Calculation of Energy Exchange between Lattice Oscillators

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The rate of transfer of energy between lattice oscillators due to anharmonic perturbations is computed when different portions of the frequency spectrum are not in thermal equilibrium. This calculation is needed for the preceding paper and is not to be confused with that of ordinary thermal conductivity, since the present article is concerned with the flow of energy between oscillators at the same point of space, rather than that associated with spatial temperature gradients. The mean free paths for the two problems are shown to be unrelated, particularly at low temperatures, inasmuch as spatial thermal resistivity can be created by boundary or mosaic reflections, free from energy exchange, but does not arise from energy-transferring collisions between oscillators unless they are of the abnormal "umklapp" type in which momentum is imparted to the grating framework. The force constants needed for the calculation for the alums are furnished by Bridgman's compressibility data. The rate of flow of energy between a band of low frequency oscillators and the main body of lattice vibrations when the two are at slightly different temperatures proves to be proportional to T^4 at low temperatures. The corresponding collision frequency between oscillators is about 10^5 sec.$^{-1}$ even at helium temperatures and thus is of such a magnitude that equilibrium between the different vibrations can be considered as secured instantaneously from the standpoint of macroscopic acoustical experiments, but not at all as far as paramagnetic dispersion is concerned.

INTRODUCTION

IT is the purpose of the present paper to calculate the transfer of energy between lattice oscillators at different temperatures. We shall suppose that the oscillators at the low frequency end of the spectrum are at a different temperature than that of the rest and shall determine the rate at which the temperatures become equalized. It is to be emphasized that we are thus concerned with a different kind of conductivity than in the ordinary theory of heat conduction, for in the latter one studies the passage of heat between two spatial portions of the lattice at different temperatures, whereas we are interested in the flow of heat between different vibrations at the same position in space. Most physical problems involve spatial inhomogeneity in the temperature distribution, but permit the assumption that all vibrations at the same point in space are at the same temperature. The reason for the latter supposition is that the transfer of energy between vibrations at the same point is more rapid than the spatial flow. Thus, for instance, in his interesting theory of the internal friction of solids, Zener[1] supposes that the rarefactions and condensations are at

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[1] C. Zener, Phys. Rev. **52**, 230 (1937); **53**, 90 (1938).

different temperatures, but that the temperature distribution over the frequency spectrum at a given point in space is uniform, because, as he says, "thermal equilibrium between the different normal vibrations is established so rapidly." It is our intent to calculate how great the latter rapidity really is, as its numerical value is needed in connection with our preceding article on paramagnetic relaxation, though it is so great that the equilibrium can be considered instantaneous for a macroscopic elastic problem such as Zener's. On the other hand, we are not concerned with spatial inhomogeneity. Thus our mathematical problem is quite different in nature from that involved in ordinary conduction theory and is in many ways a simpler one, for spatial inhomogeneity in temperature is achieved only as a sort of "wave packet" or interference effect between waves of different frequency. In the present calculation, we regard an oscillation of given frequency as having the same temperature throughout the crystal, and neglect the phase effects associated with the superposition of waves of different frequency. Thus with our model the spatial conductivity would be infinite. Nevertheless our approximations appear legitimate because we are concerned with a much shorter relaxation time than in the spatial problem. We

can apply our results to problems in which the spatial distribution of temperatures is not uniform, because the spatial interference between different waves is essentially a coarse-grained effect not affecting the total strength of the matrix elements connecting oscillators of different frequencies.

