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The thermal conductivity of dielectric solids at low temperatures (Theoretical)

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The statistical equilibrium of phonons in the presence of a temperature gradient is investigated, and a general formula for the thermal conductivity of dielectric solids is obtained. This is applied to quartz glass, giving good agreement with values observed by Berman (1951), and to crystals. Comparison between theory and experiment are made for alkali-halides and quartz, and conclusions are drawn about the defects in neutron-irradiated quartz.

We shall discuss the thermal conductivity of dielectric solids, i.e. solids in which the heat transfer is mainly through the elastic vibrations of the lattice. The solid may be a crystal or it may be amorphous, but each atom has a fixed equilibrium position and the thermal vibrations can thus be resolved into normal modes. For a perfect crystal these normal modes are plane travelling waves. Departures from the perfect lattice result in interactions which are responsible for the statistical equilibrium between the normal modes.

The normal modes of a perfect lattice can be quantized (Peierls 1929, 1935), giving rise to the concept of phonons analogous to the photons of radiation theory. The phonons obey Bose-Einstein statistics. The heat current is determined by the distribution of phonons, which in turn is obtained as a solution of a Boltzmann equation. We shall obtain an approximate solution, and thus obtain an expression for the thermal conductivity. This will be similar, though not quite the same, as expressions given, but without derivation, by Pomeranchuk (1942). The approach here developed can be regarded as a link between the rigorous theory of Peierls and the approach of Pomeranchuk.

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THE BOLTZMANN EQUATION

Let N_i be the number of phonons per unit volume pertaining to a normal mode of wave-number k_i , frequency ω_i . The average value of N is determined by the following equation:

$$-v_G \cdot \text{grad } T \frac{dN}{dT} = \frac{\partial N}{\partial t}, \tag{1}$$

where T is the temperature and v_G the classical group velocity (velocity of phonon wave-packet). The left-hand side represents the rate of change of N due to convection; this is balanced on the right-hand side by the rate of change due to discontinuous processes. These processes are additive, i.e.

$$\frac{\partial N}{\partial t} = \sum_{(\alpha)} \frac{\partial N}{\partial t}_{(\alpha)}, \tag{2}$$

where $\frac{\partial N}{\partial t}_{(\alpha)}$ is the rate of change due to process (α) . We have the following processes:

- (1) Three-phonon processes in which energy $\hbar\omega$ and momentum $\hbar k$ is conserved.
- (2) Three-phonon processes in which energy is conserved, but one component of momentum altered by \hbar/a , a being the lattice constant (Umklapprozesse, U -processes).
- (3) 'Elastic scattering' of a phonon by a lattice defect or boundary. The energy is unaltered, but the momentum is changed.
- (4) 'Inelastic scattering.'
- (5) Higher-order phonon interaction, as treated by Pomeranchuk (1941).

Processes (1) and (2) arise from anharmonicities of the interatomic forces. According to Peierls the perturbation results in a transition in which one phonon is destroyed and two created, or vice versa. The rate of change of the i th mode is given by

$$\frac{\partial N_i}{\partial t} = \sum_j \sum_k D_{ijk} \{N_i N_j (N_k + 1) - (N_i + 1) (N_j + 1) N_k\}, \tag{3}$$

where the coefficient D_{ijk} depends on the anharmonicities and vanishes unless energy is conserved

$$\omega_i + \omega_j = \omega_k, \tag{4}$$

and momentum is conserved for (1)-processes

$$\mathbf{k}_i + \mathbf{k}_j = \mathbf{k}_k, \tag{5}$$

while for U -processes

$$\mathbf{k}_i + \mathbf{k}_j = \mathbf{k}_k + \epsilon 2\pi/a, \tag{6}$$

where ϵ is a unit vector capable of six orientations.

Processes (3) and (4) arise from defects in the lattice, boundaries, microcrystalline structure, etc. We shall disregard the effects of processes (5), since the higher-order processes will be unimportant at low temperatures (Pomeranchuk 1942), becoming appreciable at the highest temperatures only. We shall also assume that there is no correlation between the directions of the initial and final phonons in processes (3) and (4).

Although the Boltzmann equation determines the average value of N , it gives us no information about fluctuations. Also in setting it up one assumes the phonons

to behave like classical particles, i.e. one disregards the limitations of the uncertainty principle. A criterion for the validity of this has been given by Peierls (1934).

THE HOMOGENEOUS EQUATION

In the absence of a temperature gradient we have as condition of equilibrium

$$\sum_{(\alpha)} \left. \frac{\partial N}{\partial t} \right]_{(\alpha)} = 0. \quad (7)$$

The solution of this homogeneous equation \mathcal{N} gives us the equilibrium distribution, and we know from general considerations that this is the Planck distribution

$$\mathcal{N}_i = \frac{1}{e^{\hbar\omega_i/KT} - 1}. \quad (8)$$

If we put separately

$$\left. \frac{\partial N}{\partial t} \right]_{(\alpha)} = 0, \quad (9)$$

then the solution of each of these equations consists of a wider class of functions $\mathcal{N}'_{(\alpha)}$. A singular solution $\mathcal{N}'_{(\alpha)}$ is a solution of (9) for one process (α) which is not at the same time a solution for all other processes, and is thus not a solution of (7). It can be shown that (8) is a solution for all processes.

For example, it was shown by Peierls (1935) that a solution of (9) common to processes (1) and (2) is

$$\mathcal{N}'_{(1,2)} = (e^{\alpha\omega} - 1)^{-1},$$

where α is some constant, since $\alpha\Sigma\omega$ is conserved for these processes. For (1)-processes alone, however, we have a wider class of solutions

$$\mathcal{N}'_{(1)} = (e^{\alpha\omega + \beta \cdot \mathbf{k}} - 1)^{-1}, \quad (10)$$

since $\Sigma(\alpha\omega + \beta \cdot \mathbf{k})$ is conserved in (1)-processes, where β is some constant vector. If $|\beta|$ is small, this can be written

$$\mathcal{N}'_{(1)} = -\frac{\beta \cdot \mathbf{k} e^{\alpha\omega}}{(e^{\alpha\omega} - 1)^2}. \quad (11)$$

Similarly, a singular solution for process (3) is

$$\mathcal{N}'_{(3)} = f(\omega), \quad (12)$$

where f is any function, since the number of phonons of a given frequency is not altered by (3)-processes.

THE FIRST-ORDER APPROXIMATION TO THE INHOMOGENEOUS EQUATION

More generally if there is a temperature gradient,

$$-v_G \cdot \text{grad } T \frac{dN}{dT} = \sum_{(\alpha)} \left. \frac{\partial N}{\partial t} \right]_{(\alpha)}. \quad (13)$$

The right-hand side is an integral expression. Owing to the complicated form of (3) a rigorous solution seems impracticable, but we shall find an approximate solution. If \mathcal{N} is the equilibrium distribution for uniform temperature, let

$$N = \mathcal{N} + n, \quad (14)$$

and assume that $n \ll \mathcal{N}$. In particular, assume $\frac{dn}{dT} \ll \frac{d\mathcal{N}}{dT}$, and thus

$$-v_G \cdot \text{grad } T \frac{d\mathcal{N}}{dT} = \sum_{(\alpha)} \left[\frac{\partial N}{\partial t} \right]_{(\alpha)}. \tag{15}$$

If in the expression for $\left[\frac{\partial N}{\partial t} \right]$ we neglect all powers of n higher than the first, then in consequence of (15) the deviation from equilibrium n is proportional to the temperature gradient.

The heat current is the energy flux due to the transport of phonons, each of which carries energy $\hbar\omega$. If $f(\mathbf{k}) d\mathbf{k}$ is the number of normal modes in the wave-number interval \mathbf{k} , $d\mathbf{k}$, we get for the energy flux in the direction of $\text{grad } T$

$$Q = \sum_j \iiint N_j(\mathbf{k}) \hbar\omega \frac{\mathbf{k} \cdot \text{grad } T}{|k| \times |\text{grad } T|} v_{Gj}(\mathbf{k}) f(\mathbf{k}) d\mathbf{k}, \tag{16}$$

where we now specify a mode by its wave-number \mathbf{k} and its polarization j . Since $N = \mathcal{N} + n$, and since $\mathcal{N}(\mathbf{k}) = \mathcal{N}(-\mathbf{k})$ in all cases, we can replace $N_j(\mathbf{k})$ by $n_j(\mathbf{k})$ in (16), i.e. only the deviation n contributes to the energy current. Also since to a first approximation $n \propto \text{grad } T$, Q is also proportional to $\text{grad } T$.

The first-order approximation is valid provided n , and hence $\text{grad } T$, is sufficiently small. From (23), an equation correct to the first order, a criterion of the validity of the first-order approximation is easily deduced, namely, that the temperature gradient be so small that the temperature difference associated with the relaxation length v_{GT} is much smaller than the absolute temperature. This is always fulfilled at high temperatures, and has always been considered a desirable criterion in experimental work even at lowest temperatures.

The results up till now are valid for all solids. If we restrict ourselves to isotropic solids, a considerable simplification is possible. Consider an isotropic body. Introduce spherical polar co-ordinates in \mathbf{k} -space with the axis of symmetry in the direction of the temperature gradient and let μ be the cosine of the angle between \mathbf{k} and $\text{grad } T$. Then (13) becomes

$$-\mu v_G \frac{dT}{dz} \frac{d\mathcal{N}}{dT} = \sum_{(\alpha)} \left[\frac{\partial N}{\partial t} \right]_{(\alpha)}. \tag{17}$$

We can expand n into spherical harmonics

$$n = A_0 + A_1 P_1(\mu) + A_2 P_2(\mu) + \dots, \tag{18}$$

where the coefficients A depend on $|k|$ only. Then substituting into (16) and integrating over all directions, since $\mathbf{k} \cdot \text{grad } T = k \frac{dT}{dz} \mu$

$$Q = \sum_j \frac{4\pi}{3} \int n_j(k) \hbar\omega v_{Gj}(k) f(k) dk, \tag{19}$$

where now $n_j(k) = A_1(k)$ and depends on the magnitude of k only. Thus only the first harmonic in the expansion (18) contributes to the energy flux.

