d\omega \quad (22)$$

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The assumption that $v_g(\omega) = v_o$, a constant, is equivalent to the Debye approximation for $g(\omega)$ and we accordingly designate ω_{\max} by ω_D , the Debye cutoff frequency or

$$K_\ell = \frac{K}{2\pi^2 v_o} \int_0^{\omega_D} \omega^2 \tau(\omega) d\omega \quad (23)$$

This expression allows one to calculate K_ℓ provided one has an expression for τ . Equation (4) suggests that one can do this provided $dn(k)/dt \Big|_{\text{scatt}}$ can be determined. The dependence of the relaxation time for phonon-phonon scattering on frequency will now be calculated for a one-dimensional lattice. The correct relation between relaxation time and frequency is obtained even though a rigorous application of the selection rules for energy and wave vector cause the thermal resistance to vanish for this model.

$\tau(\omega)$ FOR PHONON-PHONON SCATTERING IN ONE DIMENSION

The Hamiltonian operator for the lattice is

$$H = H_o + H_1$$

where H_o is the Hamiltonian for the lattice in the harmonic oscillator approximation and H_1 is the perturbation due to the anharmonic terms in the potential energy. The Hamiltonian out to cubic anharmonic terms in the potential energy of the lattice was shown in Technical Documentary Report No. ASD-TDR-62-74, Part I to be

$$H = \frac{1}{2} \sum_k \hbar \omega(k) (a_k a_k^* + a_k^* a_k) + \frac{1}{3!} \sum_{k, k', k''} 2G(k, k', k'') (a_k^* - a_{-k}) \times (a_{k'}^* - a_{-k'}) (a_{k''}^* - a_{-k''}) \quad (24)$$

with

$$2G(k, k', k'') = - \left(\frac{2 \hbar^3}{8 f^3 N} \right)^{1/2} \delta_{k+k'+k''}^b [\omega(k)\omega(k')\omega(k'')]^{1/2} \quad (25)$$

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where a_k^* and a_k are creation and annihilation operators, f and g are the harmonic and anharmonic force constants, \hbar is Planck's constant divided by 2π , N is the number of atoms in the lattice, $\omega(k)$ is the circular frequency of the k th mode, and $\delta_{k+k'+k''}^b$ is the kronecker delta function.

The first term on the right hand side of Equation (24) is the Hamiltonian operator, H_0 , of the unperturbed problem. The eigenvalues and eigenstates of H_0 are well known. They can be characterized by sets of positive integers (quantum numbers), $n(k)$, which tell us the number of quanta in the particular mode. If the k th mode is excited to its $n(k)$ th level, we say that there are $n(k)$ quanta in the mode and symbolize the state by $|n(k)\rangle$. $|\dots, n(k), \dots\rangle$ is then an eigenstate of H_0 for the eigenvalue $E(\dots, n(k), \dots)$. The annihilation and creation operators act on these states according to the rules

$$a_k |n(k)\rangle = \sqrt{n(k)} |n(k) - 1\rangle \quad (26)$$

$$a_k^* |n(k)\rangle = \sqrt{n(k) + 1} |n(k) + 1\rangle \quad (27)$$

where $|n(k) + 1\rangle$ means the state in which $n(k)$ has been increased by unity and so on. From the definition of H_0 [Equation (24)] and Equations (26) and (27) it is obvious that the unperturbed problem is specified by the equations

$$H_0 |\dots, n(k), \dots\rangle = E(\dots, n(k), \dots) |\dots, n(k), \dots\rangle \quad (28)$$

$$E(\dots, n(k), \dots) = \sum_k \hbar \omega(k) \left(n(k) + \frac{1}{2} \right) \quad (29)$$

The eigenstates form a complete normal and orthogonal system of states, i.e.,

$$\langle \dots, n'(k), \dots | \dots, n(k), \dots \rangle = \dots \delta_{n'(k)}^{n(k)} \dots \quad (30)$$

where $\delta_{n'(k)}^{n(k)}$ is the kronecker delta function.

Equations (26) and (27) enable one to determine the effect of the operator H_1 [the second term on the right hand side of Equation (24)] on the eigenstates

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of the unperturbed problem and to calculate by Dirac's perturbation theory the transition probability between the unperturbed states. The transition probability $P_{\dots, n(k), \dots \dots, n'(k), \dots}$ between two states $|\dots, n(k), \dots\rangle$ and $|\dots, n(k), \dots\rangle$, due to the perturbation term H_1 , is the product of the square of the absolute values of the matrix element between the two states and a delta function which expresses the conservation of energy:

$$P_{\dots, n(k), \dots \dots, n'(k), \dots} = \frac{2\pi}{\hbar} \delta[E(\dots, n'(k), \dots) - E(\dots, n(k), \dots)] \times \left| H_1_{\dots, n(k), \dots \dots, n'(k), \dots} \right|^2 \quad (31)$$

where

$$H_1_{\dots, n(k), \dots \dots, n'(k), \dots} = \left| \langle \dots, n'(k), \dots | H_1 | \dots, n(k), \dots \rangle \right| \quad (32)$$

$$E(\dots, n'(k), \dots) - E(\dots, n(k), \dots) = \sum_k \hbar \omega(k) (n'(k) - n(k)) \quad (32a)$$

The calculation of the matrix elements is fairly simple. H_1 contains only products of three a_k -operators. Each of these operators reduces or increases the quantum number of the initial state $|\dots, n(k), \dots\rangle$ for a given mode by one unit. The matrix elements, Equation (32), can, therefore, only be different from zero when each of three $n(k)$'s differs from the corresponding $n'(k)$'s by ± 1 and the other quantum numbers are unchanged. For the calculation of the matrix elements one expands the operator products in H_1 to obtain

$$H_1 = \frac{1}{3!} \sum_{k, k', k''} 2G(k, k', k'') \left\{ \begin{aligned} & a_k^* a_{k'}^* a_{k''}^* - a_k^* a_{k'} a_{k''}^* - a_k^* a_{-k'} a_{k''}^* \\ & + a_k^* a_{-k'} a_{-k''}^* - a_{-k} a_{k'}^* a_{k''}^* + a_{-k} a_{k'}^* a_{-k''}^* \\ & + a_{-k} a_{-k'} a_{k''}^* - a_{-k} a_{-k'} a_{-k''}^* \end{aligned} \right\} \quad (33)$$

and investigates the effect of the individual terms. The matrix element of the perturbing Hamiltonian, H_1 , between an initial state $|i\rangle$ and a final state $|f\rangle$

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is $\langle f | H_1 | i \rangle$. If the initial state is of the form $|i\rangle = |\dots, n(k), n(k'), n(k''), \dots\rangle$, the final states for the first and last terms on the right hand side of Equation (33) must be $|\dots, n(k) + 1, n(k') + 1, n(k'') + 1, \dots\rangle$ and $|\dots, n(-k) - 1, n(-k') - 1, n(-k'') - 1, \dots\rangle$, respectively, to have nonvanishing matrix elements because of the orthonormality of the eigenstates [Equation (30)]. These two terms, however, represent final states in which the number of quanta in the k th, k' th, and k'' th modes have all either increased or decreased by one unit. Conservation of energy for phonon-phonon interactions then requires in both cases (since $\omega(-k) = \omega(k)$, etc.)

$$\omega(k) + \omega(k') + \omega(k'') = 0 \quad . \quad (34)$$

Since the frequencies are always positive, Equation (34) can only be true if $k = k' = k'' = 0$, and then $G(k, k', k'') = 0$ as was shown in Technical Documentary Report No. ASD-TDR-62-74, Part I. These two terms, therefore, make no contribution to the transition probability.

The matrix elements and transition probabilities for all the interaction processes indicated in Equation (33) are collected in Table 1. As discussed above, the first and last rows (I and VIII) of the table vanish since these transitions violate the conservation of energy. We will consider only row V which corresponds to the transition

$$n'(k) = n(k) - 1, \quad n'(k') = n(k') + 1, \quad n'(k'') = n(k'') + 1 \quad (35)$$

Because each of the k 's runs over the same range of values this term occurs in Equation (33) exactly six times. The individual contributions and the terms in Equation (33) from which they arise are given in Table 2. Because the $G(k, k', k'')$'s are symmetrical with respect to an interchange of index pairs the contributions are all equal and the factor $1/3!$ drops out. One thus obtains the matrix element belonging to a definite transition. The square of the matrix element together with the conservation of energy condition gives the transition probability. Since the occupation numbers of the initial and final states can only differ by ± 1 , Equation (32a) shows that the conservation of energy

