Theory of the Thermal Conductivity of Superconductors*

J. BARDEEN, G. RICKAYZEN, AND L. TEWORDT†
Physics Department, University of Illinois, Urbana, Illinois
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A theory of the thermal conductivity of superconductors is presented, based on the theory of superconductivity due to Bardeen, Cooper, and Schrieffer. The excited states of the system are treated as quasi-particles, allowing a Boltzmann equation to be set up. The electronic contribution to the thermal conductivity when the dominant scatterers are impurities has been calculated exactly. The result is very close to that of the Heisenberg-Koppe theory which is in fair agreement with experiment. The variational principle of Wilson has been used to find the electronic conductivity when the dominant scatterers are lattice waves. It is concluded that the theory fails to predict the sharp drop in the ratio κ_{es}/κ_{en} as the temperature is lowered below T_c, a feature which is characteristic of the experimental results. The effect of the electrons on the lattice conductivity has also been calculated. The theoretical values may be too large.

1. INTRODUCTION

IN recent years many experiments have been performed[1–9] to determine accurately the thermal conductivity of superconductors and so to provide insight into the mechanism of superconductivity. In many cases interpretation of the experimental results is complicated because both the electrons and the lattice contribute to the thermal conductivity and because both contributions can be limited by several scattering mechanisms. A full discussion of these points and further references are given in the review articles of Olsen and Rosenberg,[10] Klemens,[11] and Serin.[12] In some cases one can be certain that there is only one contribution to the thermal conductivity and that one scattering mechanism is dominant. From these cases a number of results have been established for which a theoretical explanation is desired.

In the first place, except for the most impure specimens, the main contribution to the thermal conductivity (near the critical temperature, T_c) comes from the electrons. As the temperature is lowered, the electronic contribution decreases while the lattice contribution increases, until at about $0.2T_c$ to $0.3T_c$ the lattice contribution is dominant. These features are in qualitative agreement with the two-fluid model in which it is assumed that only the normal electrons carry heat or scatter phonons and that the number of these electrons decreases from the number in the normal state at T_c to zero at the absolute zero of temperature. Accordingly one expects the electronic conductivity to decrease as the temperature is lowered while, as long as the lattice waves are scattered mainly by electrons, the lattice conductivity will increase. The exact temperature dependence of the thermal conductivity depends on the details of the theory and should be a good test of the theory.

Another outstanding feature of the experimental results is the different behavior of the electronic conductivity according to whether the dominant scatterers are impurities or phonons. The ratio of the thermal conductivity in the superconducting state to that in the normal state plotted against (T/T_c) has a zero slope at T_c if the scattering is predominantly by the impurities, but it has a large slope, of order 5, if the scattering is predominantly by phonons. This important difference has long been a puzzle and is not explained by the present theory.

Previous theories of thermal conduction in superconductors have been based on the two-fluid model, the most complete being that of Heisenberg and the later modification by Koppe.[13] Although these theories were based on a microscopic theory now known to be incorrect, the applications to specific heats and thermal conduction do not depend on the details of the theories and they may be regarded as particular types of phenomenological two-fluid models. The version of Koppe may be interpreted as giving an energy gap with an exponential variation of specific heat at low temperatures, not far from that observed. When applied to thermal conduction limited by impurity scattering, the theory gives a reasonably good fit to experimental data but fails to account for the large drop in κ_s near T_c observed for phonon scattering. As we shall see, our

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† Present address: Institut für Theoretische Physik, Universität, Münster (Westf.), Germany.
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results for impurity scattering, although based on quite different concepts, are close to those of the Heisenberg-Koppe theory.

According to the theory of superconductivity presented by Bardeen, Cooper, and Schrieffer,[14] a state with energy lower than that of the normal state can be formed by taking a linear combination of normal-state configurations in which states of electrons of equal but opposite momentum and spin ($\mathbf{k}\uparrow$, $-\mathbf{k}\downarrow$) are both either occupied or unoccupied. This state is identified with the superconducting ground state. Excited states are formed when only one state of a pair is occupied in all configurations or when pair excitations are formed so as to be orthogonal to the ground state. Valatin[15] and Bogolyubov[16] have shown independently that the two kinds of excitations can be handled in the same way and that they behave like quasi-particles which obey the Fermi-Dirac statistics. At the low temperatures at which the phenomenon of superconductivity is found, the system is not highly excited so that it is reasonable to treat the excitations as independent. The mean free path for scattering of one quasiparticle by another is large. The fact that the excitations behave like a set of independent quasi-particles simplifies the treatment for one can set up a Boltzmann equation for the transport problem and borrow many of the results of single-particle theories. It is evident that these quasi-particles correspond to the normal electrons of the two-fluid theory. The energy gap accounts for the exponential decay of the excitations with decreasing temperature. Thus the microscopic theory certainly accounts for those qualitative features which were adequately described by the two-fluid model.

The theory of BCS is based on a simplified model. Comparison with experiment is based on the law of corresponding states for superconductors. This law implies that the ratio of the thermal conductivity in the superconducting state to that in the normal state should be a universal function of (T/T_c) for the electronic contribution and the lattice contribution separately when one scattering mechanism predominates. Experimental results indicate that such universal functions exist[3] only as a rough approximation and that there are marked deviations for particular metals. (For instance the ratio for tin is not even isotropic.) It is only in this sense that one can expect agreement between the present idealized theory and experiment.

Section 2 is devoted to the properties of the quasi-particle excitations of the system and succeeding sections are devoted to the calculation of the electronic conductivity when impurity scattering or lattice scattering predominates and of the lattice conductivity when electronic scattering predominates. In Sec. 6 we return to a discussion of the results and a comparison of theory with experiment.

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In accordance with the established notation κ denotes the thermal conductivity, subscripts e and g denote electronic and lattice contributions, respectively, and subscripts n and s indicate whether we are referring to the normal or superconducting state of the metal.

2. GROUP VELOCITY OF EXCITATIONS

In order to calculate the heat carried by the excitations of the superconducting system it is necessary to know the group velocity of the excitations. The ground state of the system is given by the wave function Ψ_{gN} which is that component of the wave function Ψ_g, which contains exactly N electrons, the number of electrons present.

$$\Psi_g=\{\prod_{\mathbf{k}}[(1-h_{\mathbf{k}})^{\frac{1}{2}}+h_{\mathbf{k}}^{\frac{1}{2}}b_{\mathbf{k}}^*]\}\Phi_0, \tag{2.1}$$

where Φ_0 is the vacuum state. The operators $b_{\mathbf{k}}$ are defined by

$$b_{\mathbf{k}}=C_{\mathbf{k}\uparrow}C_{-\mathbf{k}\downarrow},$$

where the C's are destruction operators for electrons. The definition of $h_{\mathbf{k}}$ is

$$h_{\mathbf{k}}=\tfrac{1}{2}(1-\epsilon_{\mathbf{k}}/E_{\mathbf{k}}), \tag{2.2}$$

where $\epsilon_{\mathbf{k}}$ is the energy of the electron with wave-vector $\mathbf{k}$ in the normal metal,

$$E_{\mathbf{k}}=+(\epsilon_{\mathbf{k}}^2+\epsilon_0^2)^{\frac{1}{2}}, \tag{2.3}$$

and $2\epsilon_0$ is the energy gap for the formation of excitations. In the future we shall ignore the subscripts N. The notation is that of BCS. States in which two particles are excited in states $(\mathbf{k},\uparrow)$ and $(-\mathbf{l},\downarrow)$ are given by the wave functions

$$\Psi_{\mathbf{k},\mathbf{l}}=\{\prod_{\mathbf{k}'\neq\mathbf{k},\mathbf{l}}[(1-h_{\mathbf{k}'})^{\frac{1}{2}}+h_{\mathbf{k}'}^{\frac{1}{2}}b_{\mathbf{k}'}^*]\}C_{-\mathbf{l}\downarrow}^*C_{\mathbf{k}\uparrow}^*\Psi_0. \tag{2.4}$$