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We now define a relaxation time $\tau_{(\alpha)}$ by

$$\left. \frac{\partial N}{\partial t} \right]_{(\alpha)} = -\frac{N - \mathcal{N}}{\tau_{(\alpha)}} = -\frac{n}{\tau_{(\alpha)}}, \quad (20)$$

i.e. we assume that the discontinuous processes tend to obliterate exponentially any deviations from equilibrium. We assume that $\tau_{(\alpha)}$ depends on the magnitude, but not on the direction, of \mathbf{k} . We define an overall relaxation time

$$\frac{1}{\tau} = \sum_{(\alpha)} \frac{1}{\tau_{(\alpha)}}, \quad (21)$$

and substituting into (17) we get

$$v_G \mu \frac{dT}{dz} \frac{d\mathcal{N}}{dT} = \frac{n}{\tau}, \quad (22)$$

whence we can obtain the deviation from equilibrium using (8):

$$n = v_G \frac{dT}{dz} \tau \mu \frac{\hbar\omega}{KT^2} \frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT} - 1)^2}, \quad (23)$$

so that n is proportional to τ . We can substitute this into (19), and dividing by the temperature gradient we get for the conductivity of an isotropic solid

$$\kappa = \frac{4\pi}{3} \sum_j \int \tau(k) \frac{\hbar^2 \omega^2}{KT^2} v_G(k)^2 \frac{e^{\hbar\omega/KT}}{(e^{\hbar\omega/KT} - 1)^2} f(k) dk. \quad (24)$$

In the case of an anisotropic solid the position is more complicated, and the present theory cannot predict quantitatively the effect of the anisotropy.

Now since the contribution to the energy-content per unit volume from the normal modes of wave-number k , dk is

$$E(K, T) = \frac{\hbar\omega}{(e^{\hbar\omega/KT} - 1)} f(k) 4\pi, \quad (25)$$

we can, on defining the relaxation length

$$l(k) = v_G(k) \tau(k), \quad (26)$$

rewrite (24) in the form

$$\kappa = \frac{1}{3} \sum_j \int \frac{\partial}{\partial T} (E(k, T))_j l(k) v_G(k) dk. \quad (27)$$

This is formally equivalent to the generalized formula of Debye (1914) as used by Pomeranchuk (1941, 1942). However, $l(k)$ is defined by (26) and (20) and is not the mean free path, as commonly stated. For (1)-processes the concept of mean free path is obviously inapplicable, since owing to the high probability of interaction with phonons of small energy the mean free path is very much smaller than the effective relaxation length. The problem is to find the latter quantity.

THE EFFECTIVE RELAXATION LENGTH

For all processes for which there is no correlation between the directions of the phonons involved, i.e. processes (3) and (4), the effective relaxation length is equal to the mean free path for these processes, for to the first order in $\text{grad } T$ all deviations from equilibrium will be such that the total number of phonons of a given frequency

remains unaltered, only the distribution in direction is changed. Hence the number of phonons entering a particular mode per unit time will be unchanged and is $\mathcal{N}v/\lambda$, where λ is the mean free path. The number of phonons leaving a mode will be—by definition of mean free path— Nv/λ . In equilibrium the net rate of change will be zero, but in general

$$\left. \frac{\partial N}{\partial t} \right]_{(3,4)} = \frac{(\mathcal{N} - N) v_G}{\lambda}, \tag{28}$$

and comparing this with (20) we see that the mean free path λ equals the relaxation length $l = v_G \tau$ for processes without directional correlation.

The situation is more complicated for (1)-processes. We can divide these processes into three classes. Let phonons \mathbf{k} and \mathbf{k}_1 combine to form a phonon \mathbf{k}_2 ,* where we are interested in the rate of change of N . We then have

- (a) processes such that $|k_1| \ll |k|$; hence $\mathbf{k} \sim \mathbf{k}_2$;
- (b) processes such that $|k_1| \gg |k|$; hence $|k_2| \gg |k|$;
- (c) processes such that $|k_1| \sim |k| \sim |k_2|$.

The rate of change of N is given by equation (3)

$$\left. \frac{\partial N}{\partial t} \right] = \sum_{(1)} A_{012} [N N_1 (N_2 + 1) - (N + 1) (N_1 + 1) N_2], \tag{29}$$

where the conservation relations (4) and (5) are obeyed

$$\omega + \omega_1 = \omega_2, \quad \mathbf{k} + \mathbf{k}_1 = \mathbf{k}_2. \tag{30}$$

It will be shown that the major contribution to $\left. \frac{\partial N}{\partial t} \right]_{(1)}$ comes from processes of class (b) and (c).

Consider processes of class (a): regarding \mathbf{k} as fixed and \mathbf{k}_2 determined by \mathbf{k}_1 we must sum over all allowed \mathbf{k}_1 . Putting $N = \mathcal{N} + n$, and noting that the condition of equilibrium requires

$$\mathcal{N} \mathcal{N}_1 - \mathcal{N} \mathcal{N}_2 - \mathcal{N}_1 \mathcal{N}_2 = 0, \tag{31}$$

we can rewrite the expression inside the bracket of (29), regrouping and neglecting products of the n 's

$$N N_1 (N_2 + 1) - (N + 1) (N_1 + 1) N_2 = n_1 (\mathcal{N} - \mathcal{N}_2) + \mathcal{N}_1 (n - n_2) - (n \mathcal{N}_2 + n_2 \mathcal{N}). \tag{32}$$

We can neglect $n - n_2 = \frac{\partial n}{\partial \omega} \omega_1$ as a second-order quantity. Likewise

$$(\mathcal{N} - \mathcal{N}_2) n_1 = \frac{\partial \mathcal{N}}{\partial \omega} \omega_1 n_1$$

vanishes when summed over all \mathbf{k}_1 , since to every interaction $\mathbf{k}_2 = \mathbf{k} + \mathbf{k}_1$, $\omega_2 = \omega + \omega_1$ there also corresponds an interaction $\mathbf{k} = \mathbf{k}'_2 + \mathbf{k}_1$, $\omega = \omega'_2 + \omega_1$; i.e. n_1 is unchanged in sign since \mathbf{k}_1 is in the same sense, but ω_1 is now of opposite sign. Finally, $\mathcal{N} \sim \mathcal{N}_2$ and $n \sim n_2$ since $\mathbf{k} \sim \mathbf{k}_2$; hence

$$\left. \frac{\partial N}{\partial t} \right] = - \sum_{(1)} A_{012} 2n \mathcal{N}. \tag{33}$$

* The other case $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}$ can be taken account of by letting ω_1 become negative.

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Now the simultaneous solutions of (30) for small ω_1 are uniformly spaced over an ellipsoid or hyperboloid of revolution in \mathbf{k} -space; the number of solutions in the range $\omega_1, \Delta\omega_1$ is proportional to $\omega_1 \Delta\omega_1$, and thus

$$\left. \frac{\partial N}{\partial t} \right]_{\Delta\omega_1} \sim -n \, 2A \mathcal{N} \omega_1 \Delta\omega_1. \quad (34)$$

From this it can be seen that the greatest contribution comes from large ω_1 ; hence (c)-processes are more important than (a)-processes owing to the larger measure of solutions of (30).

Consider now processes of class (b). We regroup expression (32) to

$$n(\mathcal{N}_1 - \mathcal{N}_2) + \mathcal{N}(n_1 - n_2) - (n_1 \mathcal{N}_2 + n_2 \mathcal{N}_1). \quad (35)$$

Since $\omega \ll \omega_1$ we can neglect $n_1 - n_2 = \frac{\partial n_1}{\partial \omega_1} \omega$ as a second-order quantity. Also from (23)

$$n_1 \propto \tau_1 \frac{\alpha \omega_1 e^{\alpha \omega_1}}{(e^{\alpha \omega_1} - 1)^2}, \quad (36)$$

where $\alpha = \hbar/KT$, and further

$$(\mathcal{N}_1 - \mathcal{N}_2) = \omega \frac{\partial \mathcal{N}_1}{\partial \omega_1} = \frac{\alpha \omega e^{\alpha \omega_1}}{(e^{\alpha \omega_1} - 1)^2}. \quad (37)$$

Now, $(n_1 \mathcal{N}_2 + n_2 \mathcal{N}_1) \sim 2n_1 \mathcal{N}_1$, and we find that the first and the third terms in (35) are in the ratio

$$n(\mathcal{N}_1 - \mathcal{N}_2)/2n_1 \mathcal{N}_1 = \tau \alpha^2 \omega^2 \frac{e^{\alpha \omega}}{(e^{\alpha \omega} - 1)^2} \bigg/ 2\tau_1 \frac{\alpha \omega_1}{(e^{\alpha \omega_1} - 1)}, \quad (38)$$

where τ is the effective relaxation time for \mathbf{k} -phonons, τ_1 for \mathbf{k}_1 -phonons. If $\alpha\omega > 1$, and thus $\alpha\omega_1 \gg 1$, this ratio becomes

$$n(\mathcal{N}_1 - \mathcal{N}_2)/2n_1 \mathcal{N}_1 = \tau \alpha^2 \omega^2 e^{-\alpha \omega} / 2\tau_1 \alpha \omega_1 e^{-\alpha \omega_1}, \quad (38')$$

and since $\alpha\omega_1 > \alpha\omega$, the term $2n_1 \mathcal{N}_1$ can be neglected, provided $\tau_1 \gg \tau$. This last condition is always fulfilled. Thus, for $\alpha\omega > 1$,

$$\left. \frac{\partial N}{\partial t} \right]_{\Delta\omega_1} = -An\alpha\omega e^{-\alpha \omega_1} \omega_1 \Delta\omega_1. \quad (39')$$