At first sight, it perhaps appears that the calculations of the present paper are unnecessary, as one can determine a mean free path l_K from the spatial thermal conductivity K by the usual relation $K = \frac{1}{3} C l_K v$, in which C is the total specific heat per unit volume of all oscillators and v is the velocity of sound. If one knows the mean free path, it is easy enough to make an estimate of the rate of energy transfer, for the collision frequency is the ratio v/l_K and the amount of energy transferred between colliding oscillators of temperatures T_2, T_1 is, on the average, usually supposed to be of the order $\frac{1}{2}c(T_2 - T_1)$, where c is some sort of a mean specific heat per oscillator. However, this way of estimating energy transfer is fallacious, as the mean free path entering in the spatial thermal conductivity is irrelevant for our purposes. Namely, as Casimir[2] has emphasized, the peculiar dependence of thermal conductivity on cross section found experimentally[3] in the helium region shows very clearly. that the thermal resistivity at low temperatures is not due primarily to impacts between oscillators of different frequencies, but instead to reflection of the elastic waves at the walls, or at the surfaces of crystalline imperfections due to mosaic structure. Such reflections can have no effect on the redistribution of temperature between oscillators of different frequency, as a reflection merely alters the direction of a wave without altering its frequency or energy. On the other hand, the most common variety of collision between oscillators is the type not involving any change in the combined momentum of the two interacting vibrations. Such collisions are of importance for the reapportionment of energy between oscillations of different frequency, but do not give rise to any resistivity for spatial heat flow. As Peierls[4] shows, only the abnormal "umklapp" processes, which impart momentum to the crystal grating, can influence the spatial conductivity, and at low temperatures such phenomena are unimportant compared with the wall and mosaic effects. Thus the collisions which are important for the purposes of the present paper are not revealed at all in measurements of thermal conductivity, and conversely, the latter involves reflections irrelevant for us. In other words, the mean free path or collision frequency for energy exchange between oscillators has in principle no relation to that revealed by the thermal conductivity. Hence it is not surprising that the mean free path 1.0 cm which we calculate at 1.4°K is about ten times as large as that l_K deduced in the usual way from measurements of the thermal (spatial) conductivity in a similar temperature region. The rate of flow of energy to or from a low frequency oscillator turns out to be less than one-hundredth that which would be obtained by using the naive formula $\frac{1}{2}c(T_1 - T_2)v/l_K$, as the latter errs not only in the type of mean free path, but also in supposing that the energy of two colliding oscillators is divided equally after impact. Actually a low frequency vibration will suffer only a relatively small modulation of its energy at collision, for it can only gain or lose a quantum $h\omega$ which is small compared to its mean energy kT.

Details of Calculation

Force constants from Bridgman's compressibility data.—We shall assume that all the atoms of the solid are equivalent, and that the interatomic forces are central in character. These approximations are necessary to make the calculations tractable, and presumably do not affect orders of magnitudes. Since the potential energy V_{ij} between atoms i and j is thus supposed a function only of the distance r_{ij} between them, the total energy of the solid takes the form

$$U = \sum_{j>i} V_{ij} = \sum_{j>i} f_{ij}(r_{ij}).\tag{1}$$

[2] H. B. G. Casimir, Physica **5**, 495 (1938).
[3] W. J. de Haas and Th. Biermasz, Physica **5**, 619 (1938).
[4] R. Peierls, Ann. d. Physik **3**, 1055 (1929).

The derivatives of f_{ij} necessary for our calculations can be evaluated from Bridgman's compressibility data,[5] which he writes in the form

$$-\frac{\Delta V}{V_0}=Ap-Bp^2+\cdots, \quad \text{i.e.} \quad p=-\frac{1}{A}\frac{\Delta V}{V_0}+\frac{B}{A^3}\left(\frac{\Delta V}{V_0}\right)^2, \tag{2}$$

where V_0 is the equilibrium volume at zero pressure. For potassium chrome alum, whose compressibility is no doubt sufficiently typical of the alums used in the Dutch relaxation experiments, Bridgman's values of A and B are

$$A=64.9\times10^{-7}, \quad B=112.5\times10^{-12} \quad (p \text{ in Kg/cm}^2). \tag{3}$$

Since $p=-\partial U/\partial V$ and since $dr_{ij}/dV=\frac{1}{3}r_{ij}/V$ we have by development of (1) in the displacements Δr_{ij} from equilibrium,

$$p=-\tfrac{1}{3}V_0^{-1}\sum_{j>i}[r_{ij}^2f_{ij}''(\tfrac{1}{3}\Delta V/V_0)+(\tfrac{1}{2}r_{ij}^3f_{ij}'''-3r_{ij}^2f_{ij}'')(\Delta V/3V_0)^2+\cdots], \tag{4}$$

where $r_{ij}^2f_{ij}''$ means $[r_{ij}^2(\partial^2f/\partial r_{ij}^2)]_0$, etc. In writing (4) we have omitted terms in f_{ij}', as their effect vanishes in virtue of the fact that $p=0$ at $V=V_0$, which is equivalent to the relation $\sum r_{ij}f_{ij}'=0$. The sums $\sum r_{ij}^2f_{ij}''$ and $\sum r_{ij}^3f_{ij}'''$ needed for later work can immediately be obtained by comparison of (4) with (2) and (3).

