CONCLUSIONS

In summation, we suppose that gold impurity can take both substitutional and interstitial positions in lead. Substitutional gold migrates by a "deviated-path" vacancy model, and interstitials migrate interstitially. At low pressures both mechanisms operate simultaneously with inseparable activation energies, the former mechanism being more effective than the latter. At high pressures only interstitials keep migrating, while the contribution from the vacancy mechanism becomes negligible.

In our experiment the temperature interval of the diffusion measurements has been extended to very low values: The experimental point at 60°C in the 4000 kg cm^{-2} plot (Fig. 1), perfectly fitting the same Arrhenius straight line as all other points at the same pressure, rules out the contribution, once postulated,[5] of diffusion along internal surfaces, at least in the gold-lead system.

ACKNOWLEDGMENTS

The authors thank Dr. S. J. Rothman of Argonne National Laboratory for having suggested the subject of the present research, and Professor E. Germagnoli for encouragement and stimulating discussions. Thanks are also due to Eng. G. Weiller and his staff at C. G. E., Milano, for technical assistance during the construction of the high-pressure apparatus.

PHYSICAL REVIEW VOLUME 141, NUMBER 2 JANUARY 1966

Calculation of Thermal Conductivity by the Kubo Formula

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(Received 1 July 1965)

The Kubo expression for lattice thermal conductivity is analyzed by the method of the double-time Green's function. The usual relaxation-time formula of kinetic theory can be obtained from the Kubo formula by suitable approximations only.

1. INTRODUCTION

The Kubo formula for the thermal conductivity is

$$K=\frac{k\beta}{3\Omega}\int_0^\infty dt\int_0^\beta d\lambda\langle \mathbf{Q}\cdot\mathbf{Q}(t+i\lambda)\rangle\,, \qquad (1)$$

where $\mathbf{Q}(t)$ is the energy-flow vector operator at time t and the brackets $\langle\ \rangle$ stand for thermodynamic averaging, namely, for any operator O

$$\langle O\rangle = \mathrm{Tr}e^{-\beta H}O/\mathrm{Tr}e^{-\beta H}\,,$$

where H is the Hamiltonian of the system, and $\beta=(kT)^{-1}$.

Recently Luttinger[1] has given a "mechanical" derivation of this expression by introducing a varying gravitational field. In principle, Eq. (1) is more general than any transport equation. For a lattice, the energy-flow vector has also been rigorously deduced by Choquard[2] and for the spherically symmetric dispersion formula, it is the usual Peierls expression

$$\mathbf{Q}(t)=\sum_{\mathbf{k},j}\mathbf{v}_{\mathbf{k},j}\omega_{\mathbf{k},j}n_{\mathbf{k},j(t)}\,, \qquad (2)$$

in units with $\hbar=1$; $\mathbf{v}_{\mathbf{k},j}=\nabla_{\mathbf{k}}\omega_{\mathbf{k}j}$ is the group velocity, $\omega_{\mathbf{k}j}$ is the energy of the kth normal mode in the jth branch, and $n_{\mathbf{k},j}=a_{\mathbf{k}j}{}^\dagger a_{\mathbf{k}j}$ is the number-density operator of the phonons in the second-quantized form. Thus, by the works of Luttinger and Choquard, it is possible to compute lattice thermal conductivity from the general expression

$$K=\frac{k\beta}{3\Omega}\sum_{\mathbf{k},j}\sum_{\mathbf{q},j'}\int_0^\infty dt\int_0^\beta d\lambda \mathbf{v}_{\mathbf{k},j}\cdot\mathbf{v}_{\mathbf{q},j'} \times\omega_{\mathbf{k},j}\omega_{\mathbf{q},j'}F_{\mathbf{k},j;\mathbf{q},j'}(t+i\lambda)\,, \qquad (3)$$

where

$$F_{\mathbf{k},j;\mathbf{q}j'}(t+i\lambda)=\langle n_{\mathbf{k}j}(0)n_{\mathbf{q}j'}(t+i\lambda)\rangle\,. \qquad (4)$$

Essentially one has to calculate the correlation function of two number-density operators at different times. In this paper we shall discuss an approximation scheme which leads to the relaxation-time formula of kinetic theory for thermal conductivity as it has been reviewed and discussed by Carruthers.[3]