The energy of this state measured from the energy of the ground state is

$$W_{\mathbf{k},\mathbf{l}}=E_{\mathbf{k}}+E_{\mathbf{l}}.$$

A wave-packet $X_{\mathbf{k}o,\mathbf{l}}$ can be formed from these states by taking a sum of these excited states with $\mathbf{k}\simeq\mathbf{k}_0$, i.e.,

$$X_{\mathbf{k}o,\mathbf{l}}=\sum_{\mathbf{k}}\alpha(\mathbf{k})\Psi_{\mathbf{k},\mathbf{l}}\exp(-iW_{\mathbf{k},\mathbf{l}}t/\hbar)$$

where $\alpha(\mathbf{k})$ is zero unless $\mathbf{k}\simeq\mathbf{k}_0$. The particle density in this state is

$$\begin{aligned}\rho(\mathbf{r})&=\sum_{\mathbf{p},\mathbf{p}',\sigma}\langle X_{\mathbf{k}o\mathbf{l}},C_{\mathbf{p}'\sigma}^*C_{\mathbf{p}\sigma}X_{\mathbf{k}o\mathbf{l}}\rangle e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}}\\&=\sum_{\mathbf{k},\mathbf{k}'}\sum_{\mathbf{p},\mathbf{p}',\sigma}\alpha(\mathbf{k})\alpha^*(\mathbf{k}')\\&\qquad\times\exp\{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}+i(W_{\mathbf{k}',\mathbf{l}}-W_{\mathbf{k},\mathbf{l}})t/\hbar\}\\&\qquad\times\langle\Psi_{\mathbf{k}',\mathbf{l}},C_{\mathbf{p}'\sigma}^*C_{\mathbf{p}\sigma}\Psi_{\mathbf{k},\mathbf{l}}\rangle.\end{aligned}$$

Using the table of matrix elements of BCS, we find

$$\rho(\mathbf{r})=2\sum_{p} h_p+(1-2h_l)+\sum \alpha(\mathbf{k})\alpha^*(\mathbf{k}') \times\exp\{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}+i(E_{k'}-E_k)t/\hbar\} \times[(1-h_k)^{\frac{1}{2}}(1-h_{k'})^{\frac{1}{2}}-h_k^{\frac{1}{2}}h_{k'}^{\frac{1}{2}}].$$

If the wave function $X_{k0,1}$ is normalized to unity, then

$$\sum_k[\alpha(\mathbf{k})]^2=1,$$

and

$$\rho(r)=2\sum_{\mathbf{k}} h_k+(1-2h_l)+(1-2h_{k0})\sum_{\mathbf{k},\mathbf{k}'}\alpha^*(\mathbf{k}')\alpha(\mathbf{k}) \times\exp\{i(\mathbf{k}-\mathbf{k}')\cdot[\mathbf{r}-\nabla_{k0}E_{k0}t/\hbar]\}.$$

The first two terms represent uniform distributions of particles while the last represents a particle localized near $\mathbf{r}=\nabla_0 E_{k0}t/\hbar$. Therefore, the localized excitation moves with group velocity $\nabla_0 E_{k0}/\hbar$.

The average particle density present is

$$2\sum h_k+(1-2h_{k0})+(1-2h_l),$$

which is different from the particle density N in the ground state. This is because, in choosing the excitations $\Psi_{k,1}$ as wave functions of the excited states, the fact that the number of electrons is fixed has been ignored. If we were to take this condition into account exactly, we should have to add to the functions h_k quantities of order N^{-1}. Then, *ipso facto*, the average particle density would be N while the group velocity would be altered by an amount of order N^{-1} which could be ignored.

The amount of charge localized in the packet is only $(1-2h)e$; the remainder is spread throughout the metal. This can be interpreted as follows. A transfer of the excitation from one region to another can take place by an electron transfer in state $(\mathbf{k}\uparrow)$ with probability $(1-h_k)$ or by a transfer of $(-\mathbf{k}\downarrow)$ in the opposite direction with probability h_k. The net charge transfer is $(1-2h)e$ corresponding to transfer of the excess in the excitation, $(1-2h)e$, from one region to the other.

Valatin[15] and Bogolyubov[16] have shown independently that all the single-particle and pair excited states can be obtained from the ground state by operating on it with new operators γ_{k0}^*, γ_{k1}^* which obey the Fermi-Dirac commutation relations. These new operators are defined by the equations

$$\gamma_{k0}=(1-h_k)^{\frac{1}{2}}C_{k\uparrow}-h_k^{\frac{1}{2}}C_{-k\downarrow}^*, \tag{2.5}$$

$$\gamma_{k1}=(1-h_k)^{\frac{1}{2}}C_{-k\downarrow}+h_k^{\frac{1}{2}}C_{k\uparrow}^*. \tag{2.6}$$

The state $\Psi_{k,1}$ is given by

$$\Psi_{k,1}=\gamma_{k0}^*\gamma_{11}^*\Psi_g.$$

The state in which the excited pair of momentum $\mathbf{k}$ is present is given by $\gamma_{k0}^*\gamma_{k1}^*\Psi_g$. Thus, in this formalism there is no need to differentiate between the single-particle and pair excitations; for this reason the formalism is extremely useful. It is necessary to note that the operator γ_{k1}^* creates a particle in $(-\mathbf{k}\downarrow)$ so that the group velocity of the excitation is $(-\nabla_k E/\hbar)$.

The analogy with the normal metal is most clearly brought out if one uses the terminology of electrons and holes for that case. In the limit that $\epsilon_0\to 0$, h_k approaches 0 above the Fermi surface and 1 below the Fermi surface. Therefore, γ_{k0}^* creates an electron in $(\mathbf{k}\uparrow)$ above the Fermi surface and creates a hole in $(-\mathbf{k}\downarrow)$ below the Fermi surface while γ_{k1}^* creates an electron in $(-\mathbf{k}\downarrow)$ above the Fermi surface and a hole in $(\mathbf{k}\uparrow)$ below the Fermi surface.

3. ELASTIC SCATTERING

Let us suppose that the electrons are scattered elastically by a potential $V(\mathbf{r})$. In terms of the creation and annihilation operators for electrons, the Hamiltonian contains the scattering term

$$H_s=\sum_{\mathbf{k},\mathbf{k}',\sigma} v(\mathbf{k}-\mathbf{k}')C_{k'\sigma}^*C_{k\sigma}, \tag{3.1}$$

where

$$v(\mathbf{k}-\mathbf{k}')=\Omega^{-1}\int e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}V(\mathbf{r})d^3r. \tag{3.2}$$

In terms of the operators for the creation of the quasi-particle excitations, we have

$$H_s=\sum_{\mathbf{k},\mathbf{k}'} v(\mathbf{k}-\mathbf{k}')\{[(1-h)^{\frac{1}{2}}(1-h')^{\frac{1}{2}}-h^{\frac{1}{2}}h'^{\frac{1}{2}}] \times(\gamma_{k'0}^*\gamma_{k0}+\gamma_{k1}^*\gamma_{k'1})+[h^{\frac{1}{2}}(1-h')^{\frac{1}{2}}+h'^{\frac{1}{2}}(1-h)^{\frac{1}{2}}] \times(\gamma_{k'0}^*\gamma_{k1}^*+\gamma_{k'1}\gamma_{k0})+2h_k\delta_{k,k'}\}, \tag{3.3}$$

where h denotes h_k and h' denotes $h_{k'}$. We can now find the relaxation time of the electrons by a method similar to that used for normal metals. If the probabilities that the excited states $\mathbf{k}0$, $\mathbf{k}1$ are occupied are f_{k0}, f_{k1}, then the probability that an excitation of type "0" is scattered from $\mathbf{k}$ to $\mathbf{k}'$ is

$$(2\pi/\hbar)|v(\mathbf{k}'-\mathbf{k})|^2[(1-h)^{\frac{1}{2}}(1-h')^{\frac{1}{2}}-h^{\frac{1}{2}}h'^{\frac{1}{2}}]^2 \times f'(1-f)\delta(E'-E).$$