Expansion of the potential to the third order.—We now develop the energy (1) as a Taylor's series in the normal coordinates $q_1, \cdots, q_{3N}$ for the crystalline system. Here N is the total number of atoms composing the crystal. It would be very difficult to find the spectrum of the normal coordinates exactly, and so we shall make the usual assumption that the frequencies are distributed in accord with the standard Debye model. There are, of course, no linear terms in the expansion, and the quadratic members, together with the momentum terms expressing the kinetic energy, merely determine the normal coordinates themselves. The third-order terms in the q's make the motion slightly anharmonic, and we regard them as a perturbation. They thus furnish a mechanism for the transfer of energy from one normal mode to another. The fourth-order terms we shall omit, as their effect in coupling together the different modes of vibration is qualitatively similar to that of the third-order members, but much smaller in numerical magnitude.

We must now compute explicitly the terms of the third order in the expansion of the energy U. We write the displacement associated with a normal coordinate q_α as $\Delta r_j=\mathbf{u}_\alpha q_\alpha \exp(i\mathbf{k}\cdot\mathbf{r}_j)$ where $\mathbf{r}_j$ is the equilibrium value of the position vector of a typical atom j, while $\mathbf{k}_\alpha$ is a vector of magnitude $k_\alpha=2\pi/\lambda_\alpha$ directed along the direction of propagation of the wave associated with the vibration q_α, and $\mathbf{u}_\alpha$ is a unit vector along or perpendicular to $\mathbf{k}_\alpha$ according as the wave is longitudinal or transverse. We shall now assume that the wave-length λ_α is large compared with r_{ij} ($=|\mathbf{r}_{ij}|$). This approximation is warranted at helium and hydrogen temperatures, where only low frequencies are excited, provided, as is doubtless true, the important interactions are between adjacent, or nearly adjacent atoms. If $\lambda_\alpha/r_{ij}\ll1$, we have

$$\Delta\mathbf{r}_i-\Delta\mathbf{r}_j=\sum_\alpha \mathbf{u}_\alpha q_\alpha(i\mathbf{k}_\alpha\cdot\mathbf{r}_{ij}) \exp(i\mathbf{k}_\alpha\cdot\mathbf{r}_j). \tag{5}$$

The corresponding modulation in $\Delta r_{ij}=|\mathbf{r}_{ij}+\Delta\mathbf{r}_i-\Delta\mathbf{r}_j|-r_{ij}$ is

$$\Delta r_{ij}=r_{ij}^{-1}[\sum_\alpha (\mathbf{r}_{ij}\cdot\mathbf{u}_\alpha)(i\mathbf{k}_\alpha\cdot\mathbf{r}_{ij})q_\alpha \exp(i\mathbf{k}_\alpha\cdot\mathbf{r}_j)$$

$$+\tfrac{1}{2}\sum_{\alpha,\beta} (i\mathbf{k}_\alpha\cdot\mathbf{r}_{ij})(i\mathbf{k}_\beta\cdot\mathbf{r}_{ij})q_\alpha q_\beta\{\mathbf{u}_\alpha\cdot\mathbf{u}_\beta-r_{ij}^{-2}(\mathbf{u}_\alpha\cdot\mathbf{r}_{ij})(\mathbf{u}_\beta\cdot\mathbf{r}_{ij})\}] \exp(i\mathbf{k}_\alpha\cdot\mathbf{r}_j+i\mathbf{k}_\beta\cdot\mathbf{r}_j). \tag{6}$$

[5] P. W. Bridgman, Proc. Am. Acad. **64**, 63 (1929). Strictly speaking, we want compressibility data at the absolute zero rather than room temperatures, but the variation of the elastic constants with temperature is a second-order effect of little importance for the present type of calculation.