2. RETARDED TWO-PARTICLE GREEN'S FUNCTION

The correlation function $F_{\mathbf{k},j;\mathbf{q}j'}(t)$ is an integral over the Fourier transform of the associated Green's function

$$G_{kk,q}(t-t')=-i\theta(t-t')\langle[n_k(t),n_q(t')]\rangle \equiv\langle\langle n_k(t),n_q(t')\rangle\rangle\,.$$

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[1] J. M. Luttinger, Phys. Rev. **135**, A1505 (1964).
[2] Ph. Choquard, Helv. Phys. Acta **36**, 415 (1963).
[3] P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

For simplicity in notation we shall omit the branch indices from here onwards. The relationship between correlation functions and Green's function and their properties have been discussed by Zubarev.[4] Following Ref. 4, we shall define the Fourier transforms as

$$f(t)=\int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t} f(\omega)\,. \tag{5}$$

Then

$$F_{kq}(t)=i\int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}[G_{kk,q}(\omega+i\epsilon)-G_{kk,q}(\omega-i\epsilon)]/(e^{\beta\omega}-1)\,. \tag{6}$$

Substituting this in Eq. (3) for the thermal conductivity, we obtain

$$K=\frac{k\beta}{3\Omega}\sum_{kq}\mathbf{v}_k\cdot\mathbf{v}_q\omega_k\omega_q \lim_{\substack{\epsilon\to 0\\ \delta\to 0}}\int_{-\infty}^{+\infty}\frac{d\omega}{(\omega-i\delta)^2}[G_{kk,q}(\omega+i\epsilon)-G_{kk,q}(\omega-i\epsilon)]\,. \tag{7}$$

This expression looks badly divergent in view of the factor $(\omega-i\delta)^{-2}$. However, we shall show that symmetrized $G_{kk,q}(\omega+i\epsilon)-G_{kkq}(\omega-i\epsilon)$ is an odd function in ω. To prove this we note that

$$G_{kk,q}(\omega+i\epsilon)-G_{kk,q}(\omega-i\epsilon)=-\frac{i}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle[n(t),n_q(0)]\rangle\,, \tag{8}$$

and

$$\langle[n_k(t),n_q(0)]\rangle=\langle[n_k(0),n_q(-t)]\rangle=-\langle[n_q(-t),n_k(0)]\rangle\,. \tag{9}$$

Because of symmetry of summation over k and q, Eq. (7) can also be written as

$$K=\frac{k\beta}{3\Omega}\sum_{k,q}\mathbf{v}_k\cdot\mathbf{v}_q\omega_k\omega_q \lim_{\substack{\epsilon\to 0\\ \delta\to 0}}\int_{-\infty}^{+\infty}\frac{d\omega}{(\omega-i\delta)^2}\tfrac{1}{2}[G_{kk,q}(\omega+i\epsilon)-G_{kkq}(\omega-i\epsilon)+k\leftrightarrow q]\,. \tag{10}$$

From Eqs. (8) and (9) it follows that

$$\tfrac{1}{2}[G_{kk,q}(\omega+i\epsilon)-G_{kk,q}(\omega-i\epsilon)+k\leftrightarrow q]=\frac{i}{2\pi}\int_{-\infty}^{+\infty}\sin\omega t\langle[n_k(t),n_q(0)]\rangle dt\,, \tag{11}$$

and this is an odd function of ω. Hence the expression for thermal conductivity reduces to

$$K=\frac{k\beta}{3\Omega}\sum_{k,q}\mathbf{v}_k\cdot\mathbf{v}_q\omega_k\omega_q\frac{i\pi}{2}\left(\frac{\partial}{\partial\omega}[G_{kkq}(\omega+i\epsilon)-G_{kkq}(\omega-i\epsilon)+k\leftrightarrow q]\right)_{\omega=0} \tag{12}$$

$$=-\frac{1}{4}\frac{k\beta}{3\Omega}\sum_{k,q}\mathbf{v}_k\cdot\mathbf{v}_q\omega_k\omega_q\int_{-\infty}^{+\infty} t\, dt\langle[n_k(t),n_q(0)]\rangle\,. \tag{13}$$

Equation (12) is a very useful exact form for actual calculation of thermal conductivity. It is generally believed[5] that the correlation function dies out exponentially. From Eq. (13) we note that the commutator of the number-density operators at different times should decrease as $t^{-2-\delta}$ with $\delta>0$ for calculating a finite thermal conductivity. To put it more explicitly, there may exist dissipative forces in nature which do not lead to an exponential decay law, but they are still responsible for observable effects. Such processes can be easily discussed using the formulation of Kubo.