Table 1
MATRIX ELEMENTS AND TRANSITION PROBABILITIES FOR H₁

x final state 0 initial state k k' k''	Matrix Element	Transition Probability	Change of n(k); Δ n(k)
I $\begin{matrix} \times & 0 \\ \times & 0 \\ \times & 0 \end{matrix}$	$\left\{ [n(k) + 1] n(k') + 1 n(k'') + 1 \right\}^{1/2} 2G(k, k', k'')$	$[n(k) + 1] n(k') + 1 n(k'') + 1 2G(k, k', k'') ^2 \frac{2\pi}{h} \delta[\omega(k) + \omega(k') + \omega(k'')]$	+ 1
II $\begin{matrix} \times & 0 \\ \times & 0 \\ \times & 0 \end{matrix}$	$-\left\{ [n(k) + 1] n(k') + 1 n(k'') \right\}^{1/2} 2G(k, k', -k'')$	$[n(k) + 1] n(k') + 1 n(k'') 2G(k, k', -k'') ^2 \frac{2\pi}{h} \delta[\omega(k) + \omega(k') - \omega(k'')]$	+ 1
III $\begin{matrix} \times & 0 \\ \times & 0 \\ \times & 0 \end{matrix}$	$-\left\{ [n(k) + 1] n(k') n(k'') + 1 \right\}^{1/2} 2G(k, -k', k'')$	$[n(k) + 1] n(k') n(k'') + 1 2G(k, -k', k'') ^2 \frac{2\pi}{h} \delta[\omega(k) - \omega(k') + \omega(k'')]$	+ 1
IV $\begin{matrix} \times & 0 \\ \times & 0 \\ \times & 0 \end{matrix}$	$\left\{ [n(k) + 1] n(k') n(k'') \right\}^{1/2} 2G(k, -k', -k'')$	$[n(k) + 1] n(k') n(k'') 2G(k, -k', -k'') ^2 \frac{2\pi}{h} \delta[\omega(k) - \omega(k') - \omega(k'')]$	+ 1
V $\begin{matrix} \times & 0 \\ \times & 0 \\ 0 & \times \end{matrix}$	$-\left\{ n(k) n(k') + 1 n(k'') + 1 \right\}^{1/2} 2G(-k, k', k'')$	$n(k) n(k') + 1 n(k'') + 1 2G(-k, k', k'') ^2 \frac{2\pi}{h} \delta[-\omega(k) + \omega(k') + \omega(k'')]$	- 1
VI $\begin{matrix} \times & 0 \\ \times & 0 \\ 0 & \times \end{matrix}$	$\left\{ n(k) n(k') + 1 n(k'') \right\}^{1/2} 2G(-k, k', -k'')$	$n(k) n(k') + 1 n(k'') 2G(-k, k', -k'') ^2 \frac{2\pi}{h} \delta[-\omega(k) + \omega(k') - \omega(k'')]$	- 1
VII $\begin{matrix} \times & 0 \\ 0 & \times \\ 0 & \times \end{matrix}$	$\left\{ n(k) n(k') n(k'') + 1 \right\}^{1/2} 2G(-k, -k', k'')$	$n(k) n(k') n(k'') + 1 2G(-k, -k', k'') ^2 \frac{2\pi}{h} \delta[-\omega(k) - \omega(k') + \omega(k'')]$	- 1
VIII $\begin{matrix} \times & 0 \\ 0 & \times \\ 0 & \times \end{matrix}$	$-\left\{ n(k) n(k') n(k'') \right\}^{1/2} 2G(-k, -k', -k'')$	$n(k) n(k') n(k'') 2G(-k, -k', -k'') ^2 \frac{2\pi}{h} \delta[-\omega(k) - \omega(k') - \omega(k'')]$	- 1

Table 2

CALCULATION OF THE MATRIX ELEMENTS OF H_1
FOR THE TRANSITION $-k + k' + k'' = b$

k	k'	k''	Coefficients of $a_{-k} a_{k'} a_{k''}$ in Equation (7)
- k	k'	k''	$\frac{1}{3!} 2G(-k, k', k'')$ fifth term in Equation (7)
- k	k''	k'	$\frac{1}{3!} 2G(-k, k'', k')$
k'	- k	k''	$\frac{1}{3!} 2G(k', -k, k'')$ third term in Equation (7)
k''	- k	k'	$\frac{1}{3!} 2G(k'', -k, k')$
k'	k''	- k	$\frac{1}{3!} 2G(k', k'', -k)$ second term in Equation (7)
k''	k'	- k	$\frac{1}{3!} 2G(k'', k', -k)$

condition can be expressed in the form

$$\delta_n \left(\pm \omega(k) \pm \omega(k') \pm \omega(k'') \right)$$

with the sign before the different frequencies depending on whether the number of quanta in the particular mode increases (+ sign) or decreases (- sign) during the transition. The transition probabilities can then be expressed in the form given in Table 1 if one recalls that $\delta(ax) = \delta(x)/a$ and $\delta(-x) = \delta(x)$. In the processes corresponding to Table 2 the occupation number $n(k)$ changes by -1 ($\Delta n(k) = -1$). The other rows of Table 1 are obtained in the same way.

The allowed processes are limited by two selection rules. The conservation of energy is contained in the δ -function while the conservation rule for the wave vectors is given by the quantities $\delta_{k+k'+k''}^b$ included in $G(k, k', k'')$ [Equation (25)]. Thus, row V of Table 1 includes only processes which fulfill the conditions

$$\omega(k) = \omega(k') + \omega(k'') \tag{36}$$

and

$$-k + k' + k'' = b \tag{37}$$

For the processes of row VII the corresponding conditions are

$$\omega(k) + \omega(k') = \omega(k'') \tag{38}$$

and

$$-k - k' + k'' = b \tag{39}$$

The processes which occur can be described in the following way. According to Equation (36) the wave k loses one quanta while each of the waves k' and k'' gain a quanta owing to the interaction. The wave k thus splits into the waves k' and k'' . The relations between the participating k vectors are not unique. Following Peierls, one denotes processes with $b = 0$ as normal processes. These are the only processes which would occur in an elastic continuum. All other

processes with $b \neq 0$ are denoted as umklapp processes because the direction of the vectors, contrary to what is expected from the normal momentum law for phonons, are reversed. Figure 1 shows the positions of the propagation vectors for a normal and an umklapp process.

Another possible process according to Equations (38) and (39) is the collision of two waves k and k' and the resulting generation of a wave k'' . In this case one can also distinguish between normal and umklapp processes (Figure 1).

In Figure 1 a square net is taken as the basis in each case. The edges of the squares are the basis vectors of the reciprocal lattice. The square itself is the elementary cell of the reciprocal lattice. In the description of lattice states by k vectors one must select a definite elementary cell of the reciprocal lattice since the waves k and $k + b$ are identical. When one considers a collision it may happen that the vector $k + k'$ falls outside the selected region. In this case the excited wave $k + k'$ in Figure 1d is identical with the wave k'' since k'' and $k + k'$ differ only by $-b$. Processes of this kind are umklapp processes.

In each of the processes of Table 1 which are caused by H_1 three waves participate and the quantum number $n(k)$ increases or decreases by one unit. The time rate of change of $n(k)$ is given by $\Delta n(k)$ multiplied by the transition probability from Table 1 and summed over all k', k'' . $dn(k)/dt$ thus consists of the six nonvanishing processes (II-VII) of Table 1. The processes with $\Delta n(k) = +1$ appear with positive sign, the others with negative sign. One finally obtains

$$\begin{aligned} \frac{dn(k)}{dt} = & \sum_{k', k''} \frac{2\pi}{\hbar^2} |2G(k, k', k'')|^2 \\ & \times \left\{ \delta(\omega(k) + \omega(k') - \omega(k'')) \left[\begin{aligned} & [n(k) + 1] [n(k') + 1] n(-k'') \\ & - n(k)n(k') [n(-k'') + 1] \end{aligned} \right] \right. \\ & + \delta(\omega(k) - \omega(k') + \omega(k'')) \left[\begin{aligned} & [n(k) + 1] n(-k') [n(k'') + 1] \\ & - n(k) [n(-k') + 1] n(k'') \end{aligned} \right] \\ & \left. + \delta(\omega(k) - \omega(k') - \omega(k'')) \left[\begin{aligned} & [n(k) + 1] n(-k') n(-k'') \\ & - n(k) [n(-k') + 1] [n(-k'') + 1] \end{aligned} \right] \right\} \quad (40) \end{aligned}$$