The terms of the third order in the expansion of the energy (1) in terms of the q's are thus

$$U_3 = \sum_{j>i} \sum_{\alpha,\beta,\gamma} \left[\{ \tfrac{1}{2} f_{ij}'' r_{ij}^{-2} (\mathbf{u}_\alpha \cdot \mathbf{u}_\beta)(\mathbf{r}_{ij} \cdot \mathbf{u}_\gamma) - \tfrac{1}{2} f_{ij}'' r_{ij}^{-4}(\mathbf{r}_{ij} \cdot \mathbf{u}_\alpha)(\mathbf{r}_{ij} \cdot \mathbf{u}_\beta)(\mathbf{r}_{ij} \cdot \mathbf{u}_\gamma) \right.$$

$$\left. + \tfrac{1}{6} f_{ij}''' r_{ij}^{-3}(\mathbf{r}_{ij} \cdot \mathbf{u}_\alpha)(\mathbf{r}_{ij} \cdot \mathbf{u}_\beta)(\mathbf{r}_{ij} \cdot \mathbf{u}_\gamma)\}(i\mathbf{k}_\alpha \cdot \mathbf{r}_{ij})(i\mathbf{k}_\beta \cdot \mathbf{r}_{ij})(i\mathbf{k}_\gamma \cdot \mathbf{r}_{ij})\right] q_\alpha q_\beta q_\gamma \exp[i(\mathbf{k}_\alpha + \mathbf{k}_\beta + \mathbf{k}_\gamma) \cdot \mathbf{r}_j]. \quad (7)$$

The rather formidable expression inclosed in heavy brackets in (7) is a periodic function of j when summed[6] over i, since all atoms are assumed identical. Hence, by the usual argument,[7] the expression (7) vanishes unless

$$\mathbf{k}_\alpha + \mathbf{k}_\beta + \mathbf{k}_\gamma = (2\pi/d)\mathbf{m}, \quad (8)$$

where $\mathbf{m} = (m_1, m_2, m_3)$, with m_1, m_2, m_3 integers, and where d is the lattice constant. Since the matrix elements of q_α are of the form $\Delta n_\alpha = \pm 1$, nonvanishing elements of (7) can arise only if each of the quanta changes by one unit. The energy associated with the vibration α, of frequeucy ω_α, is $(n+\tfrac{1}{2})\hbar\omega_\alpha$. From standard perturbation theory,[8] it is known that an appreciable matrix element for energy transfer between different members of the system exists only if there is conservation of the total energy, i.e.,

$$k_\alpha \Delta n_\alpha + k_\beta \Delta' n_\beta + k_\gamma \Delta n_\gamma = 0, \quad (9)$$

where $k_\alpha = |\mathbf{k}_\alpha| = 2\pi\omega_\alpha/v$ and where each of the Δn's can only be ± 1. It is possible to have a simultaneous solution of (8) and (9) with $\mathbf{m} \neq 0$ in (8) only if two (or more) of the k's are large enough to be comparable with $2\pi/d$, and involve Δn's of opposite sign in (9). Destruction of a large quantum at low temperatures, however, is virtually impossible, for the corresponding initial Boltzmann factor is negligible. Hence we can set $\mathbf{m} = 0$ in (8), so that (8) reduces to the familiar condition for the conservation of momentum. In other words we can neglect the so-called[4, 7] "umklapp" processes corresponding to $\mathbf{m} \neq 0$. Clearly Eqs. (8) and (9), with $\mathbf{m} = 0$, are compatible only if the three vectors $\mathbf{k}_\alpha, \mathbf{k}_\beta, \mathbf{k}_\gamma$ are collinear, and if one of the k's is the algebraic sum of the other two, and has the opposite sign for its Δn. In other words the destruction (or creation) of a quantum of one frequency is offset by the creation (or destruction) of two quanta of lower frequency. The transfer process is thus essentially a needle-like one, as all three quanta are directed along the same line.

In the preceding paragraph, and elsewhere, we have assumed that the velocity of sound is the same for all frequencies, so that the wave number k is proportional to the frequency ω. This assumption involves no serious error. If different waves have different velocities, the vectors $\mathbf{k}_\alpha, \mathbf{k}_\beta, \mathbf{k}_\gamma$ cease to be collinear, but our estimates of the magnitudes of transition probabilities are not much affected, as the order of magnitude of the density factor $\rho(\omega_\alpha)$ in our later Eq. (11) is not greatly influenced by the non-collinearity.