Hence, taking into account the possibility that the excitation can be scattered into $\mathbf{k}$, we have

$$\left.\frac{\partial f_{k0}}{\partial t}\right]_{\text{coll}}=\frac{2\pi}{\hbar}\sum_{k'}|v(\mathbf{k}-\mathbf{k}')|^2[(1-h)^{\frac{1}{2}}(1-h')^{\frac{1}{2}} -(hh')^{\frac{1}{2}}]^2[f'(1-f)-f(1-f')]\delta(E'-E). \tag{3.4}$$

(Since the collisions are elastic no pairs of excitations can be created.) If the departure from equilibrium is given by

$$f_{k0}=f_k^0-k_zC(E)\frac{\partial f_{k0}^0}{\partial E},$$

where f_k^0 is the equilibrium value of f_{k0}, namely

$[e^{E/kT}+1]^{-1}$,[11] and z is the direction of the disturbance, then

$$\left.\frac{\partial f_{\mathbf{k}0}}{\partial t}\right]_{\text{coll}}=\frac{N(0)}{2\hbar}\int d\epsilon' d\Omega' |v(\mathbf{k}-\mathbf{k}')|^2 \times\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)\left[k_zC(E)\frac{\partial f^0}{\partial E}-k_z'C(E')\frac{\partial f_0'}{\partial E'}\right]\delta(E-E'),$$

where $N(0)$ is the density of states at the Fermi surface. Hence

$$\left.\frac{\partial f_{\mathbf{k}0}}{\partial t}\right]_{\text{coll}}=\frac{N(0)}{2\hbar}k_0C(E)\frac{\partial f^0}{\partial E}\left|\frac{E}{\epsilon}\right|\frac{\epsilon^2}{E^2} \times\int d\Omega' |v(\mathbf{k}-\mathbf{k}')|^2\left(\frac{k_z}{k}-\frac{k_z'}{k'}\right)_{k=k'=k_0},$$

where k_0 is the wave-vector at the Fermi surface. Therefore

$$\left.\frac{\partial f_{\mathbf{k}0}}{\partial t}\right]_{\text{coll}}=\left|\frac{\epsilon}{E}\right|\frac{f_{\mathbf{k}0}-f_k{}^0}{\tau_n},$$

where τ_n is the relaxation time in the normal state. Therefore, there exists a relaxation time, τ_s, in the superconducting state given by

$$\tau_s=|E/\epsilon|\tau_n. \tag{3.5}$$

In the same way we find that the distribution of the "1" excitations relaxes with the same relaxation time τ_s. It follows from this result and the formula obtained in Sec. 2 for the group velocity that the mean free path of the excitations is the same in the normal state as in the superconducting state.

Now let us consider the heat flow by transfer of excitations from one region to another in a superconductor in the presence of a temperature gradient parallel to the z axis. Along some xy plane in the metal the excitations are in equilibrium at a temperature T. The number of excitations per unit volume at the plane with energy between E and $E+dE$ is

$$[2f(E)2N(0)(d\epsilon/dE)dE]_T.$$

The speed of these excitation is $v=|\epsilon/E|v_0$, where v_0 is the velocity of electrons at the Fermi surface in the normal metal. Therefore the energy flow to the right away from the plane is

$$W_R=\int_{\epsilon_0}^{\infty}dE\int_0^{\pi/2}\left.\sin\theta\frac{d\theta\cos\theta}{2}E\frac{\epsilon}{E}v_0 2f(E)2N(0)\frac{E}{\epsilon}\right]_T.$$

On the average the electrons which flow to the plane have come a distance l. Those that flow at an angle θ to the z axis have come from a region that was at the temperature $(T+\Delta T)$ where

$$\Delta T=l\cos\theta\frac{\partial T}{\partial z}.$$

Hence the flow of energy from the right to the plane is

$$W_L=\int_{\epsilon_0}^{\infty}dE\int_0^{\pi/2}\left.\sin\theta\, d\theta\cos\theta\, 2N(0)v_0Ef(E)\right]_{T+\Delta T},$$

and the thermal conductivity is

$$\kappa_{es}=\frac{W_R-W_L}{\partial T/\partial Z}=\frac{2N(0)v_0}{\partial T/\partial z}\int_{\epsilon_0}^{\infty}EdE\int_0^1\times d\mu\,\mu\,\Delta T\left[\frac{\partial f}{\partial T}\right]_{E\text{ const}}$$

$$=-\frac{2N(0)v_0l}{3T}\int_{\epsilon_0}^{\infty}dE\,E^2\frac{\partial f}{\partial E}.$$

The thermal conductivity of the normal metal is given by the same expression but with $\epsilon_0=0$. Therefore

$$\frac{\kappa_{es}}{\kappa_{en}}=\int_{\epsilon_0}^{\infty}E^2\frac{\partial f}{\partial E}dE\Big/\int_0^{\infty}E^2\frac{\partial f}{\partial E}dE =\frac{2F_1(-y)+2y\ln(1+e^{-y})+y^2/(1+e^y)}{2F_1(0)}, \tag{3.6}$$

where

$$y=\epsilon_0/kT,$$

and

$$F_n(-y)=\int_0^{\infty}\frac{z^ndz}{1+e^{z+y}}.$$

The function $F_n(-y)$ has been tabulated by Rhodes.[17]

4. THERMAL SCATTERING

The interaction between the electrons and the phonons gives rise to the term in the Hamiltonian[17,18]

$$H_I=\sum_{\mathbf{k},\mathbf{q},\sigma}(V_\mathbf{q}C_{\mathbf{k}+\mathbf{q},\sigma}{}^*C_{\mathbf{k},\sigma}b_\mathbf{q}{}^*+V_\mathbf{q}{}^*C_{\mathbf{k}'\sigma}{}^*C_{\mathbf{k}+\mathbf{q},\sigma}b_\mathbf{q}), \tag{4.1}$$

where $b_\mathbf{q}{}^*$ is the operator which creates a phonon of wave-vector $\mathbf{q}$ and energy $h\nu_\mathbf{q}$, and $V_\mathbf{q}$ is a c number which is proportional to $q^{\frac{1}{2}}$. Part of this interaction has been used already in forming the superconducting ground state. However, the parts of H_I that can lead to real transitions remain. (See Fröhlich[18] and Bardeen and Pines[19] for a discussion of this point.) We shall suppose that we are dealing only with this remainder

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of H_I. In terms of the operators γ_0, γ_1, we have

$$H_I=\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} V_\mathbf{q}b_\mathbf{q}^*\{[(1-h)^{\frac{1}{2}}(1-h')^{\frac{1}{2}}-(hh')^{\frac{1}{2}}]\times(\gamma_{\mathbf{k}'0}^*\gamma_{\mathbf{k}0}+\gamma_{\mathbf{k}1}^*\gamma_{\mathbf{k}'1})+[h^{\frac{1}{2}}(1-h')^{\frac{1}{2}}+h'^{\frac{1}{2}}(1-h)^{\frac{1}{2}}]\times(\gamma_{\mathbf{k}'0}^*\gamma_{\mathbf{k}1}^*+\gamma_{\mathbf{k}'1}\gamma_{\mathbf{k}0})\}+\text{comp. conj.} \quad (4.2)$$

We can now obtain a Boltzmann equation in the usual way by equating the total rate of change of the distribution function to zero.