The maximum contribution comes from frequencies $\alpha\omega_1 \sim 1$, i.e. from processes of class (c), owing to the exponential factor. If, however, $\alpha\omega < 1$, we have

$$n(\mathcal{N}_1 - \mathcal{N}_2)/2n_1 \mathcal{N}_1 = \tau/2\tau_1 \frac{\alpha \omega_1}{e^{\alpha \omega_1} - 1} \simeq \tau/\tau_1, \quad (38'')$$

and the term $2n_1 \mathcal{N}_1$ can only be neglected if the effective mean free path decreases sufficiently rapidly with frequency. If this is fulfilled

$$\left. \frac{\partial N}{\partial t} \right]_{\Delta\omega_1} = -An\alpha\omega \frac{e^{\alpha \omega_1}}{(e^{\alpha \omega_1} - 1)^2} \omega_1 \Delta\omega_1. \quad (39'')$$

The maximum contribution comes again from $\alpha\omega_1 \sim 1$, but since $\alpha\omega < 1$ this will now be a process of class (b).

We can summarize the above:

(1) Processes of class (a) are always unimportant.

(2) If $\hbar\omega/KT > 1$, the important contribution to $\left. \frac{\partial N}{\partial t} \right]_{(a)}$ comes from processes of class (c), irrespective of the form of $\tau(\omega)$.

(3) If $\hbar\omega/KT < 1$, the important processes will be of class (b), interacting with phonons of frequency of order $\omega_1 \sim KT/\hbar$. If $\tau(\omega)$ decreases sufficiently rapidly with ω , i.e. if $\tau(\omega_1) \ll \tau(\omega)$, this rate of change will be proportional to n .

But if we cannot neglect $\tau(\omega_1)$, i.e. we cannot neglect $2n_1\mathcal{N}_1$ in (35), there are not only processes of class (b) tending to reduce the deviation n , but since there is an appreciable deviation n_1 for frequency $\omega_1 = KT/\hbar$, there will be reverse processes tending to increase the deviation n . If $\tau(\omega) \sim \tau(\omega_1)$ these two processes will counter-balance each other. Another way of looking at it is to say that $\tau(\omega) = \text{const.}$ corresponds to a singular solution—compare (11) and (23)—and thus $\left. \frac{\partial N}{\partial t} \right]_{(a)} = 0$ for constant τ .

It is convenient to introduce the concept of the relaxation length of a single mode. This is defined as in (20), but we assume that all modes are excited to their equilibrium value, except the one mode whose rate of change we want to calculate. Thus the relaxation length of a single mode is the absorption length for a sound wave of the same frequency. For example, for processes (1) we put into (29) $N_1 = \mathcal{N}_1$, $N_2 = \mathcal{N}_2$, i.e. $n_1 = n_2 = 0$. We get then for the rate of change of N

$$\left. \frac{\partial N}{\partial t} \right]_{(a)} = \sum_1 A_{012} n(\mathcal{N}_1 - \mathcal{N}_2) = -\frac{n}{\sigma}, \tag{40}$$

and $v_G\sigma$ is the relaxation length of a single mode. It is a quantity whose calculation is straightforward in principle, involving only an integration over \mathbf{k}_1 , but, of course, we require a knowledge of the coefficient A . Approximate calculations have been made by Landau & Rumer (1937) and by Pomeranchuk (1941) for transverse and longitudinal waves respectively.

A similar quantity could also be defined for scattering processes (3) and (4); but for these processes there is no need to draw a distinction between the concepts of mean free path, effective relaxation length and relaxation length of a single mode. Furthermore, we need not draw any distinction between τ and σ for all processes for which $\left. \frac{\partial N}{\partial t} \right]$ is proportional to n only, namely, processes of type (1) class (a) and class (b) if $\hbar\omega/KT > 1$; but we must distinguish between τ and σ for class (c), and for class (b) if $\hbar\omega/KT < 1$.

Consider the latter case: the term $n(\mathcal{N}_1 - \mathcal{N}_2)$ in (35), when suitably summed, gives us $\left. \frac{\partial N}{\partial t} \right]$; but the term $2n_1\mathcal{N}_1$ gives us a contribution of opposite sign. We have seen that these two contributions are in the ratio $\tau(\omega)/\tau(\omega_1)$; hence we have in general for $\hbar\omega < KT$, where (b)-processes are more important than (c)-processes, that

$$\left. \frac{\partial N}{\partial t} \right]_{(a)} = \left. \frac{\partial N}{\partial t} \right]_{(a)} \left(1 - \frac{\tau(\omega_1)}{\tau(\omega)} \right), \tag{41}$$

where $\omega_1 = KT/\hbar$. Thus
$$\frac{1}{\tau_{(1)}(\omega)} = \frac{1}{\sigma_{(1)}(\omega)} \left(1 - \frac{\tau(\omega_1)}{\tau(\omega)} \right). \quad (41')$$

If now $\tau_0(\omega)$ is the combined mean free time due to all other processes, i.e. processes not conserving momentum, disregarding U -processes for the time being, then

$$\frac{1}{\tau(\omega)} = \frac{1}{\tau_{(1)}(\omega)} + \frac{1}{\tau_0(\omega)}, \quad (42)$$

and substituting this into (41') we get

$$\tau(\omega) = \frac{\tau_0(\omega) [\sigma_{(1)}(\omega) + \tau(\omega_1)]}{\tau_0(\omega) + \sigma_{(1)}(\omega)}, \quad (43)$$

and, in particular, if $\omega = \omega_1$ from (43)

$$\tau(\omega_1) = \tau_0(\omega_1). \quad (43')$$

Hence this gives us the effective relaxation time of low-frequency phonons in terms of the relaxation time of a single mode for (1)-processes.

We shall now show that no great error is made by neglecting processes of class (c). For low frequencies $\hbar\omega < KT$, we have shown that they are less important than class (b) and can therefore be neglected. For high frequencies $\hbar\omega > KT$ they form the major contribution. The quantitative effect of (c)-processes is difficult to estimate, but the following argument makes it plausible that the effect of (c)-processes is even then small compared with the effect of processes not conserving momentum.

Processes of class (c) only link modes of similar frequency. Thus if we assume that (41) holds for (c)-processes as well as for (b)-processes, since we can write $\omega_1 = \omega + \Delta\omega_1$ we have for a given $\Delta\omega_1$

$$\left. \frac{\partial N}{\partial t} \right]_{\Delta\omega_1} = \left. \frac{\partial N}{\partial t} \right]_{\Delta\omega_1} \frac{d\tau(\omega)}{d\omega} \Delta\omega, \quad (44)$$

and summing over all $\Delta\omega_1$, which can be positive or negative, we have in the average $\left. \frac{\partial N}{\partial t} \right]_{(c)} = 0$ except for terms in $\frac{d^2\tau}{d\omega^2}$. The general validity of (41) can be demonstrated from considerations of the singular solution of (1)-processes, as will be done in the next section.

Thus for $\hbar\omega/KT > 1$ we have, since the major contribution to (1)-processes comes from class (c) and since $\left. \frac{\partial N}{\partial t} \right]_c = 0$, that

$$\tau(\omega) = \tau_0(\omega). \quad (45)$$

We can thus summarize: If τ_0 is the relaxation time due to all processes except (1)-processes, and if $\sigma_{(1)}$ is the relaxation time of a single mode due to (1)-processes, then the effective relaxation time is

$$\tau(\omega) = \frac{\tau_0(\omega) [\sigma_{(1)}(\omega) + \tau_0(\omega_1)]}{\tau_0(\omega) + \sigma_{(1)}(\omega)} \quad \text{for } \omega \leq \omega_1 = KT/\hbar, \quad (43'')$$

$$= \tau_0(\omega) \quad \text{for } \omega \geq \omega_1. \quad (45)$$

LONGITUDINAL PHONONS

So far we have neglected polarization. Peierls has already pointed out that in a three-phonon process not all the phonons can have the same polarization, if conservation of energy (4) and momentum (5) are to be simultaneously satisfied. It was further pointed out by Pomeranchuk (1941) that waves of that polarization which have the greatest phase-velocity, henceforth called 'longitudinal' waves, behave quite differently from transverse waves with respect to three-phonon interactions. The two conditions (4) and (5) cannot be fulfilled for interactions of class (b) if the low-frequency phonon is longitudinal, or at least can only be fulfilled so rarely as to make such interactions unimportant. Thus a longitudinal mode of vibration will tend to return to its equilibrium value mainly as a result of processes 1(c) and of processes not conserving momentum.* The relaxation length of a single mode, which can be calculated by integrating (40) over all frequencies, is therefore different for longitudinal and transverse waves, and will be considerably larger for longitudinal waves.