The fact that $\mathbf{k}_\alpha, \mathbf{k}_\beta, \mathbf{k}_\gamma$ are collinear greatly facilitates the summing in (7). We will suppose that the $\mathbf{r}_{ij}$ can be regarded as directed at random. This assumption introduces no error of consequence, as a cubic crystal is very nearly isotropic. It is readily seen that then a nonvanishing result is obtained only either if all three of the vibrations α, β, γ are longitudinal, or else if two are transverse and one longitudinal. The averaging over the random orientations of $\mathbf{r}_{ij}$ is readily performed. To do this, we use the fact that the mean values of expressions of the type forms $(\mathbf{r} \cdot \mathbf{e})^4$, $(\mathbf{r} \cdot \mathbf{e})^6$, and $(\mathbf{r} \cdot \mathbf{e})^4(\mathbf{r} \cdot \mathbf{e}')(\mathbf{r} \cdot \mathbf{e}'')$ are respectively $r^4/5$, $r^6/7$ and $r^6(\mathbf{e}' \cdot \mathbf{e}'')/35$ if $\mathbf{r}$ is random, and $\mathbf{e}, \mathbf{e}', \mathbf{e}''$ are unit vectors, with $\mathbf{e}', \mathbf{e}''$ both perpendicular to $\mathbf{e}$. It is thus found that (7) becomes

$$U_3 = (6/210) \sum_{j>i} \{6 f_{ij}'' r_{ij}^2 + 5 f_{ij}''' r_{ij}^3\} \sum_{\alpha>\beta>\gamma} i k_\alpha i k_\beta i k_\gamma q_\alpha{}^l q_\beta{}^l q_\gamma{}^l$$

$$+ (6/210) \sum_{j>i} \{4 f_{ij}'' r_{ij}^2 + f_{ij}''' r_{ij}^3\} \sum_{\alpha>\beta} \sum_\gamma (i\mathbf{k}_\alpha \cdot i\mathbf{k}_\beta) i k_\gamma q_\alpha{}^t q_\beta{}^t q_\gamma{}^l (\mathbf{u}_\alpha \cdot \mathbf{u}_\beta). \quad (10)$$

[6] The variable of summation i is not to be confused with the factor $i = \sqrt{-1}$ preceding the wave number $\mathbf{k}$ in Eq. (7) and elsewhere.

[7] Cf. N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press), p. 256.

[8] Cf., for instance, P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press), first edition, p. 166.

A superscript l or t attached to a q means that it is a normal coordinate of longitudinal or transverse type, respectively. The factor 6 preceding the summations arises from ordering considerations, as in (10) the factors are arranged in a definite order, whereas this was unrestricted in (7). The inequality $\alpha > \beta > \gamma$, etc., does not necessarily refer to the relative sizes of ω_α, ω_β, ω_γ and is merely a device for excluding redundant terms. (The probability of repetitive cases such as $\alpha = \beta$ is negligible.)

We will now suppose that we are interested in a particular vibration of frequency ω_0. We wish to compute the rate at which this oscillator changes its quantum states due to interaction with the other vibrations of the crystal. The latter will have frequencies mostly of the order kT/h, and will be supposed in thermal equilibrium. On the other hand, we will suppose that ω_0 is at a different temperature from the main body of the lattice spectrum. In other words, we are dealing with a particular oscillator which is out of step thermally with the great bulk of vibrations of the crystal, and wish to determine how rapidly it acquires the prevalent temperature of the lattice.

First let us consider the case that ω_0 is a longitudal vibration. Then we, say, associate ω_0 with γ in (10) i.e. take $k_\gamma = 2\pi\omega_0/v$. To determine the total probability $A(n_\gamma \rightarrow n_\gamma - 1)$ of a transition of the form $n_\gamma \rightarrow n_\gamma - 1$, we must integrate over all possible values of ω_α. If we suppose that $n_\alpha \rightarrow n_\alpha + 1$, then we may take $n_\beta \rightarrow n_\beta - 1$, so that $\omega_\alpha = \omega_\beta + \omega_0$. Namely, if ω_0 is small compared with kT/h (the case of greatest interest in the study of paramagnetic relaxation), the great bulk of collisions will involve values of ω_α, ω_β larger than $\omega_0 = \omega_\gamma$, so that considerations of energy balance will prohibit n_α, n_β from both decreasing or both increasing simultaneously. Even if ω is comparable with kT/h, omission of the case $\Delta n_\alpha = \Delta n_\beta$ will not impair the orders of magnitudes of our results. By perturbation theory,[8] we have

$$A(n_\gamma \rightarrow n_\gamma - 1) = 4\pi^2 h^{-1} \int_0^{k\theta/h} \langle |U_3(n_\alpha n_\beta n_\gamma; \; n_{\alpha+1} n_{\beta-1} n_{\gamma-1})|^2 \rangle_{Av} \, \rho(\omega_\alpha) d\omega_\alpha. \tag{11}$$