[4] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].
[5] W. C. Schieve and R. L. Peterson, Phys. Rev. **126**, 1458 (1962).

3. APPROXIMATION TO THE GREEN'S FUNCTION

$G_{kk,q}(t)$ is a two-particle Green's function. One can write an integrodifferential equation for it and relate it to still higher order Green's functions. It is not possible to solve these chains of equations and so one is forced to make approximations. We shall try to relate the two-particle Green's function to the one-particle Green's function by an approximation method. This scheme essentially follows from the observation that the commutator $[n_k(t),n_q]$ can be written as

$$[n_k(t),n_q]=a_k^\dagger(t)[a_k(t),a_q^\dagger]a_q+[a_k^\dagger(t),a_q^\dagger]a_k(t)a_q +a_q^\dagger a_k^\dagger(t)[a_k(t),a_q]+a_q^\dagger[a_k^\dagger(t),a_q]a_k(t)\,. \tag{14}$$

The commutators on the right-hand side of this equation in general contain creation and annihilation operators besides a c-number part. We ignore the operator part of the commutator and assume that the contribution from these operator parts is negligible. In such an approximation, since the commutator equals its thermal average, we can write

$$\langle[n_k(t),n_q]\rangle\cong\langle[a_k(t),a_q^\dagger]\rangle\langle a_k^\dagger(t)a_q\rangle+\langle[a_k^\dagger(t),a_q^\dagger]\rangle\langle a_k(t)a_q\rangle+\langle a_q^\dagger a_k^\dagger(t)\rangle\langle[a_k(t),a_q]\rangle+\langle a_q^\dagger a_k(t)\rangle\langle[a_k^\dagger(t),a_q]\rangle. \quad (15)$$

The method of decoupling the correlation function[6,7] $\langle abcd\rangle\cong\langle ab\rangle\langle cd\rangle\pm\langle ac\rangle\langle bd\rangle+\langle ad\rangle\langle bc\rangle$ also yields Eq. (15). The correlation function of Eq. (1) can be directly decoupled in this way to yield the final result, which will be shown in an Appendix. The purpose of going through the commutator argument is to emphasize that there exists at least one physical system, e.g., the isotope-defect system, where Eq. (15) can be shown to be exact.

We define the one-particle Green's functions and the associated correlation functions as

$$G_{kq}(t-t')=\langle\langle a_k(t),a_q^\dagger(t')\rangle\rangle,\quad n_{kq}(t-t')=\langle a_q^\dagger(t')a_k(t)\rangle, \quad (16a)$$

$$D_{kq}(t-t')=\langle\langle a_k^\dagger(t),a_q^\dagger(t')\rangle\rangle,\quad d_{kq}(t-t')=\langle a_q^\dagger(t')a_k^\dagger(t)\rangle, \quad (16b)$$

$$E_{kq}(t-t')=\langle\langle a_k(t),a_q(t')\rangle\rangle,\quad e_{kq}(t-t')=\langle a_q(t')a_k(t)\rangle, \quad (16c)$$

and from Eq. (15),

$$G_{kk,q}(t)\cong G_{kq}(t)n_{qk}(-t)+D_{kq}(t)e_{qk}(-t)-E_{qk}(-t)d_{kq}(t)-G_{qk}(-t)n_{kq}(t). \quad (17)$$

By taking the Fourier transform of Eq. (15), we get from Eq. (8)

$$\begin{aligned}G_{kkq}(\omega+i\epsilon)-G_{kkq}(\omega-i\epsilon)=i\int_{-\infty}^{+\infty}\frac{d\omega_2}{(e^{\beta\omega_2}-1)}\{&[G_{kq}(\omega_2+\omega+i\epsilon)-G_{kq}(\omega_2+\omega-i\epsilon)][G_{qk}(\omega_2+i\epsilon)-G_{qk}(\omega_2-i\epsilon)]\\&+[D_{kq}(\omega_2+\omega+i\epsilon)-D_{kq}(\omega_2+\omega-i\epsilon)][E_{qk}(\omega_2+i\epsilon)-E_{qk}(\omega_2-i\epsilon)]-[E_{qk}(\omega_2-\omega+i\epsilon)-E_{qk}(\omega_2-\omega-i\epsilon)]\\&\times[D_{kq}(\omega_2+i\epsilon)-D_{kq}(\omega_2-i\epsilon)]-[G_{qk}(\omega_2-\omega+i\epsilon)-G_{qk}(\omega_2-\omega-i\epsilon)][G_{kq}(\omega_2+i\epsilon)-G_{kq}(\omega_2-i\epsilon)]\}. \quad (18)\end{aligned}$$