To find the effective relaxation length of a longitudinal wave due to (1)-processes assume at first that these are the only processes acting on the longitudinal phonons. They interact with transverse phonons of about the same frequency, i.e. by processes 1(c). These transverse waves in turn can interact with other phonons with an effective relaxation time τ' . From (23) the deviation of the transverse phonons will be

$$n' = v_{II} F(\omega) \tau', \tag{47}$$

where $F(\omega)$ depends on ω only. The deviation of the longitudinal phonons

$$n = v_I F(\omega) \tau_{sing}$$

will be determined by n' , as singular solution equilibrium is established between the longitudinal and transverse waves. According to (11) this is

$$n/n' = v_I \tau_{sing} / v_{II} \tau' = v_I^2 / v_{II}^2, \tag{48}$$

where the suffixes I and II refer to longitudinal and transverse polarizations respectively.

Now allow the longitudinal phonons also to interact directly with other phonons by means of processes not conserving momentum with relaxation time τ_0 . The rate of change due to (1)-processes is then no longer zero, but is proportional to the deviation of n from the singular solution. It must also be proportional to $1/\sigma_{(1)}$ and would be equal to $n/\sigma_{(1)}$ if $\tau_{sing} = 0$. Hence

$$\frac{1}{\tau_{(1)}} = - \left. \frac{1}{n} \frac{\partial N}{\partial t} \right]_{(1)} = \frac{1}{\sigma_{(1)}} \left(\frac{\tau - \tau_{sing}}{\tau} \right). \tag{49}$$

This is similar in form to (41), and we obtain likewise

$$\tau(\omega) = \frac{\tau_0(\omega) [\sigma_{(1)}(\omega) + C\tau'(\omega)]}{\tau_0(\omega) + \sigma_{(1)}(\omega)}, \tag{50}$$

where $C = v_I/v_{II}$. Note that we could have derived (41) and (43) by an argument similar to the above, and thus justify (44).

* Note that this does not hold for U -processes. Hence the conclusion of Pomeranchuk that at high temperatures ($T \gg \theta$) we must take into account four-phonon processes to obtain a finite conductivity, and that therefore $\kappa \propto T^{-3}$, is not correct.

THERMAL CONDUCTIVITY

The important processes tending to restore equilibrium can now be summarized in the following scheme, illustrated by figure 1.

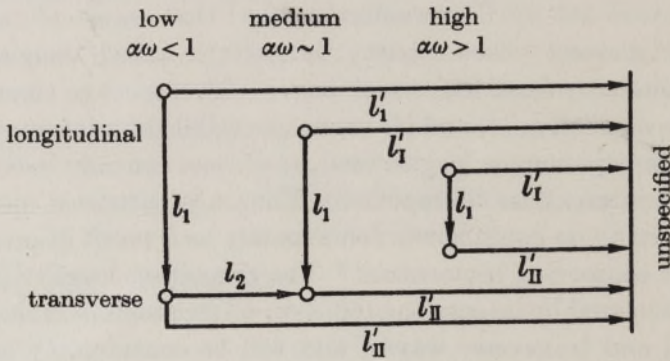


FIGURE 1. The interaction pattern, showing the important processes by which a normal mode can return to its equilibrium value of excitation. Longitudinal phonons: processes not conserving momentum l'_I ; (1)-processes l_1 . Transverse phonons: processes not conserving momentum l'_{II} ; (1)-processes l_2 .

A longitudinal phonon can interact either by a process not conserving momentum (relaxation length l'_I), or it can interact by means of an (1)-process (relaxation length of single mode l_1) with a transverse wave of the same frequency, whose effective relaxation length in turn is l_{II} . Then according to (50) its effective relaxation length is

$$l_I = \frac{l'_I(l_1 + C^2 l_{II})}{l'_I + l_1} \tag{51}$$

for all frequencies. On the other hand, we have for transverse waves according to (43) and (45)

$$l_{II}(\omega) = \frac{l'_{II}(\omega) [l_2(\omega) + l'_{II}(\omega_1)]}{l'_{II}(\omega) + l_2(\omega)} \quad \text{for } \omega \leq \omega_1 = KT/\hbar$$

$$= l'_{II}(\omega) \quad \text{for } \omega \geq \omega_1, \tag{52}$$

where l_2 is the relaxation length of a single mode for (1)-processes for transverse waves and l'_{II} the relaxation length of transverse phonons for processes not conserving momentum.

Substituting all this into (27) we get

$$\kappa(T) = \kappa_I(T) + \kappa_{II}(T)$$

$$\kappa_I(T) = \frac{1}{3} \int_0^\infty \frac{\partial}{\partial T} (E(k, T))_I v_I \frac{l'_I l_1}{l'_I + l_1} dk$$

$$\kappa_{II}(T) = \frac{1}{3} \int_0^{\omega_1} \left(\frac{\partial}{\partial T} E(k, T) \right)_{\text{eff.}} \left[\frac{l'_{II} l_2}{l'_{II} + l_2} + \frac{l'_{II}(\omega_1)}{1 + l_2/l'_{II}} \right] v_{II} dk + \frac{1}{3} \int_{\omega_1}^\infty \left(\frac{\partial}{\partial T} E(k, T) \right)_{\text{eff.}} v_{II} l'_{II} dk,$$

where
$$\left(\frac{\partial}{\partial T} E(k, T) \right)_{\text{eff.}} = \frac{\partial}{\partial T} E(k, T)_{II} \left(1 + \frac{1}{2} \frac{l'_I}{l'_I + l_1} \right). \tag{53}$$

From this we can evaluate the conductivity κ as a function of temperature if we know the relaxation lengths of the various processes and the energy spectrum $E(k, T)$. We shall now apply this formula to specific cases.

Thermal conductivity of glass

Glass is a disordered solid with a lattice structure lacking symmetry and periodicity. There is a short-range order which is similar to that of the corresponding crystalline form—if this exists. For example, quartz consists of a regular array of oxygen tetrahedra surrounding each silicon atom, each oxygen atom being shared. Quartz glass consists also of such tetrahedra, but there is a slight variation in the orientation of neighbouring tetrahedra. Since the forces between neighbouring atoms are similar, the specific heat of the glass is almost the same as that of the crystal (Simon 1922; Simon & Lange 1926), but the thermal conductivity of glass is much smaller, as is illustrated in figure 3 of Berman (1951).

Clearly the low thermal conductivity is due to the irregularity of the structure. It has been pointed out by Kittel (1949) that when substituting the known conductivity and specific heat into the simple Debye formula

$$\kappa = \frac{1}{3}Svl, \quad (53D)$$

where S is the specific heat and l an average mean free path, one obtains a value of l which is independent of temperature at room temperature and above. Thus the mean free path is independent of frequency for high frequencies, and is of the order of the size of the oxygen tetrahedra. The low frequencies, however, have a longer mean free path, for when the wave-length is large compared with the lattice constant, the lack of order is not so important, since macroscopically glass is a homogeneous substance. Thus at low temperatures the observed mean free path defined by (53D) increases. We can develop these ideas on the lines of the preceding theory and can explain the low-temperature behaviour in a more satisfactory manner.

Each atom has a fixed equilibrium position, and the thermal motion is resolvable into normal modes of vibration. These normal modes are no longer plane waves, since the structure lacks regularity. We can still resolve the instantaneous displacements into plane waves, but now there will be an interchange of energy between them. These interactions, which we call 'structure scattering', are processes of type (4). We assume the equilibrium intensity to be still given by the Planck distribution (8) and the deviation from equilibrium to be still attenuated exponentially with relaxation time $\tau_{(4)}$.

We assume, as Kittel has done, that $v\tau_{(4)} = Ca$ for $\lambda < a$, a being the lattice constant and C some constant. Such short waves describe the relative motion of neighbouring atoms. Consider now a wave of longer wave-length $\lambda > a$. We can divide its energy into two parts: the energy pertaining to the overall motion of a large region, and the energy pertaining to the relative motion of neighbours. We assume that the energy of overall motion belongs to a normal mode which is almost identical to the plane wave, and this energy is retained by the wave. But the energy of relative motion belongs to high-frequency modes and is attenuated with the constant relaxation

length Ca , which is the same as the constant relaxation length observed for high-frequency plane waves.

If q is the displacement due to a plane wave

$$q = q_0 \sin \frac{2\pi}{\lambda} (x - vt)$$

and

$$\dot{q} = -q_0 \frac{2\pi v}{\lambda} \cos \frac{2\pi}{\lambda} (x - vt), \quad (54)$$

then the relative displacement of two neighbouring atoms, distant Δx , is given by

$$\Delta q = q_0 \frac{2\pi}{\lambda} \Delta x \cos \frac{2\pi}{\lambda} (x - vt)$$

and

$$\Delta \dot{q} = -q_0 \left(\frac{2\pi}{\lambda} \right)^2 v \Delta x \sin \frac{2\pi}{\lambda} (x - vt). \quad (54')$$

The energy per unit volume is $E = \frac{1}{2} \rho q_0^2 \left(\frac{2\pi}{\lambda} \right)^2 v^2$, (55)

where ρ is the density, and the energy of relative motion is

$$E_r = \frac{1}{2} \rho q_0^2 \left(\frac{2\pi}{\lambda} \right)^4 v^2 (\Delta x)^2. \quad (56)$$

The attenuation length is thus

$$l = C \Delta x \frac{E}{E_r} = C \Delta x \left(\frac{\lambda}{2\pi \Delta x} \right)^2. \quad (57)$$

The above argument holds equally well for longitudinal as for transverse waves, but the constant C will not be the same. For our calculations we thus take the relaxation length of 'structure scattering' in glass to be

$$\begin{aligned} l &= Aa \left(\frac{1}{ak} \right)^2 & \text{if } ak < 1 \\ &= Aa & \text{if } ak \geq 1, \end{aligned} \quad (58a)$$

for longitudinal waves, while for transverse waves

$$\begin{aligned} l &= Ba \left(\frac{1}{ak} \right)^2 & \text{if } ak < 1 \\ &= Ba & \text{if } ak \geq 1, \end{aligned} \quad (58b)$$

where A and B are constants. We shall see in the case of quartz glass that $A > B$. It is not unreasonable that longitudinal waves are transmitted more easily through a disordered structure than transverse waves, and this may be a property of all glasses. Some error is, of course, introduced through (58) for frequencies $ak \sim 1$, but this is not important.