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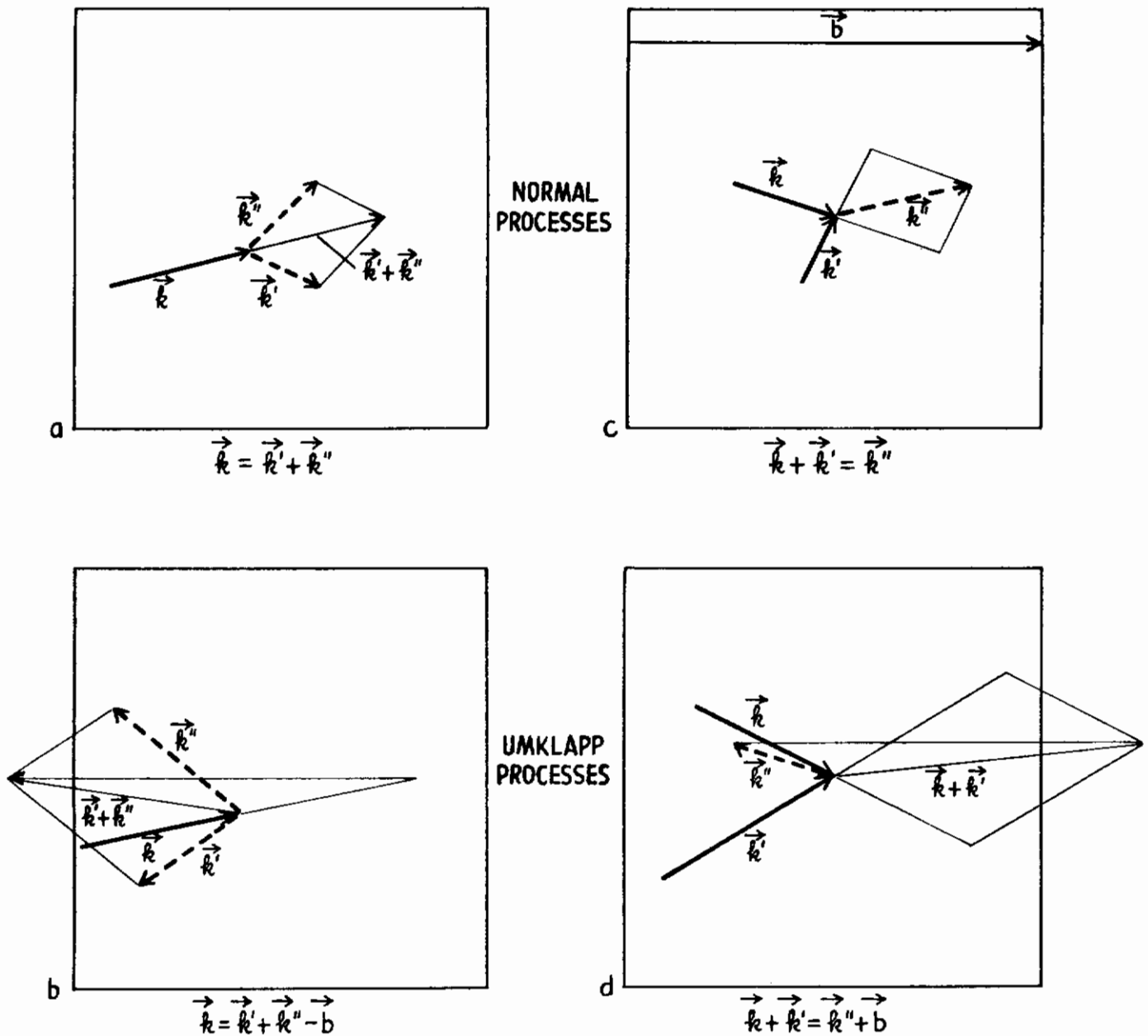


Fig. 1. Possible interaction processes for three waves. (a) Splitting of a wave \vec{k} , normal process. (b) Splitting of a wave \vec{k} , umklapp process. (c) Collision of two waves \vec{k}, \vec{k}' , normal process. (d) Collision of two waves \vec{k}, \vec{k}' , umklapp process.

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In deriving this expression we have made use of the fact that while $G(k, k', k'')$ changes sign for the symmetry operation of inversion its square does not. Thus, $|G(-k, -k', k'')|^2 = |-G(k, k', -k'')|^2 = |G(k, k', -k'')|^2$, etc. We have also used the fact that the frequencies are independent of the sign of k and that the delta function does not depend on the sign of its argument. This means that the transition probability for the process $a_{-k} a_{-k'} a_{k''}^*$ is equivalent to one for the process $a_k a_{k'} a_{-k''}^*$ and so on. Each of the three processes whose occupation number products appear after the minus signs in Equation (40) have been modified in this fashion. The first term in Equation (40) thus corresponds to the contributions of rows II and VII of Table 1, the second to rows III and VI and the third to rows IV and V.

The contributions in the first and second terms of Equation (40) are equivalent since the summation runs over the same range of values for k' and k'' . The equivalence of k' and k'' means that each of the terms of Equation (40) should be divided by two to avoid counting the same process twice. Then because terms one and two correspond to the same processes Equation (40) becomes

$$\begin{aligned} \frac{dn(k)}{dt} = & \sum_{k', k''} \frac{2\pi}{\hbar^2} |2G(k, k', k'')|^2 \\ & \times \left\{ \delta(\omega(k) + \omega(k') - \omega(k'')) \left[\left[n(k) + 1 \right] \left[n(k') + 1 \right] n(-k'') \right. \right. \\ & \qquad \qquad \qquad \left. \left. - n(k)n(k') \left[n(-k'') + 1 \right] \right] \right. \\ & \left. + \frac{1}{2} \delta(\omega(k) - \omega(k') - \omega(k'')) \left[\left[n(k) + 1 \right] n(-k')n(-k'') \right. \right. \\ & \qquad \qquad \qquad \left. \left. - n(k) \left[n(-k') + 1 \right] \left[n(-k'') + 1 \right] \right] \right\} \quad (41) \end{aligned}$$

We will now show how Equation (41) leads in the high temperature limit to the expression used in Appendix B of Technical Documentary Report No. ASD-TDR-62-74, Part I for the relaxation time in the case of phonon-phonon scattering, viz., $1/T(k) = B\omega^2(k)$. A relaxation time for phonon-phonon scattering can be defined if we assume (without physical justification) that all modes except the

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k th have their equilibrium values. The coefficient of $\delta\{\omega(k) + \omega(k') - \omega(k'')\}$ inside the braces in Equation (41) then becomes

$$\left\{n(k) + 1\right\} \left\{n^{\circ}(k') + 1\right\} n^{\circ}(-k'') - n(k)n^{\circ}(k') \left\{n^{\circ}(-k'') + 1\right\} \quad (42)$$

The equilibrium value of the occupation number $n^{\circ}(k)$ is

$$n^{\circ}(k) = \frac{1}{e^{\hbar\omega(k)/KT} - 1}$$

so that

$$1 + n^{\circ}(k) = e^{\hbar\omega(k)/KT} n^{\circ}(k)$$

and since $\omega(k)$ is an even function of k $n^{\circ}(-k) = n^{\circ}(k)$. Using these expressions for $n^{\circ}(k)$ and $1 + n^{\circ}(k)$ and the conservation of energy

$$\hbar\omega(k) + \hbar\omega(k') - \hbar\omega(k'') = 0$$

Equation (42) reduces to

$$\begin{aligned} & \left\{n(k) + 1\right\} n^{\circ}(k') e^{\hbar\omega(k')/KT} n^{\circ}(k'') - n(k)n^{\circ}(k')n^{\circ}(k'') e^{\hbar\omega(k'')/KT} \\ & = n^{\circ}(k')n^{\circ}(k'') \left[n(k) \left(1 - e^{\hbar\omega(k)/KT}\right) + 1 \right] e^{\hbar\omega(k')/KT} \end{aligned}$$

Factoring $(1 - e^{\hbar\omega(k)/KT})$ out of the expression in square brackets and noting that it is equal to $-1/n^{\circ}(k)$ gives

$$- [n(k) - n^{\circ}(k)] n^{\circ}(k') n^{\circ}(k'') \left[e^{\hbar\omega(k'')/KT} - e^{\hbar\omega(k')/KT} \right]$$

Now $1 + n^{\circ}(k') = n^{\circ}(k') e^{\hbar\omega(k')/KT}$ and $1 + n^{\circ}(k'') = n^{\circ}(k'') e^{\hbar\omega(k'')/KT}$ so that Equation (42) finally becomes

$$- [n(k) - n^{\circ}(k)] [n^{\circ}(k') - n^{\circ}(k'')]$$

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Similarly the coefficient of $\delta\{\omega(k) - \omega(k') - \omega(k'')\}$ inside the braces in Equation (41) becomes

$$- [n(k) - n^0(k)] [1 + n^0(k') + n^0(k'')]$$

Thus, when all modes except the k th are in thermal equilibrium Equation (41) takes the form

$$\begin{aligned} \frac{dn(k)}{dt} = & - [n(k) - n^0(k)] \frac{2\pi}{\hbar^2} \sum_{k', k''} \left\{ |2G(k, k', -k'')|^2 \right. \\ & \times \delta\{\omega(k) + \omega(k') - \omega(k'')\} [n^0(k') - n^0(k'')] \\ & + \frac{1}{2} |2G(k, -k', -k'')|^2 \delta\{\omega(k) - \omega(k') - \omega(k'')\} \\ & \left. \times [1 + n^0(k') + n^0(k'')] \right\} \end{aligned}$$

Comparing this expression with Equation (4) shows that $T(k)$ is given by (note $\bar{n} \equiv n^0$)

$$\begin{aligned} \frac{1}{T(k)} = \frac{2\pi}{\hbar^2} \sum_{k', k''} \left\{ |2G(k, k', -k'')|^2 \delta\{\omega(k) + \omega(k') - \omega(k'')\} [n^0(k') - n^0(k'')] \right. \\ \left. + \frac{1}{2} |2G(k, -k', -k'')|^2 \delta\{\omega(k) - \omega(k') - \omega(k'')\} [1 + n^0(k') \right. \\ \left. + n^0(k'')] \right\} \end{aligned} \quad (43)$$

In the high temperature limit

$$1 + n_{k'}^0 \approx n_{k'}^0 \approx \frac{KT}{\hbar\omega(k')} \quad , \quad n_{k''}^0 \approx \frac{KT}{\hbar\omega(k'')}$$

so that

$$\begin{aligned} \frac{1}{T(k)} = \frac{2\pi}{\hbar^2} \frac{KT}{\hbar} \sum_{k', k''} \left\{ |2G(k, k', -k'')|^2 \delta\{\omega(k) + \omega(k') - \omega(k'')\} \right. \\ \times \frac{\omega(k'') - \omega(k')}{\omega(k')\omega(k'')} + \frac{1}{2} |2G(k, -k', -k'')|^2 \\ \left. \times \delta\{\omega(k) - \omega(k') - \omega(k'')\} \frac{\omega(k'') + \omega(k')}{\omega(k')\omega(k'')} \right\} \end{aligned} \quad (44)$$