Here the subscript Av means that for given $\omega_\alpha, \omega_\beta$ we are to average over the different possible values of n_α, n_β distributed in equilibrium fashion appropriate to the temperature T. The weight factor $\rho(\omega_\alpha)d\omega_\alpha$ is the density of states, relative to energy, for the ω_α, ω_β system when ω_α takes on all possible values between ω_α and $\omega_\alpha + d\omega_\alpha$. Eq. (11) involves an integration over ω_α because transitions satisfying the conservation of energy are possible for every value of ω_α. The upper limit of integration is the cut-off frequency associated with the Debye temperature θ.

Evaluation of $\varrho(\omega_\alpha)$.—The conservation of momentum is a rigorous consequence (apart from umklapp processes) of the periodicity of the lattice, so that the vector relation (8), with $m=0$, is exact. On the other hand, the conservation of energy must not be assumed to apply in computing $\rho(\omega_\alpha)$, as calculation of the density in an energy space requires a knowledge of how states are distributed over the energy interval in the vicinity of the point in question, although $\rho(\omega_\alpha)$ is, of course, finally to be evaluated at the point at which the conservation relation (9) applies. The boundary conditions at the edge of the crystal require that $k_{\alpha x}, k_{\alpha y}, k_{\alpha z}$ be integral multiples of $2\pi/l$, where l is a dimension of the crystal, supposed for simplicity a cube, with edges parallel to the coordinate axes. There is one longitudinal vibration, for each allowed value of $\mathbf{k}_\alpha$, and furthermore, with given $\mathbf{k}_\gamma$, there is one corresponding value of k_β satisfying the conservation of momentum, viz. $\mathbf{k}_\beta = \mathbf{k}_\alpha - \mathbf{k}_\gamma$. Hence the number of states in the interval $k_{\alpha x}, k_{\alpha y}, k_{\alpha z}; \; k_{\alpha x} + dk_{\alpha x}, k_{\alpha y} + dk_{\alpha y}, k_{\alpha z} + dk_{\alpha z}$ is

$$dN = [V/(2\pi)^3] dk_{\alpha x} dk_{\alpha y} dk_{\alpha z}, \tag{12}$$

where V is the volume l^3. If we introduce elliptic coordinates $\lambda = \frac{1}{2}(k_\alpha + k_\beta)$, $\mu = \frac{1}{2}(k_\beta - k_\alpha)$, φ having as foci two extremities of $\mathbf{k}_\gamma$ which for present purposes is regarded as a fixed quantity, then the right side of (12) becomes $[2V/(2\pi)^3 k_\gamma](\lambda^2 - \mu^2) d\lambda d\mu d\varphi$. Clearly $(hv/2\pi)(k_\gamma + 2\mu)$ is the lack of energy balance ΔW. If we use ΔW, $\omega_\alpha = v k_\alpha/2\pi$ as variables in place of λ, μ respectively, we have

$$dN = \rho' d\Delta W d\omega_\alpha d\varphi \quad \text{with} \quad \rho' = \frac{4\pi^2}{hv^2} \cdot \frac{k_\alpha k_\beta}{k_\gamma} \cdot \frac{V}{(2\pi)^3}. \tag{13}$$

The quantity $\rho(\omega_\alpha)$ needed in connection with (11) is $\frac{1}{2} \cdot 2\pi\rho'$. Here the factor 2π is contributed by the trivial integration over the azimuth φ, while the factor $\frac{1}{2}$ owes its origin to the fact that $\Delta W = (hv/2\pi)(|\mathbf{k}_\alpha - \mathbf{k}_\beta| - k_\alpha + k_\beta)$ is necessarily positive, and so the Dirichlet integrals, or equivalent, involved in the familiar derivation[8] of (11) extend to only one side of the origin, instead of embracing both sides. Thus, since $k_\gamma = 2\pi\omega_0/v$, etc., we have

$$\rho(\omega_\alpha) = (\pi V\omega_\alpha\omega_\beta/v^3\omega_0 h). \qquad\qquad (\alpha, \beta \text{ longitudinal}) \quad (14)$$

This is the value of $\rho(\omega_\alpha)$ to be used when the first part of (10) is substituted in (11). For the second part of (10), where α, β are transverse, we must use a value of $\rho(\omega_\alpha)$ four times as great as (14), as there are then two transverse vibrations for each allowed value of k_α or k_β.