We can use the general formula (53) to calculate the thermal conductivity, using (58) for l'_I and l'_{II} ; we assume the same relaxation length for (1)-processes as in the case of crystals; for longitudinal waves an expression obtained by Pomeranchuk (1941)

$$l_1 = \frac{Ca}{T} \left(\frac{1}{ak} \right)^4, \quad (59)$$

and for transverse waves an expression due to Landau & Rumer (1937),

$$l_2 = \frac{Da}{T^4} \left(\frac{1}{ak} \right) \quad \text{for } T \ll \theta$$

$$= \frac{D'a}{T} \left(\frac{1}{ak} \right) \quad \text{for } T \gg \theta, \tag{60}$$

where C , D and D' are constants and θ is the Debye temperature. For $E(k, T)$ we use the expression given by the Debye theory of specific heat and we obtain finally

$$\kappa(T)_I = \frac{1}{3} \int_0^\infty \frac{2\hbar^2 v^3 k^4}{(2\pi)^4 K T^2} \frac{e^{\hbar v k / 2\pi K T}}{[e^{\hbar v k / 2\pi K T} - 1]^2} A a \left(\frac{1}{ak} \right)^2 \left\{ 1 + \frac{AT}{C} (ak)^2 \right\}^{-1} dk$$

$$= \frac{AK^2 T}{3\pi a \hbar} \int_0^\infty \frac{x^2 e^x}{(e^x - 1)^2} \left\{ 1 + \left(\frac{T}{T_0} \right)^3 x^2 \right\}^{-1} dx, \tag{61}$$

where

$$\left(\frac{1}{T_0} \right)^3 = \frac{Aa^2}{C} \left(\frac{2\pi K}{\hbar v} \right)^2 \tag{62}$$

and T_0 is a parameter of the dimension of temperature. The integral

$$\propto \int_0^\infty \frac{x^2 e^x}{(e^x - 1)^2} \frac{1}{1 + \alpha^2 x^2} dx$$

has been evaluated numerically as a function of α and $\kappa(T)_I$ obtained (see figure 2). At the lowest temperatures

$$\kappa_I(T) = 3.29 \frac{AK^2}{3\pi a \hbar} T, \tag{63}$$

and at higher temperatures the curve of κ_I against T flattens out, reaching a maximum at $T = 0.8T_0$; while at high temperatures $\kappa(T)_I \propto T^{-1}$.

The high-frequency cut-off, which is important in the expression for the specific heat, has been neglected in (61) because the integrand in (61) decreases more quickly with increasing frequency than the integrand of the specific heat integral. Also we have used for l'_I expression (58) for $ak < 1$ because for the higher frequencies $l_1 < l'_I$ and the exact form of l'_I is then unimportant.

Consider now $\kappa_{II}(T)$. At higher temperatures $l_2 \ll l'_{II}$ and the term containing l_2 can be neglected. For l'_{II} we use the high-frequency form of (58b), and if we assume

$$\left(\frac{\partial}{\partial T} E(k; T) \right)_{\text{eff.}} \sim \frac{\partial}{\partial T} E(k, T) \text{ we have}$$

$$\kappa_{II}(T) = \frac{1}{3} B a v S(T). \tag{64}$$

At high temperatures $\kappa_I(T)$ will decrease with temperature, while $\kappa_{II}(T)$ increases with T up to several hundred degrees, being proportional to the specific heat. Hence at high temperatures $\kappa \sim \kappa_{II}$ and (64) agrees with the formula proposed by Kittel. At the lowest temperatures, however, if $l'_{II} < l_2$ we get in analogy to (63)

$$\kappa_{II}(T) = 3.29 \frac{2BK^2}{3\pi a \hbar} T. \tag{65}$$

At intermediate temperatures the expression for $\kappa_{II}(T)$ is more complicated, though it can be evaluated in principle. As a rough approximation we can take the sum of

(64) and (65), though this will overestimate $\kappa_{II}(T)$ in the intermediate range. Also it is only weakly dependent on l_2 ; thus if $l_2 < l'_{II}$ the coefficient in (65) is changed to 2.63, while at higher temperature (64) holds in either case.

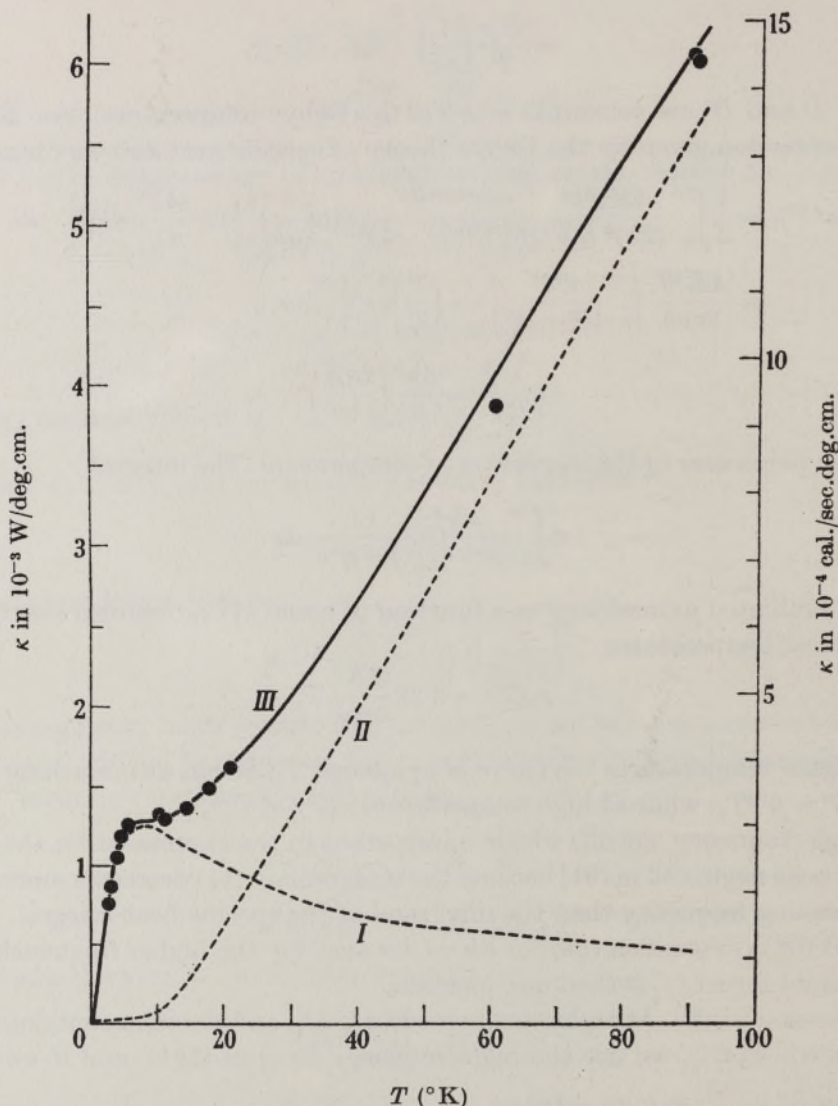


FIGURE 2. Thermal conductivity of quartz glass. Curve I denotes κ_I , curve II κ_{II} , curve III $\kappa = \kappa_I + \kappa_{II}$. Full circles denote experimental points of Berman (1951); measurements of three specimens differing slightly in their absolute value of conductivity are here brought into agreement by multiplication with an appropriate constant.

The thermal conductivity of glass thus depends on three empirical constants A , B and T_0 (or C). We have $\kappa = \kappa_I + \kappa_{II}$, where κ_I is given by (61), κ_{II} is given by (64) at high temperatures, and by (65) at low temperatures. When fitting the formula to the experimental values, B can be obtained from the high-temperature values, where κ_{II} predominates, using the values of the specific heat observed by Simon & Lange (1922). From the linear region at lowest temperatures we obtain $(A + 2B)$, and from the position of the flat region between 10 and 20° K we can obtain T_0 .

For the conductivity of quartz glass, as measured by Berman (1951), the following values are best:

$$A = 180, \quad B = 2.4, \quad T_0 = 9.8^\circ \text{K}, \quad \text{i.e. } C = 50, \quad (66)$$

taking $a = 5 \times 10^{-8}$ cm., $v_{\text{II}} = 2 \times 10^5$ cm./sec. In figure 2 are plotted the values of the conductivity observed by Berman, and the values of κ_{I} , κ_{II} and κ , calculated with the above constants. The agreement between theory and experiment is seen to be quite satisfactory.