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From Equation (25) we have

$$|2G(k, k', -k'')|^2 = \frac{g^2 \hbar^3}{8f^3 N} \delta_{k, -k', -k''}^b \omega(k) \omega(k') \omega(k'')$$

and

$$|2G(k, -k', -k'')|^2 = \frac{g^2 \hbar^3}{8f^3 N} \delta_{k, -k', -k''}^b \omega(k) \omega(k') \omega(k'')$$

Substituting these expressions into Equation (44) and noting that the conservation of energy (the $\delta(\omega)$'s) requires for the first term on the right hand side of Equation (44)

$$\omega(k) = \omega(k'') - \omega(k')$$

and for the second term

$$\omega(k) = \omega(k') + \omega(k'')$$

we obtain

$$\frac{1}{T(k)} = \frac{2\pi(KTg^2)}{8f^3 N} \omega^2(k) \sum_{k', k''} \left\{ \delta_{k+k'-k''}^b + \frac{1}{2} \delta_{k-k'-k''}^b \right\} \quad (45)$$

$$= B\omega^2(k) \quad . \quad (46)$$

In deriving Equation (46) $\omega^2(k)$ was factored out of the summation since it is independent of k' and k'' . The expression obtained for B should not be taken too literally since it is based on a one-dimensional model and we demonstrated in Technical Documentary Report No. ASD-TDR-62-74, Part I that the $G(k, k', k'')$'s vanish when the conservation of energy condition and the selection rule on the k 's are applied. However, the form in its dependence on $\omega(k)$ is the same as one would obtain for a three-dimensional model with central forces.

The introduction of a relaxation time for phonon-phonon scattering at high temperatures by the method given above is not too good an approximation because the other modes are not very likely to be in equilibrium in this temperature

range. The relaxation time concept is valid at low temperature but here we can not use a simple limiting form for $n_{k'}^0$ and $n_{k''}^0$.

SCATTERING BY POINT IMPERFECTIONS

In substitutional alloys the impurity atom may be regarded as an isolated point imperfection if the alloy is sufficiently dilute to exclude correlation effects among the impurities. The dependence of the relaxation time on the frequency of the lattice waves is then given by

$$\frac{1}{T} = A\omega^4 \quad (47)$$

where the proportionality constant A depends on the particular scattering mechanism considered. We will derive equation (47) for the case in which the phonons are scattered by an atom which differs from the normal lattice atoms by ΔM .

The one-dimensional treatment is not adequate for this case since it does not lead to the proper dependence of T on ω . However, the arguments are easier to follow in the one-dimensional case and we will employ it as far as possible in calculating the perturbing potential. In this case the Hamiltonian is increased by

$$H' = \frac{\Delta M}{2M^2} p_\ell^2 \quad (48)$$

where p_ℓ is the momentum operator and M is the mass of a lattice atom. In normal coordinate operators p_ℓ has the form

$$p_\ell = \frac{1}{\sqrt{N}} \sum_k p_k e^{ik\ell a} \quad (49)$$

so that H' becomes

$$H' = \frac{\Delta M}{2NM^2} \sum_{k,k'} p_k p_{k'} e^{i(k+k')\ell a} \quad (50)$$

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Equation (27) of the Technical Documentary Report No. ASD-TDR-62-74, Part I expressed the annihilation and creation operators a_k and a_k^* in terms of the normal coordinate momentum and displacement operators by

$$\begin{aligned} a_k &= c_k \left(\frac{P_k}{M} - i\omega(k)U_k^* \right) \\ a_k^* &= c_k \left(\frac{P_k^*}{M} + i\omega(k)U_k \right) \end{aligned} \quad (51)$$

where

$$c_k = \left(M/2\hbar\omega(k) \right)^{1/2} \quad (52)$$

Recalling that $U_k^* = U_{-k}$ and $P_k^* = P_{-k}$ we can solve Equations (51) for P_k in terms of the a_k 's. Thus,

$$P_k = \frac{M}{2c_k} (a_{-k}^* + a_k) \quad (53)$$

Substituting this expression for the P_k 's in Equation (50) gives

$$H' = \left(\frac{\Delta M}{M} \right) \frac{\hbar}{4N} \sum_{k,k'} [\omega(k)\omega(k')]^{1/2} (a_{-k}^* + a_k)(a_{-k'}^* + a_{k'}) \times e^{i(k+k')\ell a}$$

or

$$H' = \frac{\hbar}{4N} \left(\frac{\Delta M}{M} \right) \sum_{k,k'} [\omega(k)\omega(k')]^{1/2} (a_{-k}^*a_{-k'}^* + a_{-k}^*a_{k'} + a_k a_{-k'}^* + a_k a_{k'}) \times e^{i(k+k')\ell a} \quad (54)$$

The processes $a_{-k}^*a_{-k'}^*$ and $a_k a_{k'}$, are not permissible processes since they would simultaneously create or destroy phonons in the states k, k' and would, therefore, violate the law of conservation of energy. Since k and k' both run over the same range of values the remaining two processes are doubly degenerate. In addition k and k' run over positive and negative values so that $a_{-k}^*a_{k'}$, and $a_k a_{-k'}$, are equivalent when summed over positive and negative k 's.

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The transition matrix $\langle f | H' | i \rangle$ may now be evaluated from Equation (53) by taking the initial state to be $| i \rangle = | n(k), n(-k') \rangle$. One obtains for the two processes

$$\langle n(k) + 1, n(-k') - 1 | a_k^* a_{-k'} | n(k), n(-k') \rangle = \sqrt{n(k) + 1} \sqrt{n(-k')}$$

and

$$\langle n(k) - 1, n(-k') + 1 | a_k a_{-k'}^* | n(k), n(-k') \rangle = \sqrt{n(k)} \sqrt{n(-k') + 1}$$

The time rate of change of $n(k)$ due to scattering is then

$$\begin{aligned} \frac{dn(k)}{dt} &= \frac{2\pi}{\hbar^2} \sum_f |\langle f | H' | i \rangle|^2 \delta(\omega_f - \omega_i) \\ &= \frac{2\pi}{\hbar^2} \frac{\hbar^2}{4N^2} \left(\frac{\Delta M}{M} \right)^2 \sum_{k'} \omega(k)\omega(k') \delta(\omega(k) - \omega(k')) \\ &\quad \times \left\{ [n(k) + 1] [n(-k') - n(k)] [n(-k') + 1] \right\} \end{aligned} \quad (55)$$

where the sign is + or - depending on whether $\Delta n(k) = \pm 1$, and the factor $e^{i(k+k')\ell a}$ disappears in the square of the matrix element. We assume that $n(-k')$ has its thermal equilibrium value $n^0(-k')$. Then since $n^0(-k') = n^0(k')$ and the delta function requires $n^0(k') = n^0(k)$ we obtain

$$\frac{dn(k)}{dt} = - \frac{2\pi}{4N^2} \left(\frac{\Delta M}{M} \right)^2 [n(k) - n^0(k)] \sum_{k'} \omega(k)\omega(k') \delta(\omega(k) - \omega(k')) \quad (56)$$

To proceed further we must convert the sum over k' to an integral. In one dimension $\sum_{k'} \rightarrow \frac{L}{2\pi} \int dk'$ and the corresponding form for three dimensions is $\sum_{k'} = \int f(k') dk'$. The integral over dk' is now converted to an integral over $d\omega'$ by assuming an isotropic continuum and using Equation (21) times the volume V (i.e., not referred to unit volume). We finally obtain for $dn(k)/dt$ the expression

$$\begin{aligned} \frac{dn(k)}{dt} &= - [n(k) - n^0(k)] \frac{V}{N} \left(\frac{\Delta M}{M} \right)^2 \frac{2\pi}{4N} \frac{3\omega^3(k)}{2\pi^2 v_o^3} \int \omega(k') \delta(\omega(k) - \omega(k')) d\omega' \\ &= - [n(k) - n^0(k)] \frac{a^3}{N} \left(\frac{\Delta M}{M} \right)^2 \frac{\omega^4(k) 3}{4\pi v_o^3} \end{aligned}$$

where $a^3 = V/N$ is the atomic volume.

Comparing this with Equation (4) gives as the relaxation time for isotope scattering

$$\frac{1}{\tau} = 3 \frac{a^3}{N} \left(\frac{\Delta M}{M} \right)^2 \frac{\omega^4}{4\pi v_0^3} \quad (57)$$

This result is three times the value obtained by Klemens¹ and is due to the fact that we now have a three-dimensional harmonic oscillator and it is possible to choose three mutually perpendicular directions so that the oscillator is resolved into three independent one-dimensional oscillators. Unit vectors specifying these directions should appear in the expressions for the normal coordinate momentum operators. We then have terms of the form $\vec{\epsilon}(k) \cdot \vec{\epsilon}(k')$ in the expression for H' ; when the matrix element is squared and averaged over random directions we obtain

$$\overline{\cos [\vec{\epsilon}(k), \vec{\epsilon}(k')]} = \overline{\vec{\epsilon}(k) \cdot \vec{\epsilon}(k')} = \frac{1}{3}$$

so that we agree with Klemens' result.