Calculation of transition probability.—The matrix elements of the q's, and the values of the n's appropriate to thermal equilibrium are given by the usual formulas

$$q(n ; n\pm1) = (h/8\pi^2 M\omega)^{\frac{1}{2}}(n+\tfrac{1}{2}\pm\tfrac{1}{2}), \quad \langle n\rangle_{\text{Av}} = 1/[\exp(h\omega/kT) - 1], \qquad (15)$$

where M is the mass of the crystal. We can now substitute (10), (14), (15) in (11), and express the results in terms of the A and B constants, instead of the f_{ij}, by comparison of (2) and (4). In squaring the second part of (10), one may replace $(\mathbf{u}_\alpha \cdot \mathbf{u}_\beta)^2$ by its mean value $\frac{1}{3}$. One thus finally obtains

$$A(n_0 \rightarrow n_0 - 1) = n_0 DI, \qquad (16)$$

with

$$D = \tfrac{1}{2}\pi^3 v^{-9} h(V_0/M)^3 (6/35)^2 [(54A^{-1} - 45BA^{-3})^2 + 2(15A^{-1} - 9BA^{-3})^2] \qquad (17)$$

and

$$I = \int_0^{\theta k/k} \frac{\omega_\alpha^2\omega_\beta^2 \exp(h\omega_\alpha/kT)}{[\exp(h\omega_\alpha/kT) - 1][\exp(h\omega_\beta/kT) - 1]} d\omega_\alpha \sim \int_0^\infty \omega^4 e^{-h\omega/kT} d\omega = 4!k^5 T^5/h^5. \qquad (18)$$

The expression (17) is independent of crystalline size since M/V_0 is the density. The approximate value given in the second form of (18) applies to the case that $h\omega_0$ is small compared with kT, where $\omega_\beta = \omega_\alpha - \omega_0$ can be replaced by ω_α without serious error. In the preceding paper we needed primarily this case, but the approximations used to simplify (18) furnish a crude estimate of orders of magnitudes even when ω_α and ω_0 are comparable. The replacement of the upper limit of integration by infinity is legitimate since we are interested in temperatures small compared to the Debye cut-off. Then the exponentials can also be simplified because the presence of the factor $\omega_\alpha^2\omega_\beta^2$ makes most of the contributions to the integral come from values of $h\omega/kT$ somewhat greater than unity.

Equations (16, 17, 18) apply directly only in case ω_0 is a longitudinal vibration. If it is transverse, we must identify ω_0 with β rather than γ in (10), and take $\omega_\alpha = \omega_\gamma + \omega_0$. Correspondingly we replace α, β by α, γ in (14), (18), etc., and in connection with the second part of (10) we must use a density twice rather than four times the expression (14). Thus when ω_0 is transverse, the expression for the transition probability is an expression identical with (16, 17, 18), except that in (17) the terms with factors 54, 45 are deleted, in virtue of the absence of the first part of (10) for transverse waves, and the remainder of (17) is halved.

If we use Bridgman's values (3) of the constants A, B, and take $v = 2.3 \times 10^5$ cm/sec., $M/V_0 = 1.7$ g/cc, then the value of the factor DI for longitudinal oscillators ω_0 is 2.0×10^4 sec.$^{-1}$. The corresponding expression for transverse oscillators is 4.0×10^2 sec.$^{-1}$. Thus the longitudinal low frequency oscillators are much more effective intermediaries than are the transverse ones in transferring heat between the spin system and the crystal proper, and so we will henceforth in numerical estimates consider only the longitudinal type.