Thermal conductivity of crystals

In the case of crystals the conductivity is again determined by (53), but while in the case of glass $l'_1 \sim l_1$ at about 10°K , in the case of crystals the processes which do not conserve momentum are much rarer, and thus $l'_{\text{II}} \gg l_1$ except at very low temperatures (2°K in the case of quartz, using the value of l_1 as found above), and thus $\kappa_{\text{I}} \ll \kappa_{\text{II}}$. We can neglect all terms in (53) which are limited by either l_1 or l_2 and we get

$$\kappa(T) = \kappa_{\text{II}}(T) = \frac{1}{3} \int_0^{\omega_1} \left(\frac{\partial}{\partial T} E(k, T) \right)_{\text{eff.}} v_{\text{II}} l'_{\text{II}}(\omega_1) dk + \frac{1}{3} \int_{\omega_1}^{\infty} \left(\frac{\partial}{\partial T} E(k, T) \right)_{\text{eff.}} v_{\text{II}} l'_{\text{II}} dk. \quad (67)$$

A possible exception is diamond. Owing to its very high Debye temperature l_1 is very large, so that in an appreciable temperature range $l_1 > l'_1$; and if $l'_1 > l'_{\text{II}}$, $\kappa_{\text{I}} > \kappa_{\text{II}}$. It was shown by Pomeranchuk (1942) that in this case κ_{I} is temperature independent over a range of temperatures, and this explains the temperature-independent conductivity of diamond from 24 to 340°K .

In all other crystals, however, the conductivity is limited only by the processes not conserving momentum. These are U -processes, scattering by lattice defects, scattering by the external boundaries and scattering due to mosaic structure. These processes compete with each other, so that

$$\frac{1}{l'_{\text{II}}} = \sum_{(\beta)} (\rho_{\beta} l'_{\text{II}})^{-1}, \quad (68)$$

where $\rho_{\beta} l'_{\text{II}}$ is the relaxation length—or mean free path—of each of the above processes.

Scattering by defects

This may be elastic or inelastic, but it has been shown by Pomeranchuk (1942) that inelastic scattering can be neglected. With respect to its effect on long waves, a defect alters the elastic properties of the medium over a spherical region of the order of a unit cell, and can thus be regarded as a hard sphere, or a spherical hole, embedded in the substance. For long waves elastic scattering is proportional to the fourth power of frequency (Rayleigh scattering), so that the mean free path is

$$l' = \frac{Fa}{\epsilon} \left(\frac{1}{ak} \right)^4 \quad (ak \ll 1), \quad (69)$$

where ϵ is the defect-concentration and F some constant. For higher frequencies the power of the frequency will decrease, until at highest frequencies scattering is almost frequency-independent.

Boundary scattering

The mean free path L can be obtained from geometrical arguments; it is, of course, frequency-independent. Casimir (1938) has worked out the case of long cylinders of circular and square cross-section. In general, L equals approximately the smallest linear dimensions of the crystal.

Mosaic scattering

Mosaic structure of crystals is an additional source of scattering. If we assume the crystal divided into domains of slightly different orientation, it can be shown (Pomeranchuk 1942) that

$$Ml' = Ma \left(\frac{1}{ak} \right)^2, \quad (70)$$

where M is a constant depending on the size of the domains and the mean angle of disorientation.

Umklapprozesse

The rate of change due to U -processes is determined by (3), which to the first order in the n 's is

$$\left. \frac{\partial N}{\partial t} \right]_{(2)} = \sum_{1,2} D_{012} [n(\mathcal{N}_1 - \mathcal{N}_2) + \mathcal{N}(n_1 - n_2) - (n_1 \mathcal{N}_2 + n_2 \mathcal{N}_1)], \quad (71)$$

where D_{012} vanishes unless (4) and (6) are fulfilled. Consider first the case when ω is well below the Debye frequency ω_D . Since for a U -process

$$|\omega| + |\omega_1| + |\omega_2| \sim \omega_D, \quad (72)$$

we need only consider processes such that $\omega \ll \omega_1 \sim \omega_2 \sim \omega_D$. In (71) we have

$$n(\mathcal{N}_1 - \mathcal{N}_2) = n \frac{\partial \mathcal{N}_1}{\partial \omega_1} \omega, \quad (73)$$

which is the same as for processes (1b). But since the components of \mathbf{k}_1 and \mathbf{k}_2 in the direction of $\boldsymbol{\epsilon}$ have opposite sign, in the average $n_1 \sim -n_2$ and thus, except for second-order terms $n_1 \mathcal{N}_2 + n_2 \mathcal{N}_1 = 0$. Also $n_1 - n_2 \sim 2n_1$, so that

$$\left. \frac{\partial N}{\partial t} \right]_{(2)} = \sum D_{012} \left(n \frac{\partial \mathcal{N}_1}{\partial \omega_1} \omega + 2\mathcal{N}n_1 \right). \quad (74)$$

It is easily shown that the second term can be neglected provided τ decreases faster with increasing frequency than ω^{-1} . This, however, is always fulfilled, so that $\left. \frac{\partial N}{\partial t} \right]_{(2)} \propto n$, and thus U -processes acting on low-frequency phonons can be regarded as processes not conserving momentum for purposes of calculating the thermal conductivity by (67). And so

$$\frac{1}{\tau_{(2)}} = - \left. \frac{1}{n} \frac{\partial N}{\partial t} \right]_{(2)} = \sum D \alpha \omega \frac{e^{\alpha \omega_1}}{(e^{\alpha \omega_1} - 1)^2}, \quad (75)$$

where $\alpha = \hbar/KT$. If $T \ll \theta$

$$\frac{1}{\tau_{(2)}} = \sum D \alpha \omega e^{-\alpha \omega_1}. \quad (76)$$

It can be shown (Landau & Rumer 1937) that $D_{012} \propto \omega \omega_1 \omega_2$. The number of simultaneous solutions of (4) and (6) in the range $\omega_1, \Delta\omega_1$ varies as $\omega_1 \Delta\omega_1$, as for (1)-processes. Since $\omega_1 \simeq \omega_2$, $D_{012} \propto \omega \omega_1^2$; hence

$$-\frac{1}{n} \frac{\partial N}{\partial t} \Big]_{\Delta\omega_1} \propto \alpha \omega^2 e^{-\alpha\omega_1} \omega_1^3 \Delta\omega_1. \tag{77}$$

We must integrate over all possible values of ω_1 . The lowest possible value is $\frac{1}{2}\omega_D$, so that

$$\begin{aligned} \frac{1}{\tau_{(2)}} &\propto \int_{\frac{1}{2}\omega_D}^{\omega_D} \alpha \omega^2 \omega_1^3 e^{-\alpha\omega_1} d\omega_1 \\ &\propto \frac{\omega^2}{\alpha^3} \int_{\theta/2T}^{\theta/T} e^{-x} x^3 dx. \end{aligned} \tag{77a}$$

At low temperatures x is large, so that the upper limit of integration can be neglected. Hence

$$\tau_{(2)} \propto \omega^{-2} e^{\theta/2T} \left[1 + 6\frac{T}{\theta} + 24\left(\frac{T}{\theta}\right)^2 + 48\left(\frac{T}{\theta}\right)^3 \right]^{-1}.$$

If $T < \theta/6$

$$\tau_{(2)} \propto \frac{1}{\omega^2} e^{\theta/2T}$$

or

$$l_U = S a \left(\frac{1}{ak} \right)^2 e^{\theta/2T}, \tag{78}$$

where S is a constant.

We can now substitute these mean free paths into (67) to obtain the thermal conductivity. In principle the integrals occurring in this formula can be evaluated exactly, but as this involves tedious numerical work, we shall give approximations only.

Crystals without defects

At low temperatures we must consider boundary scattering as well as U -processes. Using (68) we get after substitution into (67)

$$\begin{aligned} \kappa(T) &= \frac{4\pi K^4 T^3}{h^3 v^2} \left\{ \frac{1}{L} + \frac{a}{S} \left(\frac{2\pi K T}{h v} \right)^2 e^{-\theta/2T} \right\}^{-1} \int_0^1 \frac{x^4 e^x}{(e^x - 1)^2} dx \\ &\quad + \frac{4\pi K^4 T^3}{h^3 v^2} \int_1^\infty \left\{ \frac{1}{L} + \frac{a}{S} \left(\frac{2\pi K T}{h v} \right)^2 e^{-\theta/2T} x^2 \right\}^{-1} \frac{x^4 e^x}{(e^x - 1)^2} dx. \end{aligned} \tag{79}$$

This is of the form

$$\frac{1}{A+B} \int_0^1 \frac{x^4 e^x}{(e^x - 1)^2} dx + \int_1^\infty \frac{1}{A+Bx^2} \frac{x^4 e^x}{(e^x - 1)^2} dx. \tag{80}$$

Instead of calculating this expression exactly we approximate in either of the following ways:

(a) Cut-off approximation:

If $A > B$ expression (80) is approximately

$$\frac{1}{A} \int_0^{X_1} \frac{x^4 e^x}{(e^x - 1)^2} dx, \tag{81}$$

where $X_1^2 = A/B$, or, more accurately,

$$\frac{1}{A} \left\{ \int_0^{X_1} \frac{x^4 e^x}{(e^x - 1)^2} dx + X_1^2 \int_{X_1}^{\infty} \frac{x^2 e^x}{(e^x - 1)^2} dx \right\}. \quad (82)$$

(b) Additive-resistance approximation:

If $A < B$ expression (80) is approximately

$$\frac{1}{A+B} \left\{ \int_0^1 \frac{x^4 e^x}{(e^x - 1)^2} dx + \int_1^{\infty} \frac{x^2 e^x}{(e^x - 1)^2} dx \right\}. \quad (83)$$

This approximation lends itself to easy physical interpretation since the reciprocal of (80), which is a resistance, can be written as a sum of two resistances

$$A/2.63 + B/2.63,$$

which are due to boundary scattering and U -processes respectively.