The rate of change of the distribution functions due to collisions is calculated in the following way. The probability that an excitation is scattered from $(\mathbf{k},0)$ to $(\mathbf{k}',0)$ with the absorption of a phonon of momentum $\mathbf{q}$ is

$$Q_{0a}(\mathbf{k},\mathbf{k}',\mathbf{q})=\frac{2\pi}{\hbar}|V_\mathbf{q}|^2\times\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)N_\mathbf{q}\times\delta(E'-E-h\nu_\mathbf{q})\delta(\mathbf{k}'-\mathbf{k}-\mathbf{q})f_{\mathbf{k}0}(1-f_{\mathbf{k}'0})=P_{0a}(\mathbf{k},\mathbf{k}',\mathbf{q})f_{\mathbf{k}0}(1-f_{\mathbf{k}'0}),$$

where $N_\mathbf{q}$ is the number of phonons of momentum $\mathbf{q}$ present. Similarly the probability that an excitation is scattered from $(\mathbf{k},0)$ to $(\mathbf{k}',0)$ with the emission of a phonon of momentum $\mathbf{q}$ is

$$Q_{0e}(\mathbf{k},\mathbf{k}',\mathbf{q})=\frac{2\pi}{\hbar}|V_\mathbf{q}|^2\times\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)(N_\mathbf{q}+1)\times\delta(E'-E+h\nu_\mathbf{q})\delta(\mathbf{k}'+\mathbf{q}-\mathbf{k})f_{\mathbf{k}0}(1-f_{\mathbf{k}'0})=P_{0e}(\mathbf{k},\mathbf{k}',q)f_{\mathbf{k}0}(1-f_{\mathbf{k}'0}).$$

Therefore the total probability that the excitation is scattered from $(\mathbf{k},0)$ to $(\mathbf{k}',0)$ is

$$Q_0(\mathbf{k},\mathbf{k}')=\left\{\frac{2\pi}{\hbar}|V_\mathbf{q}|^2\times\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)[\delta(E'-E-h\nu_\mathbf{q})N_\mathbf{q}+\delta(E'-E+h\nu_{-\mathbf{q}})(N_{-\mathbf{q}}+1)]\right\}_{\mathbf{q}=\mathbf{k}'-\mathbf{k}}f_{\mathbf{k}0}(1-f_{\mathbf{k}'0})=P_0(\mathbf{k},\mathbf{k}')f_{\mathbf{k}0}(1-f_{\mathbf{k}'0}).$$

The probabilities for the scattering of an excitation of type "1" are given by similar formulas. There is also the possibility that two excitations are created or destroyed, the analog of the creation or destruction of electron-hole pairs in a normal metal. For instance, the probability that the excitation $(\mathbf{k},0)$ and $(\mathbf{k}',1)$ are created with the absorption of a phonon of momentum $\mathbf{q}$ is

$$Q_{ca}(\mathbf{k},\mathbf{k}',\mathbf{q})=\frac{2\pi}{\hbar}|V_\mathbf{q}|^2\times\frac{1}{2}\left(1-\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)\delta(\mathbf{k}-\mathbf{k}'-\mathbf{q})\times\delta(E'+E-h\nu_\mathbf{q})N_\mathbf{q}(1-f_{\mathbf{k}0})(1-f_{\mathbf{k}'1})=P_{ca}(\mathbf{k},\mathbf{k}',\mathbf{q})(1-f_0)(1-f_1').$$

The total probability that the excitations $(\mathbf{k},0)$ and $(\mathbf{k}',1)$ are created is

$$Q_c(\mathbf{k},\mathbf{k}')=\sum_\mathbf{q}[Q_{ca}(\mathbf{k},\mathbf{k}',\mathbf{q})+Q_{ce}(\mathbf{k},\mathbf{k}',\mathbf{q})]=\left\{\frac{2\pi}{\hbar}|V_\mathbf{q}|^2\times\frac{1}{2}\left(1-\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)\times[\delta(E'+E-h\nu_{-\mathbf{q}})N_{-\mathbf{q}}+\delta(E'+E+h\nu_\mathbf{q})\times(N_\mathbf{q}+1)]\right\}_{\mathbf{q}=\mathbf{k}'-\mathbf{k}}(1-f_0)(1-f_1')=P_c(\mathbf{k},\mathbf{k}')(1-f_0)(1-f_1').$$

Similarly, the total probability that the excitations $(\mathbf{k},0)$ and $(\mathbf{k}',1)$ are destroyed is

$$Q_d(\mathbf{k},\mathbf{k}')=\left\{\frac{2\pi}{\hbar}|V_\mathbf{q}|^2\times\frac{1}{2}\left(1-\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)[\delta(E'+E-h\nu_{-\mathbf{q}})\times(N_{-\mathbf{q}}+1)+\delta(E'+E+h\nu_\mathbf{q})N_\mathbf{q}]\right\}_{\mathbf{q}=\mathbf{k}'-\mathbf{k}}f_{\mathbf{k}0}f_{\mathbf{k}'1}=P_d(\mathbf{k},\mathbf{k}')f_0f_1'.$$

Summing over all possible processes, we obtain for the rates of change of the distribution functions f_0, f_1, due to collisions

$$\left.\frac{\partial f_{\mathbf{k}0}}{\partial t}\right]_{\text{coll}}=\sum_{\mathbf{k}'}[-Q_0(\mathbf{k},\mathbf{k}')+Q_0(\mathbf{k}',\mathbf{k})+Q_c(\mathbf{k},\mathbf{k}')-Q_d(\mathbf{k},\mathbf{k}')], \quad (4.3)$$

$$\left.\frac{\partial f_{\mathbf{k}1}}{\partial t}\right]_{\text{coll}}=\sum_{\mathbf{k}'}[-Q_1(\mathbf{k},\mathbf{k}')+Q_1(\mathbf{k}',\mathbf{k})+Q_c(\mathbf{k}',\mathbf{k})-Q_d(\mathbf{k}',\mathbf{k})]. \quad (4.4)$$

In the usual way, we write for the distribution functions

$$f_{\mathbf{k}0}=f_k^0-\chi_{\mathbf{k}0}\frac{\partial f_k^0}{\partial E_k}, \quad (4.5)$$

$$f_{\mathbf{k}1}=f_k^0-\chi_{\mathbf{k}1}\frac{\partial f_k^0}{\partial E_k}, \quad (4.6)$$

where f_k^0 is the equilibrium value of the distribution functions and the second terms describe the small departures from equilibrium. We shall assume that we can neglect the departure from equilibrium of the phonons. One can verify easily that

$$P_0(\mathbf{k}',\mathbf{k})f_{k'}^0(1-f_k^0)=P_0(\mathbf{k},\mathbf{k}')f_k^0(1-f_{k'}^0), \quad (4.7)$$

$$P_c(\mathbf{k},\mathbf{k}')(1-f_k^0)(1-f_{k'}^0)=P_d(\mathbf{k},\mathbf{k}')f_k^0f_{k'}^0, \quad (4.8)$$

when N_q is the equilibrium number of phonons of momentum $\mathbf{q}$. It follows that

$$\left.\frac{\partial f_{\mathbf{k}0}}{\partial t}\right]_{\text{coll}} = -\frac{1}{kT}\int P_0(\mathbf{k},\mathbf{k}')f_k{}^0(1-f_{k'}{}^0)\times(\chi_{k0}-\chi_{k'0})d^3k' -\frac{1}{kT}\int P_c(\mathbf{k},\mathbf{k}')(1-f_k{}^0)(1-f_{k'}{}^0)\times(\chi_{k0}+\chi_{k'1})d^3k'. \quad (4.9)$$

Now the function $f_{\mathbf{k}1}$ gives the distribution of particles of momentum $-\mathbf{k}$. Therefore, in the presence of a temperature gradient, $(f_{\mathbf{k}1}-f_k{}^0)$ and $(f_{\mathbf{k}0}-f_k{}^0)$ are equal in magnitude and opposite in sign, i.e.,

$$\chi_{\mathbf{k}1}=-\chi_{\mathbf{k}0}=-\chi_{\mathbf{k}}(\text{say}), \quad (4.10)$$

and

$$\left.\frac{\partial f_{\mathbf{k}0}}{\partial t}\right]_{\text{coll}} = -\int W(\mathbf{k},\mathbf{k}')(\chi_{\mathbf{k}}-\chi_{\mathbf{k}'})d^3k' = -\Lambda\chi_{\mathbf{k}}, \quad (4.11)$$

where

$$W(\mathbf{k},\mathbf{k}') = (kT)^{-1}\{P_0(\mathbf{k},\mathbf{k}')f_k{}^0(1-f_{k'}{}^0) +P_c(\mathbf{k},\mathbf{k}')(1-f_k{}^0)(1-f_{k'}{}^0)\}, \quad (4.12)$$

and Λ is the integral operator defined by the identity. As there will be no chance of confusion, we shall in the future drop the superscript zero from $f_k{}^0$. It is easy to see that

$$W(\mathbf{k}',\mathbf{k}) = W(\mathbf{k},\mathbf{k}').$$

The rate of change of $f_{\mathbf{k}0}$ due to the temperature gradient is given by

$$v_z\left[\frac{\partial f_k}{\partial T}\right]_{E\,\text{const}}\frac{dT}{dz},$$

where the z axis is taken along the direction ∇T. Using the result of Sec. 2 for the group velocity, one obtains the Boltzmann equation

$$\frac{\hbar k_z}{m}\frac{\epsilon}{E}\frac{E}{T}\frac{df}{dE}\frac{dT}{dz}=\Lambda\chi_{\mathbf{k}}. \quad (4.13)$$

One obtains the same equation for $\chi_{\mathbf{k}}$ from a consideration of the rate of change of $f_{\mathbf{k}1}$. This confirms Eq. (4.10).