CALCULATION OF THE LATTICE THERMAL CONDUCTIVITY OF SIMPLE ALLOYS

The lattice conductivity of Ge-Si alloys was calculated in Technical Documentary Report No. ASD-TDR-62-74, Part I by assuming that the only effect of substituting Si for Ge in the diamond cubic lattice was to change the mass of the atoms. We then have essentially an isotope effect, and the relaxation time associated with the mass defect scattering is, except for a factor of three, given by Equation (57). This relaxation time may be combined with that for phonon-phonon scattering (Ref. section "Expression for K_ℓ ") to give an effective relaxation time for both processes acting simultaneously as indicated in Equation (2). The resultant relaxation time is then substituted in Equation (23) to calculate K_ℓ . If the cubic anharmonic terms in the potential energy, and mass defects are the only processes effective in scattering phonons, K_ℓ is given by

$$K_\ell = K_u \frac{\omega_0}{\omega_D} \tan^{-1} \frac{\omega_D}{\omega_0} \quad (58)$$

where K_u is thermal conductivity in the absence of point defect scattering arising from those processes which do not conserve crystal momentum, viz., "umklapp" processes, ω_D is the Debye cutoff frequency, and ω_0 is the frequency at which phonons are scattered with equal probability by umklapp processes and mass defects. In general

$$\frac{\omega_D}{\omega_0} = \left(\frac{\omega_D^3 K_u \epsilon \pi}{2Kv_0^2} \right)^{1/2} \quad (59)$$

where ϵ is the mean square mass fluctuation parameter and the other quantities are as defined above. As indicated in the Technical Documentary Report No. ASD-TDR-62-74, Part I, v_0 may be expressed in terms of ω_D and ω_D in turn in terms of the Debye temperature so that we finally obtain

$$\frac{\omega_D}{\omega_0} = (395.5)(n)^{1/3} \left(\frac{\bar{M}}{\rho} \right)^{1/6} \left(\frac{K_u}{\theta_D} \right)^{1/2} \epsilon^{1/2} \quad (60)$$

where n is the number of particles per unit cell, θ_D is the Debye temperature, \bar{M} is the mean molecular weight and ρ is the density. All of these quantities except n are a function of the composition of the alloy so that the thermal conductivity as a function of composition is determined by the variation of ω_D/ω_0 with composition. In particular, for the diamond cubic lattice, $n = 8$ and $a^3 = \bar{M}/\rho N_0$ where a is now the cube edge and N_0 is Avogadro's number so that ω_D/ω_0 may be expressed in the form

$$\frac{\omega_D}{\omega_0} = (726.9)(a \times 10^8)^{1/2} \left(\frac{K_u}{\theta_D} \right)^{1/2} \epsilon^{1/2} \quad (61)$$

These results may be generalized by noting that the relaxation for mass defect scattering may be expressed in the form

$$\frac{1}{\tau} = \left(\frac{3a^2 \omega^4}{\pi v_0^3} \right) S_1^2$$

where $S_1^2 = (\Delta M/\bar{M})^2/12$. In particular, since alloys are not a case of simple isotropic substitution but at best the substitution of one chemically similar element for another, we should expect changes in the force constants and lattice distortion.

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Klemens¹ has considered the composition of different point defect scattering mechanisms in cubic crystals. The general form of the relaxation time associated with point defect scattering is

$$\frac{1}{\tau_i} = \left(\frac{3a^3 \omega^4}{\pi v_o^3} \right) S^2 \quad (62)$$

where S^2 is a constant of the order unity whose form depends on the scattering mechanisms considered and the way in which they are composed. Klemens in his approximation obtains

$$S^2 = S_1^2 + (S_2 + S_3)^2 \quad (63)$$

where $S_1^2 = (\Delta M / \bar{M})^2 / 12$, $S_2 = \Delta f / \sqrt{6} \bar{f}$ and $S_3 \approx -4.2 \sqrt{\frac{2}{3}} \Delta r / \bar{r}$. \bar{M} is the mean molecular weight; \bar{f} is the mean force constant of a linkage; \bar{r} is the mean distance to nearest neighbors for an alloy of a given composition; and ΔM , Δf , Δr are the changes in them. Δr is positive if the nearest neighbors are displaced outwards (this is not the case when Si is substituted for Ge). For an alloy system in which $\Delta r < 0$ we thus obtain

$$\begin{aligned} \frac{1}{\tau_i} &= \left(\frac{3a^3 \omega^4}{\pi v_o^3} \right) \left\{ \frac{1}{12} \left(\frac{\Delta M}{\bar{M}} \right)^2 + \left(\frac{1}{\sqrt{6}} \frac{\Delta f}{\bar{f}} + 4.2 \sqrt{\frac{2}{3}} \frac{\Delta r}{\bar{r}} \right)^2 \right\} \\ &= \left(\frac{a^3 \omega^4}{4\pi v_o^3} \right) \left\{ \left(\frac{\Delta M}{\bar{M}} \right)^2 + 2 \left(\frac{\Delta f}{\bar{f}} + 8.4 \frac{\Delta r}{\bar{r}} \right)^2 \right\} = \left(\frac{a^3 \omega^4}{4\pi v_o^3} \right) \epsilon \end{aligned} \quad (64)$$

In general ϵ may be expressed in the form

$$\epsilon = \epsilon_{\Delta M} + 2 \epsilon_{\Delta f, \Delta r} \quad (65)$$

where

$$\epsilon_{\Delta M} = x_{\text{Ge}} \left(\frac{\Delta M_{\text{Ge}}}{\bar{M}} \right)^2 + x_{\text{Si}} \left(\frac{\Delta M_{\text{Si}}}{\bar{M}} \right)^2 \quad (66)$$

and

$$\epsilon_{\Delta f, \Delta r} = x_{\text{Ge}} \left(\frac{\Delta f}{\bar{f}} + 8.4 \frac{\Delta r}{\bar{r}} \right)^2 + x_{\text{Si}} \left(\frac{\Delta f}{\bar{f}} + 8.4 \frac{\Delta r}{\bar{r}} \right)^2 \quad (67)$$

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with x_{Ge} , x_{Si} the mole fractions of Ge and Si in the alloy. Since $x_{\text{Ge}} + x_{\text{Si}} = 1$, $\bar{M} = x_{\text{Ge}} M_{\text{Ge}} + x_{\text{Si}} M_{\text{Si}}$, and $\Delta M_{\text{Ge}} = M_{\text{Ge}} - \bar{M}$, $\Delta M_{\text{Si}} = M_{\text{Si}} - \bar{M}$, $\epsilon_{\Delta M}$ may be expressed in the form

$$\epsilon_{\Delta M} = x_{\text{Ge}} x_{\text{Si}} \frac{(M_{\text{Ge}} - M_{\text{Si}})^2}{\bar{M}^2} \quad (68)$$

To reduce $\epsilon_{\Delta f, \Delta r}$ we express it in the form

$$\begin{aligned} \epsilon_{\Delta f, \Delta r} = & \left\{ x_{\text{Ge}} \left(\frac{\Delta f_{\text{Ge}}}{\bar{f}} \right)^2 + x_{\text{Si}} \left(\frac{\Delta f_{\text{Si}}}{\bar{f}} \right)^2 \right\} + 16.8 \left\{ x_{\text{Ge}} \left(\frac{\Delta f_{\text{Ge}}}{\bar{f}} \right) \left(\frac{\Delta r_{\text{Ge}}}{\bar{r}} \right) \right. \\ & \left. + x_{\text{Si}} \left(\frac{\Delta f_{\text{Si}}}{\bar{f}} \right) \left(\frac{\Delta r_{\text{Si}}}{\bar{r}} \right) \right\} - 70.56 \left\{ x_{\text{Ge}} \left(\frac{\Delta r_{\text{Ge}}}{\bar{r}} \right)^2 + x_{\text{Si}} \left(\frac{\Delta r_{\text{Si}}}{\bar{r}} \right)^2 \right\} \end{aligned}$$

Since $x_{\text{Ge}} + x_{\text{Si}} = 1$ and assuming that $\bar{f} = x_{\text{Ge}} f_{\text{Ge}} + x_{\text{Si}} f_{\text{Si}}$, $\bar{r} = x_{\text{Ge}} r_{\text{Ge}} + x_{\text{Si}} r_{\text{Si}}$, $\Delta f_{\text{Ge}} = f_{\text{Ge}} - \bar{f}$, $\Delta f_{\text{Si}} = f_{\text{Si}} - \bar{f}$, $\Delta r_{\text{Ge}} = r_{\text{Ge}} - \bar{r}$, and $\Delta r_{\text{Si}} = r_{\text{Si}} - \bar{r}$, $\epsilon_{\Delta f, \Delta r}$ becomes

$$\begin{aligned} \epsilon_{\Delta f, \Delta r} = x_{\text{Ge}} x_{\text{Si}} \left\{ \frac{(f_{\text{Ge}} - f_{\text{Si}})^2}{\bar{f}^2} - 16.8 \frac{(r_{\text{Ge}} - r_{\text{Si}})(f_{\text{Ge}} - f_{\text{Si}})}{\bar{r} \bar{f}} \right. \\ \left. - 70.56 \frac{(r_{\text{Ge}} - r_{\text{Si}})^2}{\bar{r}^2} \right\} \quad (69) \end{aligned}$$

The justification for expressing \bar{f} , \bar{M} , and \bar{r} as we did is mainly to facilitate the calculation of \mathcal{K} . However, we may approximately justify the procedure for \bar{f} and \bar{M} by means of the virtual crystal approximation. The lattice vibrational Hamiltonian operator for a Ge-Si alloy has the form

$$\begin{aligned} H = & -\frac{\hbar^2}{2} \left\{ \sum_{\text{Ge}} \frac{1}{M_{\text{Ge}}} \frac{\partial^2}{\partial X_{\text{Ge}}^2} + \sum_{\text{Si}} \frac{1}{M_{\text{Si}}} \frac{\partial^2}{\partial X_{\text{Si}}^2} \right\} \\ & + \frac{1}{2} \left\{ \sum_{\text{Ge}} \sum_{\text{Ge}} x_{\text{Ge}} x_{\text{Ge}} \frac{\partial^2 v}{\partial X_{\text{Ge}} \partial X_{\text{Ge}}} + \sum_{\text{Ge}} \sum_{\text{Si}} x_{\text{Ge}} x_{\text{Si}} \frac{\partial^2 v}{\partial X_{\text{Ge}} \partial X_{\text{Si}}} \right. \\ & \left. + \sum_{\text{Si}} \sum_{\text{Si}} x_{\text{Si}} x_{\text{Si}} \frac{\partial^2 v}{\partial X_{\text{Si}} \partial X_{\text{Si}}} \right\} \quad (70) \end{aligned}$$

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where M_{Ge} and M_{Si} are the masses of Ge and Si atoms, X the nuclear displacement from equilibrium and V the vibrational potential energy. The summations are carried out over all lattice sites as indicated. The virtual crystal approximation replaces the disordered crystal by an equivalent ordered crystal in which each lattice site is occupied by the same type of hypothetical atom. This atom is known as the virtual atom.