We have thus for the resistance due to U -processes

$$W_U = \frac{a\pi h}{2.63SK^2T} e^{-\theta/2T}, \quad (84)$$

while the resistance due to boundaries is

$$W_B = \frac{h^3 v^2}{2.63K^4 L T^3}. \quad (85)$$

While W_U increases with increasing T , W_B decreases. Note that W_B is about ten times as large as the boundary resistance calculated by Casimir (1938) on the assumption that boundary scattering is the only process. The additive-resistance approximation holds good as long as $W_U > W_B$. At lower temperatures we must use the cut-off approximation with

$$X_1^2 = \frac{S}{aLT^2} \left(\frac{hv}{2\pi K} \right)^2 e^{\theta/2T}, \quad (86)$$

and X_1 increases with decreasing T . At lowest temperatures, when X_1 is large, we have

$$\kappa(T) = 25.9 \frac{4\pi K^4 L T^3}{h^3 v^2}, \quad (87)$$

which is equivalent to Casimir's result. The conductivity attains a maximum near $X_1 \sim 1$.

Since (78) is valid only for frequencies well below the Debye frequency, (79) and all subsequent approximations are valid only for low temperatures, well below the Debye temperature. The increase of resistance due to U -processes becomes less strong at higher temperatures, until eventually at temperatures above the Debye temperature W_U is proportional to T . For at those temperatures

$$\mathcal{N}_i = \frac{1}{e^{\alpha\omega_i} - 1} \sim \frac{1}{\alpha\omega_i} \propto T/\omega_i, \quad (88)$$

and thus $\left[\frac{1}{n} \frac{\partial N}{\partial t} \right]_{(2)} \propto T$ and $\tau_U \propto \omega/T$. Hence

$$\begin{aligned} \kappa(T) &\propto \int_0^{\omega_D} \frac{e^{\alpha\omega}}{(e^{\alpha\omega} - 1)^2} \frac{\omega^4}{T^2} \frac{\omega}{T} d\omega \sim \int_0^{\omega_D} \frac{\omega^2}{\alpha^2 T^2} \frac{\omega}{T} d\omega \\ &\propto 1/T, \end{aligned} \quad (89)$$

a result already deduced by Peierls (1929).

Crystals with lattice defects

If there are an appreciable number of lattice defects, the resistance due to them will be more important at low temperatures than the resistance due to U -processes. Consider boundary and defect scattering only, then substituting $F'L'$ of (69) and L into (68) and (67) we obtain an expression for the conductivity in the form

$$\frac{1}{A+B} \int_0^1 \frac{x^4 e^x}{(e^x - 1)^2} dx + \int_1^\infty \frac{1}{A+Bx^4} \frac{x^4 e^x}{(e^x - 1)^2} dx, \tag{90}$$

and a similar expression containing also a term in x^2 if mosaic scattering or U -processes are also important. Again if $B > A$ we can use the additive resistance approximation, where now

$$\left. \begin{aligned} W_F &= \frac{(2\pi)^3 a^3 \epsilon T}{2hv^2 F \times 0.90}, \\ W_B &= \frac{h^3 v^2}{4\pi K^4 \times 0.90} \frac{1}{LT^3}, \\ W_M &= \frac{ha\pi}{MK^2 \times 0.90} \frac{1}{T}, \end{aligned} \right\} \tag{91}$$

where W_F , W_B and W_M are the resistances due to defect, boundary and mosaic scattering respectively, and

$$W = W_F + W_B + W_M. \tag{92}$$

It will be seen that at very low temperatures the resistance decreases to a minimum, but then increases again, while at temperatures above this minimum W_F predominates. The constant in (91) is different from the constant in (83), being the integral

$$\int_0^1 \frac{x^4 e^x}{(e^x - 1)^2} dx + \int_1^\infty \frac{e^x}{(e^x - 1)^2} dx = 0.90,$$

At high temperatures, however, W_U will become important, and W will increase faster than T , except when departures from Rayleigh scattering again offset this effect. At temperatures well above θ , W will again be proportional to T , but before this temperature is reached, the crystal may start to melt. At high temperatures $W_U > W_F$, and the conductivity is less sensitive to defects, as is generally observed.

At low temperatures when W_B exceeds W_F , the additive-resistance approximation breaks down and must again be replaced by the cut-off approximation (81), or by the analogue of (82), with

$$X_1^4 = \frac{F}{\epsilon a^3 L} \left(\frac{hv}{2\pi KT} \right)^4, \tag{93}$$

and at very low temperatures, when X_1 is large, we again approximate to Casimir's expression (87).

Alkali halides

The thermal conductivity of potassium chloride and potassium bromide crystals (shaped as rods) was measured by de Haas & Biermasz (1935, 1937, 1938) down to 2° K, though there is a gap in their measurements from 5 to 15° K. Above 15° K

the resistance is approximately proportional to temperature, and for potassium chloride

$$W = \frac{0.77}{20} T W^{-1} \text{ cm. sec.} \quad (94)$$

If we assume that this resistance is mainly due to lattice defects, then by comparing with W_F of (91), taking $v = 2 \times 10^5$ cm./sec.

$$\frac{\epsilon a^3}{F} = 7.4 \times 10^{-27}. \quad (95)$$

We take $a = 4 \text{ \AA}$, and assuming the defect to be a spherical hole of radius $R = aX$, whose scattering cross-section is

$$\sigma = \frac{256\pi^5 R^6}{9\lambda^4} \quad \text{for } \lambda \gg 2\pi R, \quad (96)$$

we get

$$\epsilon X^6 = 6.4 \times 10^{-5}. \quad (97)$$

The potassium chloride crystals used by de Haas & Biermasz contained as impurities about 10^{-4} per atom of Na and less than 10^{-4} of Mg. If only divalent impurities act as scattering centres, i.e. only the Mg^{++} ions, then if $X \sim 1$ the observed thermal resistance at liquid-hydrogen temperatures agrees roughly with the concentration of divalent impurities. This is what we would expect, for such a divalent impurity must have associated with it a hole in the alkali lattice in order to preserve electrical neutrality. On the other hand a monovalent impurity would only scatter weakly, since the only perturbing effect would be the mass-difference at the point of the impurity, the structure as such being intact.

This view is born out by the experiments of Eucken & Kuhn (1928), where a 10% addition of monovalent Br increases the resistance only by a factor of six, so that a monovalent impurity scatters less than a divalent impurity by a factor of more than 100. Again we can rule out Frenkel defects as an important source of resistance, for according to experiments by Koch & Wagner (1938) their concentration in silver chloride at 480°K is already less than 10^{-4} , and is still decreasing strongly with decreasing temperature. The concentration of Frenkel defects in KCl is probably also very small at low temperatures.

At higher temperatures the defect-resistance increases slower than T , but the resistance due to U -processes increases fast at first, and then gradually more slowly. The net effect is to approximate to the law $\kappa \propto T^{-n}$, where n is near unity.

At very low temperatures, however (below 10°K), the boundary resistance becomes important. The conductivity is then size-dependent, and can be calculated from the cut-off approximation (82). In table 1 the values calculated by the cut-off approximation are compared with the values observed by de Haas & Biermasz. It will be seen that the size-dependent conductivity in the liquid-helium region does agree quite well with the calculated values. The systematic discrepancy is due to the uncertainty in the values of v and L . However, all departures from the Casimir law $\kappa \propto LT^3$ are thus explained, and it does not seem necessary to assume mosaic scattering to explain these departures, as had been suggested by de Haas & Biermasz.

A similar state of affairs seems to hold for the other alkali halides. de Haas & Biermasz have also measured potassium bromide crystals. Their defect-resistance is larger by a factor of about four—otherwise the same explanation seems to hold.

TABLE I. THERMAL CONDUCTIVITY OF POTASSIUM CHLORIDE
AT LIQUID-HELIUM TEMPERATURES

T (°K)	L (cm.)	κ (in W/deg.cm.)			
		X_1	J	(calc.)	(obs.)
2	0.25	3.75	9.51	0.80	0.65
3		2.50	6.98	1.98	1.62
4		1.87	3.91	2.64	2.56
5	0.75	1.50	2.16	2.83	3.05
2		2.75	8.35	2.12	1.82
3		1.83	3.90	3.50	3.30
4		1.38	1.90	3.95	3.56
5		1.1	1.16	4.6	4.1

where

$$J = \int_0^{X_1} \frac{x^4 e^x}{(e^x - 1)^2} dx + X_1^4 \int_{X_1}^{\infty} \frac{e^x}{(e^x - 1)^2} dx.$$

Quartz

Since quartz is a strongly anisotropic crystal, the present theory is not strictly applicable, but we should nevertheless expect qualitative agreement with experiments. The conductivity, both along the principal axis, and in the direction of a bisector of the two binary axes, has been measured by de Haas & Biermasz (1935, 1937, 1938). In the latter direction it was also measured by Berman (1951), who also obtained values in the range 5 to 15° K. Berman's measurements are shown in figure 3. de Haas & Biermasz obtained a size-effect at liquid-helium temperatures which approximates Casimir's law better than the alkali halides. Since the ratio of the conductivities in the parallel and the perpendicular direction is fairly constantly

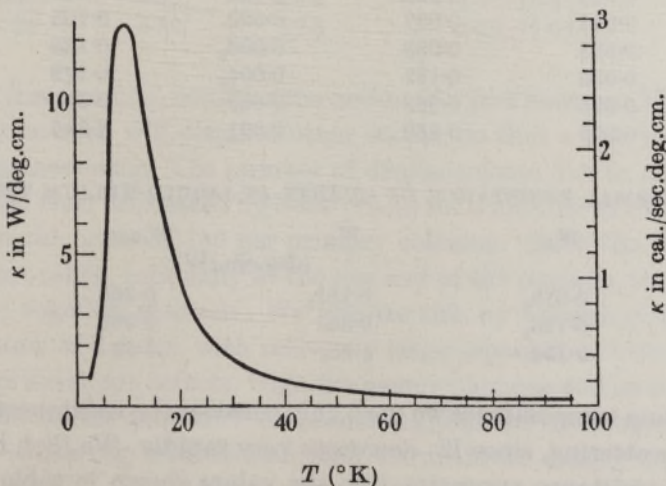


FIGURE 3. Thermal conductivity of crystalline quartz. In direction perpendicular to the principal axis, according to Berman (1951) and de Haas & Biermasz (1935, 1937, 1938).