This is easily seen to be an odd function of ω. After some manipulations, we get

$$\begin{aligned}&\frac{d}{d\omega}[G_{kkq}(\omega+i\epsilon)-G_{kkq}(\omega-i\epsilon)]|_{\omega=0}\\&=i\int\frac{d\omega}{e^{\beta\omega}-1}\left\{\frac{d}{d\omega}[(G_{kq}(\omega+i\epsilon)-G_{kq}(\omega-i\epsilon))\right.\\&\qquad\left.\times(G_{qk}(\omega+i\epsilon)-G_{qk}(\omega-i\epsilon))+(D_{kq}(\omega+i\epsilon)-D_{kq}(\omega-i\epsilon))(E_{qk}(\omega+i\epsilon)-E_{qk}(\omega-i\epsilon))]\right\}\\&=2i\beta\int_0^\infty\frac{e^{\beta\omega}}{(e^{\beta\omega}-1)^2}d\omega\{[G_{kq}(\omega+i\epsilon)-G_{kq}(\omega-i\epsilon)]\\&\qquad\times[G_{qk}(\omega+i\epsilon)-G_{qk}(\omega-i\epsilon)][D_{kq}(\omega+i\epsilon)-D_{kq}(\omega-i\epsilon)][E_{qk}(\omega+i\epsilon)-E_{qk}(\omega-i\epsilon)]\}. \quad (19)\end{aligned}$$

We have assumed that the Green's function vanishes for $\omega\rightarrow\pm\infty$. This approximate expression (Eq. 19) is used in Eq. (12) to obtain a fairly good estimate of the thermal conductivity.

In most normal processes the functions D_{kq} and E_{kq}, which depend on the correlation between two creation or two annihilation operators, are negligibly small (in superconductivity[6] or superfluidity they are no longer so negligible). Confining ourselves to normal matter we write the one-particle Green's function as

$$G_{kq}(\omega)=\delta_{kq}[2\pi(\omega-\omega_k+M_k(\omega))]^{-1}, \quad (20)$$

where $M_k(\omega)$ gives the effect of perturbation on the self-energy of one particle. The real part of $M_k(\omega+i\epsilon)$ is the shift in energy of the kth mode, and the imaginary part is interpreted as the half-width of the mode. We can write approximately

$$G_{kq}(\omega+i\epsilon)\sim\delta_{kq}[2\pi(\omega-\epsilon_k+i\Gamma_k)]^{-1}, \quad (21)$$

[6] C. Bloch and C. De Dominicis, Nucl. Phys. **7**, 459 (1958).

[7] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)]. D. N. Zubarev, Dokl. Akad. Nauk SSSR **132**, 1055 (1960) [English transl.: Soviet Phys.—Doklady **5**, 570 (1960)].

where ϵ_k is the perturbed energy of the kth mode. Substituting Eq. (21) in Eq. (19) we get

$$\frac{d}{d\omega}[G_{kk,q}(\omega+i\epsilon)-G_{kk,q}(\omega-i\epsilon)]|_{\omega=0}=-\frac{i\beta}{\pi^2}\delta_{kq}\int_{-\infty}^{+\infty}\frac{e^{\beta\omega}}{(e^{\beta\omega}-1)^2}\frac{\Gamma_k{}^2}{[(\omega-\epsilon_k)^2+\Gamma_k{}^2]^2}d\omega. \tag{22}$$

For small values of Γ_k, the integrand in Eq. (22) is peaked around $\omega=\epsilon_k$ and we can fairly accurately represent

$$\frac{d}{d\omega}[G_{kkq}(\omega+i\epsilon)-G_{kkq}(\omega-i\epsilon)]|_{\omega=0}\simeq-\frac{i\beta}{\pi^2}\delta_{kq}\frac{e^{\beta\epsilon_k}}{(e^{\beta\epsilon_k}-1)^2}\frac{\pi}{2\Gamma_k}.$$