Consider an alloy of composition $\text{Ge}_f\text{Si}_{1-f}$ then if N is the total number of sites a fraction fN is occupied by Ge atoms and a fraction $(1-f)N$ by Si atoms. The summations over Ge and Si may then be written

$$\sum_{\text{Ge}} \frac{\partial^2}{\partial X_{\text{Ge}}^2} = \sum_{i=1}^{fN} \frac{\partial^2}{\partial X_i^2} = f \sum_{i=1}^N \frac{\partial^2}{\partial X_i^2}$$

where X_i is a general site. Similarly

$$\sum_{\text{Si}} \frac{\partial^2}{\partial X_{\text{Si}}^2} = (1-f) \sum_{i=1}^N \frac{\partial^2}{\partial X_i^2}$$

The potential energy terms may be similarly expressed so that the Hamiltonian becomes

$$H = -\frac{\hbar^2}{2M_f} \sum_i \frac{\partial^2}{\partial X_i^2} + \frac{1}{2} \sum_i \sum_j X_i X_j \left(\frac{\partial^2 V}{\partial X_i \partial X_j} \right)_f \quad (71)$$

where the summations over i and j are carried out over all lattice sites of the virtual crystal, and where M_f and $(\partial^2 V / \partial X_i \partial X_j)_f$ are defined by

$$M_f^{-1} = fM_{\text{Ge}}^{-1} + (1-f)M_{\text{Si}}^{-1} \quad (72)$$

$$\begin{aligned} (\partial^2 V / \partial X_i \partial X_j)_f &= f^2 \partial^2 V / \partial X_{\text{Ge}} \partial X_{\text{Ge}} + 2f(1-f) \partial^2 V / \partial X_{\text{Ge}} \partial X_{\text{Si}} \\ &+ (1-f)^2 \partial^2 V / \partial X_{\text{Si}} \partial X_{\text{Si}} \end{aligned} \quad (73)$$

According to the virtual crystal model, an atom with suitably averaged mass, M_f , is placed at each lattice site, and the coupling between any pair of such

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atoms is described by the average force constant given by Equation (73). In Equation (63), the right hand side contains the force constants between Ge-Ge, Ge-Si, and Si-Si pairs in the original alloy. If the Ge-Si force constant is assumed to be the arithmetic average of the Ge-Ge and the Si-Si force constants, Equation (73) reduces to

$$\left(\frac{\partial^2 v}{\partial x_i \partial x_j}\right)_f = f \frac{\partial^2 v}{\partial x_{\text{Ge}} \partial x_{\text{Ge}}} + (1-f) \frac{\partial^2 v}{\partial x_{\text{Si}} \partial x_{\text{Si}}} \quad (74)$$

This result is equivalent to our definition of the average force constant used in deriving Equation (59).

The number of independent force constants is determined by the symmetry of the crystal, the type of forces considered, and the extent of the interactions. We considered a two constant model developed originally by Born² with radial and angular forces and nearest neighbor interactions. The force constants may then be determined in the long wave length limit from the elastic constants. Since there are three elastic constants and only two force constants, Born's model leads to a relation between the elastic constants known as "Born's relation". The relations are

$$\begin{aligned} c_{11} &= \alpha/2a \\ c_{12} &= (2\beta - \alpha)/2a \\ c_{44} &= (\alpha - \beta^2/\alpha)/2a \end{aligned} \quad (75)$$

where α and β are the force constants, $2a$ is the lattice constant and c_{11} , c_{12} , and c_{44} are the elastic constants. Eliminating α and β from Equation (75) gives the Born relation

$$4c_{11}(c_{11} - c_{44})/(c_{11} + c_{12})^2 = 1 \quad (76)$$

We have followed the work of Hsieh³ in calculating the force constants from the elastic constant data of Bond and his collaborators⁴ for Ge and of McSkimin and

his collaborators⁵ for Si. The force constants are then

Table 3
Force Constants for Si and Ge

	$\alpha \times 10^{-4}$ dynes/cm	$\beta \times 10^{-4}$ dynes/cm
Ge	7.307	5.046
Si	8.925	6.322

and the Born relation [Equation (76)] gives 1.017 for Ge and 1.087 for Si.

For the two force constant model we are using Equation (69) becomes

$$\begin{aligned}
 \epsilon_{\Delta f, \Delta r} = x_{\text{Ge}} x_{\text{Si}} \left\{ \frac{(\alpha_{\text{Ge}} - \alpha_{\text{Si}})^2}{\bar{\alpha}^2} + \frac{(\beta_{\text{Ge}} - \beta_{\text{Si}})^2}{\bar{\beta}^2} + 70.56 \frac{(r_{\text{Ge}} - r_{\text{Si}})^2}{\bar{r}^2} \right. \\
 + 16.8 \frac{(r_{\text{Ge}} - r_{\text{Si}})}{\bar{r}} \left[\frac{(\alpha_{\text{Ge}} - \alpha_{\text{Si}})}{\bar{\alpha}} + \frac{(\beta_{\text{Ge}} - \beta_{\text{Si}})}{\bar{\beta}} \right] \\
 \left. + 2 \frac{(\alpha_{\text{Ge}} - \alpha_{\text{Si}})}{\bar{\alpha}} \frac{(\beta_{\text{Ge}} - \beta_{\text{Si}})}{\bar{\beta}} \right\} \quad (77)
 \end{aligned}$$

The composite ϵ is then the sum of Equations (68) and (77). This expression for ϵ in Equation (64) would give the relaxation time for point defect scattering for any two component cubic alloy described by a two force constant model and for which $\Delta r > 0$. There is no difficulty in generalizing the result to more components, more force constants or in changing the sign of Δr .

The distortion of the lattice has been estimated from the change in tetrahedral radii between Ge and Si. The tetrahedral radius is given by

$$r = \frac{\sqrt{3}}{8} a$$

where a is the lattice constant. Instead of calculating r from this relation we used Pauling's values⁶ of 1.22×10^{-8} cm for Ge and 1.17×10^{-8} cm for Si.

The expression within the braces of Equation (77) varies from about 0.017 for pure Ge to 0.001 for pure Si. This small value is due to the fact the fourth term in the brackets is opposite in sign to the sum of the first three and last terms and of about the same magnitude. ϵ is thus dominated by the behavior of ϵ_{Δ_M} as a function of composition in the Ge-Si system. The relative contributions of ϵ_{Δ_M} and $2\epsilon_{\Delta_f, \Delta_r}$ to ϵ are shown in Table 4.

The values of a and θ_D used in calculating K were the same as those used before but K_u was changed to 0.6 watt/cm°C for Ge and 1.5 watt/cm°C for Si on the basis of newer experimental data. These values are lower than those used before but are still higher than the most recent experimental data.⁷ The results for K together with the values of a , K_u , θ_D and ω_D/ω_o used in calculating it are given in Table 5. The calculations are compared with the experimental data of Abeles, Beers, Cody, and Dismukes⁸ where possible. It should be emphasized that the experimental values are estimated from their thermal resistance versus temperature curves at 300°K and are subject to considerable error because of the crudeness of the scales on the graph. The theoretical results are plotted in Figure 2. The experimental points are indicated on the figure by crosses.

Note that agreement between theory and experiment is quite good. One reason for this is that a numerical error in the previous results (Technical Documentary Report No. ASD-TDR-62-74, Part I) reduced the ω_D/ω_c values by a factor of ten. The agreement could be further improved by adjusting some of the constants so that the theoretical and experimental curves fitted at some intermediate alloy composition. However, this would require knowledge of the thermal conductivity in one of the alloy compositions and would defeat the goal of predicting the conductivity of alloys from a knowledge of the conductivity of the components.