2:1 at all temperatures, even in the size-dependent range, we conclude that the anisotropy is due to an asymmetrical grouping of the normal modes, rather than an anisotropy in the relaxation length.

In the liquid-hydrogen region the resistance increases faster than T , which suggests that in the case of quartz the resistance is due mainly to U -processes even at these low temperatures. This is not surprising, since quartz has an open structure of SiO_4 tetrahedra. There are large interstitial spaces into which chemical impurities can fit without disturbing the main silica network. Since the crystal is non-ionic, the presence of atoms of different valency has no significant effect on the structure. The energy required to create a vacancy is fairly large, and the number of such vacancies at room temperature must be very small, especially with crystals created during geological processes. Frozen-in vacancies can perhaps be created by heat treatment, and de Haas & Biermasz have indeed increased the thermal resistance in the liquid-hydrogen region in this way, but the effect was small, and thus the resistance due to U -processes is probably predominant.

In order to fit the theory to the observed conductivity it is necessary to assume U -processes, boundary scattering and in addition either mosaic or defect scattering. This last-mentioned is necessary to prevent the conductivity between 5 and 10° K from exceeding the observed value of 12W/deg.cm., as it would for U -processes and boundary scattering only. Taking $S = 11,600$ and choosing W_M suitably we get the values shown in table 2 for the resistance on the additive-resistance approximation. The agreement with the observed values is not very good, and the theory obviously breaks down at higher temperatures. This is expected, since (78) holds only for frequencies well below the Debye frequency.

TABLE 2. THERMAL RESISTANCE OF QUARTZ AT LIQUID-HYDROGEN TEMPERATURES

T (°K)	W_M	W_U	W_B (deg.cm./W)	$W_{\text{calc.}}$	$W_{\text{obs.}}$
10	0.050	0.008	0.023	0.081	0.080
12	0.042	0.029	0.013	0.084	0.088
13.5	0.037	0.057	0.009	0.103	0.106
15.3	0.033	0.088	0.006 ₅	0.128	0.132
17	0.030	0.137	0.004 ₅	0.172	0.161
20	0.025	0.263	0.003	0.291	0.249
34	0.015	0.830	0.001	0.846	1.07

TABLE 3. THERMAL RESISTANCE OF QUARTZ AT LIQUID-HELIUM TEMPERATURES

T (°K)	W_M	W_B (deg.cm./W)	$W_{\text{calc.}}$	$W_{\text{obs.}}$
5	0.076 ₅	0.181 ₅	0.258	0.24
3	0.126 ₅	0.841	0.968	0.70
2.5	0.134	1.45 ₅	1.59	0.95

At liquid-helium temperatures we need only consider the resistances due to mosaic and boundary scattering, since W_U decreases very rapidly. We then have according to the additive-resistance approximation the values shown in table 3. The actual resistance is less than the resistance predicted from the additive-resistance approximation, which we would expect from the nature of this approximation. Better

values may be obtained with the cut-off approximation, but as we have no real evidence about the magnitude of the mosaic resistance, such a calculation would be artificial. The size-dependence, in particular the deviation from Casimir's law, can be specified by that specimen size, for which the boundary resistance is equal to the mosaic resistance. This saturation size, calculated from the values in table 3, agrees roughly with the values obtained by de Haas & Biermasz by extrapolation.

The theory is thus able to predict the dependence of the thermal conductivity of crystalline quartz on temperature and size only qualitatively. But considering that quartz is an anisotropic solid and that the formulae used are only very rough approximations, the disagreement between theory and experiment does not invalidate the basic ideas of the theory.

Neutron-irradiated quartz crystals

When quartz crystals are irradiated with neutrons, lattice defects are formed through the ejection of atoms from their lattice positions by fast neutrons. The thermal conductivity of neutron-irradiated quartz was measured by Berman (1951), and is plotted on a logarithmic scale in his figure 3.

In table 4 is given the thermal resistance after three irradiations of cumulative dosage in the ratio 1:2.4:18.9, having subtracted the resistance of the original crystal, which is due to *U*-processes. The ratios of these additional resistances are also given. This analysis can be criticized, since the presence of additional scattering will change the multiplicative factor of the Umklapp-resistance, but to a first approximation we treat all resistances as simply additive.

TABLE 4. THERMAL RESISTANCE OF NEUTRON-IRRADIATED QUARTZ CRYSTALS

<i>T</i> (°K)	<i>W</i> ₁	<i>W</i> ₂ (deg.cm./W)	<i>W</i> ₃	ratio	
				$\overbrace{W_1:W_2:W_3}$	dosage
95	2.6 ₃	4.5 ₄	30.4	1:1.73:11.5 1:1.77:18.9 1:1.73:17.0	1:2.4:18.9
14	1.9 ₂	3.3 ₉	36.3		
5	3.08	5.32	52.5		

To interpret these results, consider the action of a fast neutron. This will displace an atom, which in turn will displace other atoms, so that a fast neutron initiates a cascade of displacements. The number of displacements due to a fast neutron of 2 MeV energy has been calculated by Seitz (1949) for a number of substances, whose estimates are of the order of 100 per primary collision. Since the displaced atoms have a very short range, especially at the low end of the cascade, the displacements will be grouped together spatially. We idealize this by assuming that there are a number of clusters of defects, with relatively large separations between them, and in between there are single defects. High-frequency phonons will be mostly scattered by the single defects, for they are more numerous, but low-frequency phonons have a small defect-scattering cross-section, and they will be mainly scattered by the clusters.

If clusters are regarded as regions of radius *R*, in which the substance is vitrified, then these clusters are opaque to transverse waves. If there are *n* clusters per unit

volume, the mean free path due to cluster scattering is $1/(\pi R^2 n)$, and is frequency-independent. The resistance due to cluster scattering is thus similar to the boundary resistance, but L is much smaller. For the first irradiation we find from the conductivity below 15°K that $L = 10^{-2}\text{cm.}$, hence taking the lattice constant $a = 5 \times 10^{-8}\text{cm.}$ as unit of length, we have

$$1/L = \pi R^2 n = 5 \times 10^{-6}. \quad (98)$$

If we knew the size of the clusters, we could calculate their concentration, or vice versa. Making reasonable assumptions about their size, we find that the cluster concentration is of the order of 10^{-7} per atom.

The resistance at higher temperatures is due to the single defects. For the small irradiations the resistance above 15°K increases with temperature; but not as fast as T , which is a result of the departures from Rayleigh scattering. At the highest defect concentration, however, there is already interference between the defects, resulting in still larger deviations from Rayleigh scattering, so that the resistance slightly decreases with increasing temperature. When the defect concentration is even larger, scattering will be frequency independent, and we revert to the case of glass. The defect concentration of the first irradiation seems to be of order 10^{-4} , estimated by comparison with the resistance of alkali halides.

In the case of the third irradiation the transverse conductivity is already so small that the longitudinal conductivity becomes appreciable, resulting in a small peak at 10°K . This can be understood from expression (61). The constant A must now be about five times as large as in the case of glass, which is reasonable, since the clusters, which are partially transparent to longitudinal waves, will scatter according to (58a), so that we have a 'dilute glass'. The temperature T_0 defined by (62) is now reduced by a factor $5^{1/2}$ to 7°K , hence the maximum of the longitudinal conductivity is at 6°K . However the maximum of κ_{\parallel} is fairly broad, and since the transverse conductivity at this point increases strongly with temperature, the maximum of the total conductivity is displaced to higher temperatures.

It is seen from table 4 that the resistance induced is not proportional to the dosage, but increases more slowly. Apparently some reordering is taking place during irradiation. On the other hand, for low dosages, to a given dosage ratio there corresponds a ratio of the induced resistances which is the same for all temperatures; this suggests that both the clusters and the single defects arise from the same process. Only for high dosages does this cease to hold, owing to the mutual interference of single defects.

We thus see that the model of clusters and single defects gives a reasonable explanation of the observed phenomena.

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A note on the errors involved in the calculation of elevations of the geoid

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The paper discusses the errors likely to occur in calculations of the elevation of the geoid by Stokes's formula when gravity data outside a given cap are neglected, and it is shown that they are comparable with the root-mean-square elevation. It is shown that these estimates and those of similar errors in deflexions of the vertical made earlier (Cook 1950) are not seriously affected by the assumptions made about the distribution of gravity anomalies between the harmonics up to degree 18.

1. INTRODUCTION

The errors likely to occur in calculations of deflexions of the vertical from gravity anomalies when gravity data outside a certain region are excluded have been discussed in a previous paper (Cook 1950), and in this note errors in calculations of the elevation of the geoid are estimated by the same method and on the same assumptions as were used for the deflexions of the vertical.

It was suggested that the most efficient way of using the existing gravity data is to take the components of deflexions (and geoid elevations) due to harmonics up to degree 3 in the spherical harmonic expression of the free-air anomalies from Jeffreys's (1943) formula for the free-air anomalies, and to apply Stokes's integral formula for deflexion and elevation to the anomalies from Jeffreys's formula. If gravity data were