Equation (4.13) cannot be solved exactly, so we shall employ a variational principle to put a bound on κ_s. We have seen that $W(\mathbf{k}',\mathbf{k})$ is positive definite and symmetric in $\mathbf{k}$ and $\mathbf{k}'$. Therefore, of all the functions $\chi_{\mathbf{k}}$ for which $\int\chi_{\mathbf{k}}\Lambda\chi_{\mathbf{k}}d^3k$ exists, that which makes the functional

$$\int\chi_k\Lambda\chi_{\mathbf{k}}d^3k \Big/ \left\{\int\chi_{\mathbf{k}}\frac{\hbar k_z}{m}\epsilon_{\mathbf{k}}\frac{df_{\mathbf{k}}{}^0}{dE}d^3k\right\}^2$$

a minimum satisfies Eq. (4.13).[20] As pointed out by Ziman,[21] this principal has a simple physical interpretation. The thermal current is

$$W=\int Ev_z(f_{\mathbf{k}0}-f_{\mathbf{k}1})d^3k=-2\int\chi_k\frac{\hbar k_z}{m}\epsilon_k\frac{df_k{}^0}{dE}d^3k.$$

Therefore if $\chi_{\mathbf{k}}$ is the solution of (4.13), one can write

$$\frac{1}{\kappa}=-\frac{\partial T/\partial z}{W} =T\int\chi_{\mathbf{k}}\Lambda\chi_{\mathbf{k}}d^3k \Big/ 2\left\{\int\chi_{\mathbf{k}}\frac{\hbar k_z}{m}\epsilon_k\frac{df_k{}^0}{dE}d^3k\right\}^2. \quad (4.14)$$

Thus we have to determine the function $\chi_{\mathbf{k}}$ which makes the thermal resistivity (written in the above form) a minimum. By using this variational principle we shall obtain at least a lower bound to the thermal conductivity.

Our next task is to guess a functional form for $\chi_{\mathbf{k}}$ which should give a fair approximation to the thermal conductivity κ. A guide to the choice of χ is the fact that as $T\rightarrow T_c$, χ should tend to the corresponding function of the normal metal. A good approximation for χ in the normal metal is $b\epsilon\cos\theta$,[22] where θ is the angle between $\mathbf{k}$ and the z axis, and b is a constant. This χ is antisymmetric about the Fermi surface and has the property that in any direction in $\mathbf{k}$ space, the increase in the number of electrons above the Fermi surface is equal to the increase in the number of holes at the same distance below the Fermi surface. This property is physically reasonable and we would expect it to hold true for $\chi_{\mathbf{k}}$ in the superconductor. This suggests that we try the following possibilities for $\chi_{\mathbf{k}}$:

$$\text{(a)}\quad \chi_{\mathbf{k}}=b\epsilon_k\cos\theta,\quad \text{(b)}\quad \chi_{\mathbf{k}}=b\epsilon_k\left|\frac{\epsilon_k}{E_k}\right|\cos\theta,\quad \text{(c)}\quad \chi_{\mathbf{k}}=b\epsilon_k\left|\frac{E_k}{\epsilon_k}\right|\cos\theta. \quad (4.15)$$

All of these tend to $b\epsilon_k\cos\theta$ as $T\rightarrow T_c$. We shall first restrict our calculations to the form (a). κ is independent of b, so we shall take b to be unity.

The numerator of (4.14) is given by (4.11) and (4.12). That part which arises from $P_0(\mathbf{k},\mathbf{k}')$ we denote by η_0. It is given by

$$\eta_0=\frac{2\pi}{\hbar kT^2}\int d^3k\int d^3k'|V_{\mathbf{q}}|^2\times\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0{}^2}{EE'}\right) \times f(E)[1-f(E')][\delta(E'-E-h\nu_q)N_q +\delta(E'-E+h\nu_q)(N_q+1)]\epsilon\cos\theta(\epsilon\cos\theta-\epsilon'\cos\theta').$$

[20] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1954), p. 301, second edition.

[21] J. M. Ziman, Can. J. Phys. 34, 1256 (1956).

[22] H. Jones, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), p. 281, Chap. VI, Vol. 19.

We set

$$d^3k' = \sin\psi\, d\psi d\varphi'\, k'^2 dk',$$

where ψ is the angle between $\mathbf{k}$ and $\mathbf{k}'$ and φ' is the azimuthal angle from the plane given by $\mathbf{k}$ and the z direction. Then

$$\cos\theta' = \cos\psi\, \cos\theta + \sin\psi\, \sin\theta\, \cos\varphi',$$

$$\cos\psi = (k'^2 + k^2 - q^2)/2kk'.$$

When we integrate over φ', the part containing $\cos\varphi'$ vanishes. The integral over ψ can be changed into an integral over $q = |\mathbf{k}' - \mathbf{k}|$. This leads to

$$\eta_0 = \frac{1}{kT^2} \int d^3k \int_0^\infty k'^2 dk' \int_{|k'-k|}^{k'+k} \frac{2\pi q}{kk'} dq |V_q|^2 \times \frac{1}{2}\left(1 + \frac{\epsilon\epsilon' - \epsilon_0^2}{EE'}\right) f(E)[1 - f(E')] \times [\delta(E' - E - h\nu_q)N_q + \delta(E' - E + h\nu_q)(N_q + 1)] \times \epsilon \cos^2\theta \left[\epsilon - \epsilon'\left(\frac{k'^2 + k^2 - q^2}{2kk'}\right)\right].$$

Now the important values of q are such that $h\nu_q \sim kT$. Therefore, when the temperature is near T_c,

$$q/k_0 \sim 10^{-2},$$

and

$$\frac{|\mathbf{k}' - \mathbf{k}|}{q} \sim \frac{|\epsilon' - \epsilon|}{\hbar^2 k_0 q/m} = \frac{h\nu}{E_F} \frac{k_0}{q} \sim 10^{-2}.$$

Hence one can take the lower limit of the integral over q to be zero and the upper limit to be infinity ($\theta_D \gg T_c$). Moreover,

$$\epsilon - \epsilon'\left(\frac{k'^2 + k^2 - q^2}{2kk'}\right) = (\epsilon - \epsilon') - \epsilon'[O(\epsilon_0/E_F) + O(q^2/k_0^2)],$$

so that except at the very lowest temperatures which are not of interest here, the second term can be neglected in comparison with the first. Using the fact that $|V_q|^2$ is proportional to $h\nu_q$ and replacing the variables of integration k, k', q by ϵ, ϵ', $h\nu$, respectively, one obtains

$$\eta_0 = \frac{C}{2kT^2} \int_0^\infty (h\nu)^2 d(h\nu) \iint_{-\infty}^{+\infty} d\epsilon d\epsilon' \frac{1}{2}\left(1 + \frac{\epsilon\epsilon' - \epsilon_0^2}{EE'}\right) \times f(E)[1 - f(E')][\delta(E' - E - h\nu)N_q + \delta(E' - E + h\nu)(N_q + 1)]\epsilon(\epsilon - \epsilon'),$$

where C is a constant. Using the fact that some terms of the integrand are even in ϵ, ϵ' and some odd in ϵ, ϵ', one obtains

$$\eta_0 = \frac{C}{kT^2} \int_0^\infty (h\nu)^2 d(h\nu) \int_0^\infty d\epsilon \int_0^\infty d\epsilon' \times \left[\epsilon^2\left(1 - \frac{\epsilon_0^2}{EE'}\right) - \frac{\epsilon^2\epsilon'^2}{EE'}\right] f(E)[1 - f(E')] \times [\delta(E' - E - h\nu)N_q + \delta(E' - E + h\nu)(N_q + 1)].$$