Therefore, the thermal conductivity is given by

$$K=\frac{k\beta^2}{3\Omega}\sum_k \omega_k{}^2 v_k{}^2\frac{e^{\beta\epsilon_k}}{(e^{\beta\epsilon_k}-1)^2}\frac{1}{2\Gamma_k}, \tag{23}$$

which is the familiar relaxation-time expression. The effect of the frequency shift, however, has been taken into account. We consider this derivation more satisfactory than that of the previous authors.[5]

APPENDIX

Using the decoupling scheme $\langle abcd\rangle=\langle ab\rangle\langle cd\rangle+\langle ac\rangle\langle bd\rangle+\langle ad\rangle\langle bc\rangle$ and ignoring, for simplicity, the correlations between two creation and two annihilation operators, we get

$$K=\lim_{\epsilon\to 0}\frac{k\beta}{3\Omega}\int_0^\infty dt\, e^{-\epsilon t}\sum_{k,q}\omega_k\omega_q\mathbf{v}_k\cdot\mathbf{v}_q\int_0^\beta d\beta'\langle a_k{}^\dagger(-t-i\beta')a_k(-t-i\beta')a_q{}^\dagger a_q\rangle$$

$$\cong\lim_{\epsilon\to 0}\frac{k\beta}{3\Omega}\int_0^\infty dt\, e^{-\epsilon t}\sum_{k,q}\omega_k\omega_q\mathbf{v}_k\cdot\mathbf{v}_q\int_0^\beta d\beta'\langle a_k{}^\dagger(-t-i\beta')a_q\rangle\langle a_k(-t-i\beta')a_q{}^\dagger\rangle.$$

We have further

$$n_{kq}(t-t')=\langle a_q{}^\dagger(t')a_k(t)\rangle=i\int_{-\infty}^{+\infty}d\omega\frac{1}{e^{\beta\omega}-1}e^{-i\omega(t-t')}[G_{kq}(\omega+i\epsilon)-G_{kq}(\omega-i\epsilon)],$$

and

$$\langle a_k(t)a_q{}^\dagger(t')\rangle=i\int_{-\infty}^{+\infty}d\omega\frac{e^{\beta\omega}}{e^{\beta\omega}-1}e^{-i\omega(t-t')}[G_{kq}(\omega+i\epsilon)-G_{kq}(\omega-i\epsilon)].$$

Substituting these values and performing the integration over t and β', we get

$$K=\lim_{\epsilon\to 0}\frac{ik\beta}{3\Omega}\iint_{-\infty}^{\infty}d\omega_1 d\omega_2\sum_{k,q}\omega_k\omega_q\mathbf{v}_k\cdot\mathbf{v}_q$$
$$\times\frac{1}{\omega_1-\omega_2-i\epsilon}\frac{1}{\omega_1-\omega_2}\frac{e^{\beta\omega_1}-e^{\beta\omega_2}}{(e^{\beta\omega_1}-1)(e^{\beta\omega_2}-1)}[G_{kq}(\omega_2+i\epsilon)-G_{kq}(\omega_2-i\epsilon)][G_{qk}(\omega_1+i\epsilon)-G_{qk}(\omega_1-i\epsilon)].$$

Interchanging $\omega_1\leftrightarrow\omega_2$, we can also write the above expression as

$$K=\lim_{\epsilon\to 0}\frac{ik\beta}{3\Omega}\iint_{-\infty}^{\infty}d\omega_1 d\omega_2\sum_{k,q}\omega_k\omega_q\mathbf{v}_k\cdot\mathbf{v}_q[G_{qk}(\omega_1+i\epsilon)-G_{qk}(\omega_1-i\epsilon)]$$
$$\times[G_{kq}(\omega_2+i\epsilon)-G_{kq}(\omega_2-i\epsilon)]/[(e^{\beta\omega_1}-1)(e^{\beta\omega_2}-1)]\frac{e^{\beta\omega_1}-e^{\beta\omega_2}}{\omega_1-\omega_2}\frac{1}{2}\left[\frac{1}{\omega_1-\omega_2+i\epsilon}+\frac{1}{\omega_2-\omega_1-i\epsilon}\right].$$

Since $(\omega_1-\omega_2-i\epsilon)^{-1}+(\omega_2-\omega_1-i\epsilon)^{-1}=2i\pi\delta(\omega_1-\omega_2)$, we can integrate over one of the variables. To integrate over the remaining variable, we make the same approximation for the one-particle Green's function as in the text and get Eq. (23) of the text.