THERMAL CONDUCTIVITY OF OTHER ALLOY SYSTEMS

Similar calculations were undertaken for the lattice thermal conductivity of $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$ and $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$ alloys. These systems have been previously

Table 4

The Factor Entering into Point Defect Scattering Factor

$x_{\text{Ge}} x_{\text{Si}}$	$\epsilon_{\Delta_{\text{M}}/x_{\text{Ge}} x_{\text{Si}}}$	$\epsilon_{\Delta_{\text{f}}, \Delta_{\text{r}}/x_{\text{Ge}} x_{\text{Si}}}$	$\epsilon/x_{\text{Ge}} x_{\text{Si}}$
0	0.376	0.017	0.413
0.09	0.427	0.014	0.454
0.16	0.488	0.011	0.511
0.21	0.564	0.009	0.582
0.24	0.660	0.007	0.674
0.25	0.769	0.005	0.780
0.24	0.941	0.004	0.948
0.21	1.153	0.003	1.159
0.16	1.448	0.002	1.451
0.09	1.871	0.001	1.873
0	2.511	0.0005	2.512

Table 5

The Lattice Thermal Conductivity of Ge-Si Alloys

x_{Si}	$a \times 10^8$ (cm)	K_u (watt/cm°C)	θ_D (°K)	ω_D/ω_0	K_{calc} (watt/cm°C)	K_{exp} (watt/cm°C)
0	5.657	0.60	400	0	0.60	
0.05						0.182
0.1	5.634	0.69	414	14.14	0.073	
0.2	5.611	0.78	428	21.01	0.057	
0.3	5.589	0.87	445	26.57	0.050	0.077
0.4	5.566	0.96	463	31.40	0.047	
0.5	5.544	1.05	484	35.20	0.046	
0.6	5.522	1.14	508	38.60	0.046	
0.7	5.498	1.23	536	40.28	0.047	0.063
0.8	5.474	1.32	570	39.44	0.052	
0.9	5.453	1.41	611	33.66	0.065	
1.0	5.431	1.50	661	0	1.5	

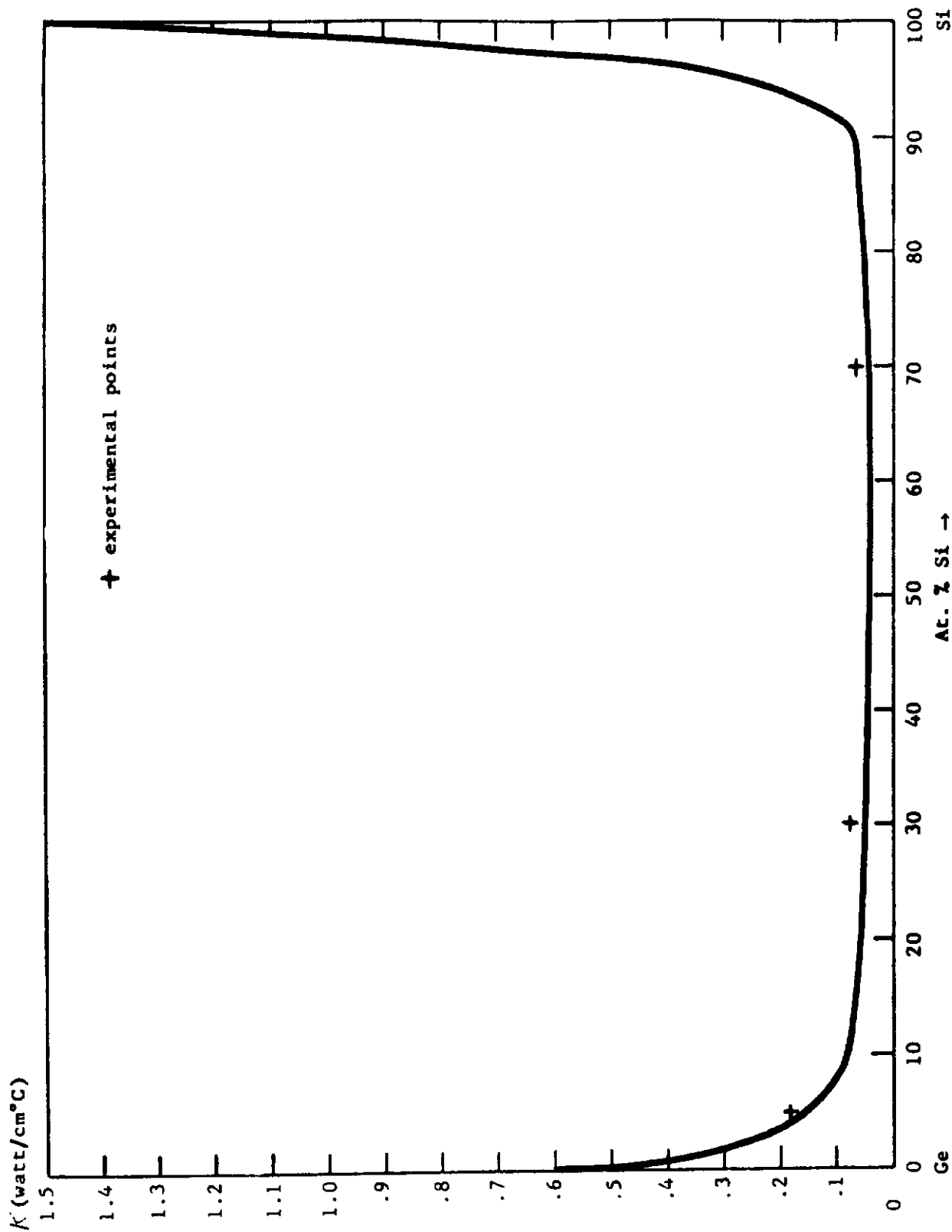


Figure 2
The Lattice Thermal Conductivity of Ge-Si Alloys

calculated by Dr. F. J. Donahoe of the Franklin Institute and by Dr. R. T. Bate of Battelle Memorial Institute. Dr. Donahoe's experimental results for the $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$ system show a much greater reduction in thermal conductivity with alloying than he calculates from the theory. In the $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$ system he shows a slight shoulder in the theoretical curve at the composition Bi_2SeTe_2 which corresponds to an ordering peak. Dr. Bate gets a strong ordering peak at this composition. Unfortunately, the only experimental data for this system that shows any structure is that of Rosi, Abeles, and Jensen⁸ and they obtain a strong peak for a 50% $\text{Bi}_2\text{Te}_3\text{-50% Sb}_2\text{Te}_3$ alloy. Theoretically this has not yet been explained.

The relative mass differences are not as great in these systems as they were in the Ge-Si system so that mass defect scattering does not necessarily dominate the effects of changes in the force constants and lattice distortion. In particular it is found that $\epsilon_{\Delta_f, \Delta_r}$ is dominated by ϵ_{Δ_M} in the $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$ system since the terms in Equation (77) tend to cancel each other because of changes of sign, but that $\epsilon_{\Delta_f, \Delta_r}$ is the dominant factor in the $\text{Bi}_2\text{Te}_3\text{-Bi}_2\text{Se}_3$ system where all the terms in Equation (77) occur with like sign.

Unfortunately we were not able to complete this work.

CALCULATION OF K_ℓ BASED ON NONEQUILIBRIUM STATISTICAL MECHANICS

We attempted to derive an expression for K_ℓ from the general theory of nonequilibrium statistical mechanics. Ordinary statistical mechanism is based on two postulates. The first postulate concerns the existence of an enormous number of atomistic states among which continual spontaneous transitions occur in the course of a macroscopic observation. The second is the assumption of equal a priori probability of each of the atomistic states. From these extremely general hypotheses follows the entire general theory of statistical mechanics.

The theory of nonequilibrium statistical mechanics is based on the two postulates of the equilibrium theory, plus the additional postulate of time symmetry of all physical laws. The additional postulate states that all laws

of physics remain unchanged if the time t is everywhere replaced by its negative $-t$ and if simultaneously the magnetic field \vec{H} is replaced by its negative $-\vec{H}$. This additional postulate permits us to treat systems which are not in thermal equilibrium and in particular lattice thermal conductivity in which the phonon distribution does not have its thermal equilibrium value. The work has not been carried to a satisfactory conclusion because at the moment we do not know how to define a suitable distribution function in the nonequilibrium case.

A. Ensemble Theory

Until recent years, the Boltzmann equation has been the fundamental tool in studying nonequilibrium phenomena. In dilute (weakly interacting) gases with short range forces the equation has been successful in producing results that agree with experiments and with phenomenological theories. However, it is inadequate for dense gases and produces divergent results for coulomb forces. In the past fifteen years a great deal of attention has been focused on the method of Gibbs, i.e., Ensemble Theory, in the hope of justifying the Boltzmann equation for dilute gases with short range forces and to obtain the appropriate generalizations for dense gases and coulomb forces. In the case of solids, the attempt is just beginning.