Similarly, the part of the numerator of κ^{-1} which comes from $P_c(\mathbf{k}, \mathbf{k}')$ is

$$\eta_c = \frac{C}{kT^2} \int_0^\infty (h\nu)^2 d(h\nu) \int_0^\infty d\epsilon \int_0^\infty d\epsilon' \times \left[\epsilon^2\left(1 + \frac{\epsilon_0^2}{EE'}\right) + \frac{\epsilon^2\epsilon'^2}{EE'}\right](1 - f)(1 - f') \times [\delta(E' + E - h\nu)N_q + \delta(E' + E + h\nu)(N_q + 1)].$$

The total result for the numerator can be written

$$\eta = \frac{C}{kT^2} \int_0^\infty (h\nu)^2 d(h\nu) \int_{-\infty}^\infty d\epsilon \int_0^\infty d\epsilon' \times \left[\epsilon^2\left(1 - \frac{\epsilon_0^2}{EE'}\right) - \frac{\epsilon^2\epsilon'^2}{EE'}\right] f(1 - f') \times [\delta(E' - E - h\nu)N_q + \delta(E' - E + h\nu)(N_q + 1)],$$

where the sign of E is conventionally taken to be the same as that of ϵ. Hence

$$\eta = \frac{C'}{kT^2} \int_{-\infty}^\infty \frac{x^2 dx}{|e^x - 1|} \int_{-\infty}^\infty d\epsilon \int_0^\infty d\epsilon' \times \left[\epsilon^2\left(1 - \frac{\epsilon_0^2}{EE'}\right) - \frac{(\epsilon\epsilon')^2}{EE'}\right] f(E)(1 - f(E')) \times \delta(E' - E - x),$$

where the energies are expressed in units of kT. The symbol x is used for $h\nu/kT$ but the other symbols have been retained despite their altered meanings. If we perform the integration over x, we obtain

$$\eta = \frac{C'}{kT^2} \int_{-\infty}^\infty d\epsilon \int_0^\infty d\epsilon' \frac{(E' - E)^2}{|e^{E'-E} - 1|} \times \left[\epsilon^2\left(1 - \frac{\epsilon_0^2}{EE'}\right) - \frac{\epsilon^2\epsilon'^2}{EE'}\right] f(1 - f')$$

$$= \frac{C'}{2kT^2} \int_{-\infty}^\infty d\epsilon \int_{-\infty}^\infty d\epsilon' \frac{(E' - E)^2}{|e^{E'-E} - 1|} \times \left[\epsilon^2\left(1 - \frac{\epsilon_0^2}{EE'}\right) - \frac{\epsilon^2\epsilon'^2}{EE'}\right] f(1 - f'), \quad (4.16)$$

where E' has the same sign as ϵ'. In the limit $T\rightarrow T_c$, $\epsilon_0\rightarrow 0$ and η tends to the value it has in the normal state with the same constant C'. Had we used the functions (b) or (c) for x, we should have found the same expression for η except that the term in square brackets would be replaced by

$$\left[\frac{\epsilon^4}{E^2}\left(1-\frac{\epsilon_0^2}{EE'}\right)-\frac{(\epsilon\epsilon')^3}{(EE')^2}\right],$$

or by

$$\left[E^2\left(1-\frac{\epsilon_0^2}{EE'}\right)-\epsilon\epsilon'\right],$$

respectively.

The heat flow in the three cases is given by

$$\text{(a)}\quad W=C''\int_0^\infty \epsilon^2 f(E)[1-f(E)]d\epsilon,$$

$$\text{(b)}\quad W=C''\int_0^\infty \frac{\epsilon^3}{E}f(E)[1-f(E)]d\epsilon,$$

$$\text{(c)}\quad W=C''\int_0^\infty \epsilon E f(E)[1-f(E)]d\epsilon.$$

C'' is independent of ϵ and ϵ_0, but it does depend on temperature. Further discussion of this thermal conductivity is left to Sec. 6.

5. THERMAL CONDUCTIVITY OF THE LATTICE

We consider here only the thermal conductivity of the lattice when it is limited by electron scattering, this being the only new feature. The Boltzmann equation for this problem is[20]

$$u_0\frac{q_z}{q}\frac{\partial N_{\mathbf{q}}}{\partial T}\frac{\partial T}{\partial z}=\left[\frac{\partial N_{\mathbf{q}}}{\partial t}\right]_{\text{coll}},\tag{5.1}$$

where $N_{\mathbf{q}}$ is the number of phonons of wave vector $\mathbf{q}$ and u_0 is the velocity of sound in the metal. We have obtained already in Sec. 4 the probabilities for absorption and admission of phonons by the electrons. To find $(\partial N_{\mathbf{q}}/\partial t)]_{\text{coll}}$, all we have to do is to sum over the possible excited states. Thus the probability per second that a phonon of momentum $\mathbf{q}$ is absorbed is

$$\sum_{\mathbf{k},\mathbf{k}'}[Q_{0a}(\mathbf{k},\mathbf{k}',\mathbf{q})+Q_{1a}(\mathbf{k},\mathbf{k}',\mathbf{q})+Q_{ca}(\mathbf{k},\mathbf{k}',\mathbf{q})+Q_{da}(\mathbf{k},\mathbf{k}',\mathbf{q})]$$

and

$$\begin{aligned}\left.\frac{\partial N_q}{\partial t}\right]_{\text{coll}}&=\sum_{\mathbf{k},\mathbf{k}'}[Q_{0e}(\mathbf{k},\mathbf{k}',\mathbf{q})-Q_{0a}(\mathbf{k},\mathbf{k}',\mathbf{q})+Q_{1e}(\mathbf{k},\mathbf{k}',\mathbf{q})\\&\quad-Q_{1a}(\mathbf{k},\mathbf{k}',\mathbf{q})+Q_{ce}(\mathbf{k},\mathbf{k}',\mathbf{q})-Q_{da}(\mathbf{k},\mathbf{k}',\mathbf{q})\\&\quad+Q_{de}(\mathbf{k},\mathbf{k}',\mathbf{q})-Q_{ca}(\mathbf{k},\mathbf{k}',\mathbf{q})]\\&=\frac{2\pi}{\hbar}|V_q|^2\sum_{\mathbf{k},\mathbf{k}'}\delta(\mathbf{k}'-\mathbf{k}-\mathbf{q})\left\{\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)\right.\\&\quad\times[\delta(E'-E-h\nu)((N_{\mathbf{q}}+1)f'(1-f)\\&\quad-N_{\mathbf{q}}f(1-f'))+\delta(E-E'-h\nu)\\&\quad\times((N_{\mathbf{q}}+1)f(1-f')-N_{\mathbf{q}}f'(1-f))]\\&\quad+\frac{1}{2}\left(1-\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)[\delta(E+E'+h\nu)\\&\quad\times((N_{\mathbf{q}}+1)(1-f)(1-f')-N_{\mathbf{q}}ff')\\&\quad+\delta(E+E'-h\nu)((N_{\mathbf{q}}+1)ff'\\&\quad\left.-N_{\mathbf{q}}(1-f)(1-f'))]\right\}.\end{aligned}$$