Rate of energy flow.—In the preceding paper, we needed the value of the conductivity for the heat flow between the low frequency oscillators and the main body of vibrations under the assumption that the former and latter are at temperatures T_L, T respectively, with $|T_L - T| \ll T$. If the low

frequency oscillators are located in the band ω_0, $\omega_0 + \Delta\omega_0$, and are $Vf(\omega_0)\Delta\omega_0$ in number this flow is

$$dQ/dt = \langle A(n_0 \to n_0 - 1) - A(n_0 - 1 \to n_0)\rangle_{\mathrm{Av}} h\omega_0 Vf(\omega_0)\Delta\omega_0, \tag{19}$$

inasmuch as an amount of energy $h\omega_0$ is added or removed from the vibration n_0 at each collision. The two transition probabilities involved in (19) differ solely in their Boltzmann weighting, i.e.,

$$A(n_0 \to n_0 - 1)/A(n_0 - 1 \to n_0) = \exp[(h\omega_0/kT) - (h\omega_0/kT_L)] \sim 1 + [(T_L - T)h\omega_0/kT^2]. \tag{20}$$

The mean value of n_0 needed in connection with averaging (16) is, by (15), very approximately $kT/h\omega_0$ since $h\omega_0/kT \ll 1$. By (16), (18), and (20), the expression (19) becomes

$$dQ/dt = b(T_L - T) \quad \text{with} \quad b = DIT^{-1}h\omega_0 Vf(\omega_0)\Delta\omega \sim 4!DT^{-1}(kT/h)^5 h\omega_0 Vf(\omega_0)\Delta\omega. \tag{21}$$

The band of longitudinal low frequency oscillators in which we were interested in the previous paper had $f(\omega_0) = 4\pi\omega_0^2/v^3$, $\omega_0 = 6 \times 10^9$, $\Delta\omega = 3 \times 10^9$ sec.$^{-1}$, $V = 4\pi R^3/3$ where R is the radius of the specimen. On combining these numerical values with the estimates of DI obtained in the preceding paragraph, it is found that $dQ/dT = 3 \times 10^{-5} R^3$ watts/deg. at $T = 1.4°$K.

Mean life.—Instead of computing the conductivity b, it is in many ways more illuminating to examine the mean free time τ_0 of the oscillator ω_0 between collisions, which is given by the formula $\tau_0 = 1/\langle 2A(n_0 \to n_0 - 1)\rangle_{\mathrm{Av}}$. Here the factor 2 appears in the denominator to allow for the fact that there are approximately equal probabilities of a low frequency oscillator absorbing and emitting a quantum. In our example, the numerical value of τ_0 is 0.5×10^{-5} sec. The corresponding mean free path $l = \tau_0 v$ is 1.0 cm.

The mean free time τ_0 is not to be confused with the relaxation time τ_e required for the temperature difference between the low frequency oscillators and the main body of lattice vibrations to reach $1/e$ of its original value, under the assumption that the specific heat of the former (viz., $kf(\omega) \cdot \Delta\omega$) is small compared to the latter. The formula for τ_e is $\tau_e = kT/h\omega DI$ and gives $\tau_e = 2 \times 10^{-4}$ instead of 0.5×10^{-5} second at $T = 1.4°$K. The distinction between the two kinds of times arises because an oscillator loses or gains only a portion of its energy at each collision.

Even a mean free time 0.5×10^{-5} sec. is not nearly as short as required if the conventional theory of paramagnetic dispersion is to function properly at helium temperatures. In consequence, this theory must be abandoned, or very materially modified, as discussed in the preceding paper. By customary standards, however, the mean life τ_0 or the relaxation time τ_e must be regarded as exceedingly brief, at least at ordinary temperatures, and hence the process of temperature equalization practically instantaneous. Thus in experiments on acoustical vibrations, etc., all the oscillators can be regarded as at the same temperature at a given point of the crystal, though spatial inhomogeneities are of course possible. Our estimate $\tau_0 = 0.5 \times 10^{-5}$ and $\tau_e = 2 \times 10^{-4}$ sec. was for $\omega_0 = 6 \times 10^9$ sec.$^{-1}$ and $T = 1.4°$K. In acoustical applications one is interested in much lower frequencies and much higher temperatures, but this will reduce τ_0 even further, since the integral I involved in (16) increases rapidly with T, and since by (16) the value of $\tau_0 = 1/\langle 2A(n \to n - 1)\rangle_{\mathrm{Av}}$ is inversely proportional to the mean number of quanta n_0. The frequencies involved in acoustical problems are so low that $\langle n_0 \rangle_{\mathrm{Av}}$ will amount to millions rather than being of the order 10 as in our example appropriate to paramagnetic relaxation in the helium domain. It will be noted that the interruption frequency due to anharmonic perturbations is much larger than the proper frequency when the latter is in the acoustic region. The resulting blurring, however, is insignificant, because acoustic vibrations have such high amplitudes that the loss or gain of a quantum at a collision represents only a minor disturbance.