Ensemble Theory has been from the time of Gibbs entirely successful, from a formal point of view, in describing equilibrium phenomena, but only in the last few years has the nonequilibrium problem started to yield results. We shall start with a brief outline of Ensemble Theory. Consider a conservative system of N particles with generalized coordinates $\{q\}$ and momenta $\{p\}$ and a Hamiltonian $H(\{qp\})$ where $\{q\}$ means all coordinates, $\{p\}$ all momenta, $\{qp\}$ all coordinates and momenta. The equations of motion are

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad , \quad \dot{p}_i = - \frac{\partial H}{\partial q_i} \quad (78)$$

Define a space, called the Γ space, whose coordinates are all the coordinates and momenta of the system. The "volume element", $d\Gamma$ in this space is $d\Gamma = \prod_i dq_i dp_i$. A given point in this space completely determines the

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state of the system since it gives all coordinates and momenta of the system. If a system is known to be at a point in Γ at a given instant of time then the future of the system (as well as the past) is uniquely determined. The motion of the system is then a curve in the Γ space, the equation of the curve is given (parametrically, with time the parameters) by the solution of Equation (78). Now one does not expect to solve Equation (78) for $N \approx 10^{23}$; rather the point of view is this: Suppose some macroscopic information is known about the system, there is a whole region of Γ space consistent with this information. As an example, suppose one knew only the energy of the system to be between E and $E + \delta E$ then there is a "region" in the Γ space, defined by $E \leq H(\{qp\}) \leq E + \delta E$ where if a system was at any point in this region its energy would be between E and $E + \delta E$. If we ask for some other property of the system, with only the knowledge of the system energy, we cannot give an answer for the property would vary depending on which point on this "energy shell" the system was actually at. However, by making a probability assumption one can give an average value to a given property. For example, one could say that since nothing else but the energy is known, the probability $P_N(\{qp\})$ of finding the system in a volume element $d\Gamma$ is constant if $d\Gamma$ is in the "energy shell" and zero if outside. This is certainly a reasonable statement. If one is now asked about a property of the system $\Omega(\{qp\})$ then the best one can give is its average value, i.e.,

$$\langle \Omega \rangle = \int \Omega P_N(\{qp\}) d\Gamma \quad (79)$$

The point of view of Ensemble Theory is this: Given a system with some information known about it, construct an ensemble (i.e., $P_N(\{qp\})$) consistent with the known information, then for all other properties Ω an average can be computed according to Equation (79) and these averages are to be identified with what is observed macroscopically.

It should be noted that if at $t = 0$ we construct $P_N(\{qp\})$ then at a later time the probability distribution P_N changes with time. The equation governing the change in time of P_N is the continuity equation in Γ space,

for probability is conserved just like a fluid. The equation, called the Liouville equation, is

$$\frac{\partial P_N(\{qp\})}{\partial t} = - \sum_k \left\{ \frac{\partial P_N}{\partial p_k} \dot{p}_k + \frac{\partial P_N}{\partial q_k} \dot{q}_k \right\} \quad (80)$$

or using Equation (78)

$$\frac{\partial P_N(\{qp\})}{\partial t} = - \sum_k \left\{ \frac{\partial P_N}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial P_N}{\partial p_k} \frac{\partial H}{\partial q_k} \right\} \quad (81)$$

a. Thermal Equilibrium

The equilibrium problem is formulated in the following way: In equilibrium all macroscopic properties are time independent; since macroscopic properties are to be identified with averages [Equation (79)] the equilibrium form for P_N should also be time independent. A time independent solution of Equation (81) is of the form $P_N(H(qp))$, i.e., P_N is a function of $\{qp\}$ only through H .

Proof:

$$\begin{aligned} \frac{\partial P_N(H)}{\partial q_k} &= \frac{dP_N}{dH} \frac{\partial H}{\partial q_k} & \frac{\partial P_N}{\partial p_k} &= \frac{dP_N}{dH} \frac{\partial H}{\partial p_k} \\ \sum_k \left\{ \frac{\partial P_N}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial P_N}{\partial p_k} \frac{\partial H}{\partial q_k} \right\} &= \frac{dP_N}{dH} \sum_k \left\{ \frac{\partial H}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial H}{\partial p_k} \frac{\partial H}{\partial q_k} \right\} = 0 \end{aligned}$$

One possible selection for P_N is (called Micro Canonical Ensemble)

$$\begin{aligned} P_N &= c & E \leq H(\{qp\}) \leq E + \delta E \\ P_N &= 0 & \text{otherwise} \end{aligned} \quad (82)$$

This corresponds to the example presented earlier, i.e., if a system is known to have an energy between E and $E + \delta E$ then the Micro Canonical Ensemble is a possible way to calculate the equilibrium properties of the system.

Another choice, usually more convenient (called Canonical Ensemble), is

$$P_N = c e^{-\beta E(\{qP\})} \quad \beta = \frac{1}{KT} \quad (83)$$

This corresponds to a system known to have a macroscopic energy \bar{E} where [using Equation (79)]

$$\bar{E} = \int P_N E d\Gamma$$

b. Nonequilibrium

There does not exist, as in the equilibrium case, a general result corresponding to the choice of (82) or (83). Each type of problem must be considered on its own, using the general notions of Ensemble Theory and any simplifying assumption suitable to the chosen problems.

B. One-Dimensional Lattice

In the one-dimensional lattice problem, Equation (81) is

$$\frac{\partial P_N(\{U,P\})}{\partial t} = \left\{ \sum_{s,k} \frac{\partial H}{\partial U_k^s} \frac{\partial}{\partial P_k^s} - \frac{\partial H}{\partial P_k^s} \frac{\partial}{\partial U_k^s} \right\} P_N \quad (84)$$

Setting $H = H_0 + H_3$ we have (85)

$$\frac{\partial P_N}{\partial t} = -L_0^N P_N - L_3^N P_N \quad (86)$$

$$L_0^N \equiv \sum_{s,k} \left\{ \frac{\partial H_0}{\partial P_k^s} \frac{\partial}{\partial U_k^s} - \frac{\partial H_0}{\partial U_k^s} \frac{\partial}{\partial P_k^s} \right\} \quad (87)$$

$$L_3^N \equiv \sum_{s,k} \left\{ \frac{\partial H_3}{\partial P_k^s} \frac{\partial}{\partial U_k^s} - \frac{\partial H_3}{\partial U_k^s} \frac{\partial}{\partial P_k^s} \right\} = - \sum_{s,k} \frac{\partial H_3}{\partial U_k^s} \frac{\partial}{\partial P_k^s} \quad (88)$$

Using the explicit form for H_0 we have

$$\frac{\partial H_0}{\partial U_k^s} = m\omega^2 U_k^s \quad ; \quad \frac{\partial H_0}{\partial P_k^s} = \frac{P_k^s}{m} \quad (89)$$

a. Equilibrium

In the case of a lattice, it is customary in discussing equilibrium properties to treat only the H_0 term in H , i.e., by assuming H_3 is a small correction to H_0 . Equation (80) is then

$$\frac{\partial P_N}{\partial t} = -L_0^N P_N \quad (90)$$

and the equilibrium solution in the Canonical Ensemble is [Equation (83)]

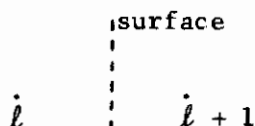
$$P_N = c e^{-\beta H_0} \quad \beta = \frac{1}{KT} \quad (91)$$

Equation (91) is a stationary solution of Equation (90) [but not of Equation (86)]. The constant in Equation (91) is determined by the normalization

$$\int P_N d\Gamma = 1 \quad d\Gamma = \prod_{s,k} dU_k^s dP_k^s \quad (92)$$

b. Nonequilibrium

The power transmitted across a "surface" may be determined as follows. Consider the l th and $(l+1)$ th particle and a surface perpendicular to the line joining them.



- $f_{l,l+1}$ = force on l due to $(l+1)$.
- $f_{l+1,l}$ = force on $(l+1)$ due to l .
- u_l, u_{l+1} displacements of (l) and $(l+1)$

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We have:

$$f_{l,l+1} = c(u_{l+1} - u_l)$$

$$f_{l+1,l} = c(u_l - u_{l+1})$$

The net instantaneous power π_l transmitted across the surface is

$$\pi_l = - (f_{l,l+1})\dot{u}_l + (f_{l+1,l})\dot{u}_{l+1} \quad (93)$$

$$\pi_l = c(u_l - u_{l+1}) (\dot{u}_{l+1} + \dot{u}_l) \quad (94)$$

Now $\dot{u}_l = p_l/m$ so that we may express \dot{u}_l in terms of the normal coordinates P_k by Equation (49). Similarly u_l is given by

$$u_l = \frac{1}{\sqrt{N}} \sum_k U_k e^{-ikla}$$

When these relations are substituted for the u 's and \dot{u} 's in Equation (94) and an ensemble average is taken we obtain $\langle \pi_l \rangle$. This is the basic equation for determining the thermal conductivity, for it is an expression for the flux of energy across the surface. One needs to find the necessary distribution function, in the non-equilibrium case, to evaluate the averages. Note: in equilibrium, the averages on the right side of Equation (94) are zero so that there is no heat current in equilibrium.

SUMMARY

The thermal conductivity of dilute simple substitutional alloys can be fairly accurately calculated by combining the scattering of the phonons due to anharmonic terms in the potential energy of the crystal with various point defect scattering mechanisms arising from the impurity atoms. If the concentration of the two constituents in a binary alloy become comparable one would expect other effects such as an ordering of the constituents or dislocation effects. Apparently good results can be obtained for Ge-Si alloys by ignoring these complications even in nondilute alloys.

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The electronic portion of the thermal conductivity is usually estimated by assuming that a Wiedemann-Franz law is valid for the ratio of thermal to electrical conductivity with a suitable value of the Lorenz number.

At very high temperatures one might expect some thermal energy to be transported by radiation and by coupled electron-hole pairs, i.e., excitations. In fairly pure material where the electron and hole concentrations are approximately equal ambipolar diffusion of electrons and holes will cause the thermal conductivity to rise with decreasing electrical conductivity. These effects were not considered in our work although presumably all of them could occur in suitable temperature ranges in the Ge-Si alloys.

We chose to consider only the lattice portion of the thermal conductivity because it can be readily separated from the other effects and should be a sensitive gauge for judging the validity of various theories of heat conduction in solids. As far as we know the attempt to calculate the lattice thermal conductivity from nonequilibrium statistical mechanics is a new approach to the problem and the investigation should be continued along these lines.

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