Therefore if $\delta N_{\mathbf{q}}$ is the departure of $N_{\mathbf{q}}$ from its equilibrium value, N_q^0, we have

$$\begin{aligned}\left.\frac{\partial N_{\mathbf{q}}}{\partial t}\right]_{\text{coll}}&=\delta N_{\mathbf{q}}\frac{2\pi}{\hbar}|V_q|^2\sum_{\substack{\mathbf{k}\\(\mathbf{k}'=\mathbf{k}+\mathbf{q})}}\left\{\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)(f'-f)\right.\\&\quad\times[\delta(E'-E-h\nu)-\delta(E-E'-h\nu)]\\&\quad+\frac{1}{2}\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)(1-f-f')\\&\quad\left.\times[\delta(E+E'+h\nu)-\delta(E+E'-h\nu)]\right\}.\end{aligned}$$

We change the sum to an integral over ϵ and the polar angles, θ and φ. The integration over φ can be performed and the integration over θ changed to one over ϵ'. Then

$$\begin{aligned}\left.\frac{\partial N_{\mathbf{q}}}{\partial t}\right]_{\text{coll}}&=\delta N_{\mathbf{q}}\,C\int_{-\infty}^{\infty}d\epsilon\int d\epsilon'\left\{\left(1+\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)(f'-f)\right.\\&\quad\times[\delta(E+h\nu-E')-\delta(E'+h\nu-E)]\\&\quad+\left(1-\frac{\epsilon\epsilon'-\epsilon_0^2}{EE'}\right)(1-f-f')\\&\quad\left.\times[\delta(E+E'+h\nu)-\delta(E+E'-h\nu)]\right\},\end{aligned}$$

where C is a constant, independent of q. The limits of the integral over ϵ' are

$$\epsilon+\frac{\hbar^2k_0q}{m}+\frac{\hbar^2q^2}{2m} \quad\text{and}\quad \epsilon-\frac{\hbar^2k_0q}{m}+\frac{\hbar^2q^2}{2m}.$$

Since the important values of q are such that $\hbar u_0 q\sim kT$ while $\epsilon,\epsilon'\sim\epsilon_0(0)$, we have that

$$(\hbar^2kq/m)\gg\epsilon,\epsilon',(\hbar^2q^2/2m).$$

Therefore the limits of the integral over ϵ' can be taken as $\pm\infty$. The integrals can then be replaced by integrals from 0 to ∞ and the variables then changed from ϵ,ϵ' to E,E', respectively. The result is

$$\left.\frac{\partial N_{\mathbf{q}}}{\partial t}\right]_{\text{coll}}=\delta N_{\mathbf{q}}\times 4C\int_{\epsilon_0}^{\infty}dE\int_{\epsilon_0}^{\infty}dE'\frac{EE'}{\epsilon\epsilon'}\times\left\{\left(1-\frac{\epsilon_0^2}{EE'}\right)(f'-f)[\delta(E+h\nu-E')-\delta(E'+h\nu-E)]+\left(1+\frac{\epsilon_0^2}{EE'}\right)(1-f-f')\times[\delta(E+E'+h\nu)-\delta(E+E'-h\nu)]\right\}$$

$$=\delta N_{\mathbf{q}}\times 4C\int\int dEdE'\left|\frac{EE'}{\epsilon\epsilon'}\right|\left(1-\frac{\epsilon_0^2}{EE'}\right)\times(f'-f)\delta(E+h\nu-E').$$

In the last step, the integrals are to be taken over all those positive and negative values of E and E' for which $|E|>\epsilon_0$, $|E'|>\epsilon_0$. Therefore

$$\left.\frac{\partial N_{\mathbf{q}}}{\partial t}\right]_{\text{coll}}=\delta N_{\mathbf{q}}\times 4C\left\{\int_{\epsilon_0}^{\infty}dE+\int_{\epsilon_0-h\nu}^{-\epsilon_0}dE+\int_{-\infty}^{-h\nu-\epsilon_0}dE\right\}\left(1-\frac{\epsilon_0^2}{EE'}\right)\times\left.\left|\frac{EE'}{\epsilon\epsilon'}\right|(f'-f)\right]_{E'=E+h\nu}$$

$$=\delta N_{\mathbf{q}}\times 4C\left\{2\int_{\epsilon_0}^{\infty}dE+\int_{\epsilon_0-h\nu}^{-\epsilon_0}dE\right\}\times\left(1-\frac{\epsilon_0^2}{EE'}\right)\left|\frac{EE'}{\epsilon\epsilon'}\right|(f'-f).$$

The second integral is to be taken into account only if $h\nu>2\epsilon_0$.

Following the procedure for normal metals we look for a solution of the Boltzmann equation of the form

$$\delta N_{\mathbf{q}}=-q_z\frac{b(u)}{kT}\frac{\partial N_q^0}{\partial u},\quad u=h\nu/kT.$$

One obtains

$$b(u)=\frac{\hbar u_0^2}{4CkT}\frac{\partial T}{\partial z}\bigg/\int dE\left|\frac{EE'}{\epsilon\epsilon'}\right|\left(1-\frac{\epsilon_0^2}{EE'}\right)(f'-f).$$

The thermal current density is

$$W_g=\sum\nolimits_{\mathbf{q}}\hbar q_z u_0^2\delta N_{\mathbf{q}}=-\sum_{\mathbf{q}}q_z^2u_0^2\frac{b(u)}{kT}\frac{\partial N_q^0}{\partial u}.$$

Therefore the thermal conductivity is

$$\kappa_{gs}=-\frac{W_g}{\partial T/\partial z}=D(T/\Theta)^2\int_0^{\infty}\frac{u^3du}{(e^u-1)(1-e^{-u})g(u)}\tag{5.2}$$

where D is a constant independent of temperature and

$$g(u)=\frac{1-e^{-u}}{u}\int dE\left|\frac{EE'}{\epsilon\epsilon'}\right|\left(1-\frac{\epsilon_0^2}{EE'}\right)f(E)f(-E'),$$

and the energies are measured in units of kT. It is shown in Appendix B that a good approximation for $g(u)$ in the low-temperature region, $\epsilon_0>2$, is

$$g(u)=(1-e^{-u})\left(\frac{2\epsilon_0}{u+2\epsilon_0}\right)^{\frac{1}{2}}e^{-\epsilon_0+u/2}\times\left\{K_1(u/2)+\frac{(3u+4\epsilon_0)u}{8\epsilon_0(u+2\epsilon_0)}[K_1(u/2)-K_0(u/2)]\right\}\tag{5.3}$$

for $u<2\epsilon_0$ and infinitely large for $u>2\epsilon_0$. K_0 and K_1 are Bessel functions of imaginary argument in the notation of Watson.[23]

The lattice thermal conductivity in the normal state is obtained from Eq. (5.2) by letting ϵ_0 tend to zero. In this limit $g(u)$ is unity and

$$\kappa_{gn}=D(T/\Theta)^2\int_0^{\infty}\frac{u^3du}{(e^u-1)(1-e^{-u})}=7.2D(T/\Theta)^2.$$

6. RESULTS AND DISCUSSIONS

We shall discuss in turn the different contributions to the thermal conductivity and the effects of different scatterers.

[23] G. N. Watson, *Treatise on the Theory of Bessel Functions* (Cambridge University Press, London, 1952), p. 78, second edition.

(a) Electronic Contribution in Impure Specimens

A plot of the thoretical $(\kappa_{es}/\kappa_{en})$ from Eq. (3.6), *versus* (T/T_c), together with a plot of $(\kappa_{es}/\kappa_{en})$ obtained from the Heisenberg-Koppe theory[13] is shown in Fig. 1. It can be seen that the two curves lie close together. As it is already known[3] that for the most impure specimens there is fair agreement between the Heisenberg-Koppe theory and experiment, at least insofar as the experimental curves can be described by a universal function, we deduce that there is the same fair agreement between the present theory and experiment. The two theories diverge very close to T_c. According to the present theory the slope of the curve near T_c is $\frac{3}{2}(1-T/T_c)^{\frac{1}{2}}$ whereas according to the Heisenberg-Koppe theory it is $4(1-T/T_c)$. More accurate measurements near T_c may show up the difference.

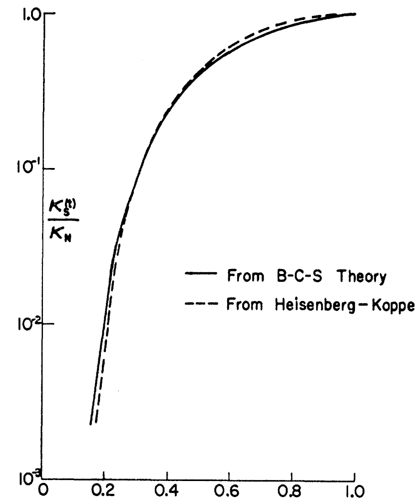

FIG. 1. The ratio of the electronic thermal conductivity in the superconductor, K_s, to that in the normal metal, K_n, when impurity scattering is predominant.

(b) Electronic Contribution in Pure Specimens

For the purest specimens of tin, lead, and mercury the experimentally determined κ_{es}/κ_{en} drops very sharply as the temperature is lowered below T_c. An indication of the size of this decrease is

$$d(\kappa_{es}/\kappa_{en})/d(T/T_c)\simeq 5,$$

at T_c. The very different shape of the plot of $(\kappa_{es}/\kappa_{en})$ *vs* (T/T_c) for these specimens from that for the impure specimens indicates that the dominant scattering mechanism is not impurity scattering. It is generally believed to be lattice scattering. In Appendix A we calculate the ratio $(\kappa_{es}/\kappa_{en})$ near T_c for the three cases of Sec. 4. The results are

$$(1)\quad \kappa_{es}/\kappa_{en}=1-0.1\epsilon_0^2,$$

$$(2)\quad \kappa_{es}/\kappa_{en}=1-0.3\epsilon_0^2,$$

$$(3)\quad \kappa_{es}/\kappa_{en}=1+0.05\epsilon_0^2.$$

Since

$$T_c d\epsilon_0^2/dT\simeq -10 \text{ at } T_c,$$

the gradient of the curve $(\kappa_{es}/\kappa_{en})$ *vs* (T/T_c) is for the three cases, (1) 1.0, (2) 3.0, and (3) -0.5. According to the variational principle the true κ_{es}/κ_{en} is greater than the greatest of our three values (assuming the approximation for κ_{en} to be accurate), so that the slope at T_c is less than (-0.5). There is therefore disagreement between theory and experiment. To see whether there is disagreement at T_c only, we have calculated $(\kappa_{es}/\kappa_{en})$ for $T=0.72T_c$ (i.e., $\epsilon_0=2$) and have found for case (1) that κ_{es}/κ_{en} is 0.75 and for case (3) that κ_{es}/κ_{en} is 0.78. The experimental value is approximately 0.3, showing that there is still disagreement at the lower temperature. The fact that the experimental value of $(\kappa_{es}/\kappa_{en})$ is smaller than the theoretical one suggests that an extra mechanism for scattering may be acting more strongly in the superconducting than in the normal state. One reason for this may be that in the superconductor the excitations near the Fermi surface have a smaller velocity than the corresponding electrons in the normal metal. Consequently, they are more likely to be scattered by larger obstacles. In this case one would have a mechanism that would be sensitive to the structure of the specimen. This possibility cannot yet be ruled out by experiment.

(c) Lattice Contribution Limited by Electronic Scattering

Unfortunately there are no experimental values of the thermal conductivity which can be unequivocally interpreted as lattice conductivity limited by electron scattering. At the lowest temperatures (less than 1°K) where it is certain that the electronic contribution is negligible, it appears that the lattice waves are scattered mainly by the boundaries of the crystal. At higher temperatures where it is certain that the lattice waves are scattered mainly by the electrons, the main contribution to the thermal conductivity comes from the electrons. In impure specimens and alloys the contribution of the lattice is not negligible at the higher temperatures, so some attempt has been made by Hulm,[3] Laredo,[5] and Sladek[7] to subtract out κ_e in order to obtain κ_g. Since κ_g is then obtained as the small difference of two large quantities this procedure is not reliable, particularly since the κ_{gn} obtained by Hulm does not have the T^2 dependence predicted by theory and the results of the experimenters differ widely. In view of this, the comparison we now make must be regarded as tentative. In Fig. 2 we have plotted the curves of Hulm and Laredo for κ_{gs}/κ_{gn} together with that obtained from Sec. 5. Laredo has suggested that

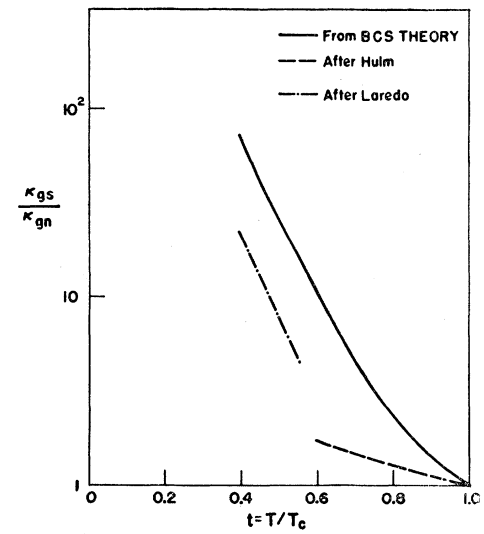

FIG. 2. The ratio of the lattice thermal conductivity in the superconductor, K_{gs}, to that in the normal metal, K_{gn}, when electronic scattering is predominant.

in the region of temperature, 0.4 T_c to 0.6 T_c, his ratio κ_{gs}/κ_{gn} may be proportional to T^{-5}. It can be seen that the theoretical curve does follow a T^{-5} law closely in this temperature range but that the theoretical values of the ratio are about three times the experimental ones.

Sladek[7] has made measurements on single-crystal and polycrystalline samples of indium-thallium alloys and has found results which cannot be fitted by a universal function $\kappa_{gs}/\kappa_{gn}(T/T_c)$. All the same, his results are greater than those of Hulm and Laredo and, particularly on the polycrystalline samples, are in fair agreement with the theory. In the temperature range from 0.4 T_c to 0.6 T_c Sladek finds that κ_{gs}/κ_{gn} varies with temperature according to $(T/T_c)^{-n}$, where $3<n<6$.

To draw a definite conclusion about the agreement of theory with experiment, we shall have to wait upon more clear-cut experimental results.

APPENDIX A

In this Appendix we calculate κ_{es}/κ_{en} near T_c, from the formulas of Sec. 4.

Case (a)

The integral η can be written

$$\eta=\frac{C'}{4kT^2}\int\int_{-\infty}^{\infty} d\epsilon\, d\epsilon'\, F(E,E',\epsilon_0), \qquad \text{(A1)}$$

where

$$F(E,E',\epsilon_0)=\frac{(E+E')^4}{|e^{-E-E'}-1|}\left(1-\frac{\epsilon_0^2}{EE'}\right)f(E)f(E').$$

Hence near T_c, where $\epsilon_0\rightarrow 0$, we have

$$\eta=\frac{C'}{4kT^2}\int\int_{-\infty}^{\infty} d\epsilon d\epsilon'\left[F(\epsilon,\epsilon',0)+2(E-\epsilon)\frac{\partial F}{\partial E}(\epsilon,\epsilon',0)+\epsilon_0^2\frac{\partial F}{\partial\epsilon_0^2}\right]$$

$$=\frac{C'}{4kT^2}\int\int_{-\infty}^{\infty} d\epsilon d\epsilon'\left[F(\epsilon,\epsilon',0)-2\left(\frac{\epsilon}{E}-1\right)\times[F(\epsilon,\epsilon',0)-F(0,\epsilon',0)]+\epsilon_0^2\frac{\partial F}{\partial\epsilon_0^2}\right],$$

where an integration by parts has been performed to obtain the second equation. Therefore

$$\eta=\frac{C'}{4kT^2}P\int\int_{-\infty}^{\infty} d\epsilon d\epsilon'\left[F(\epsilon,\epsilon',0)+\frac{\epsilon_0^2}{\epsilon^2}[F(\epsilon,\epsilon',0)-F(0,\epsilon',0)]+\epsilon_0^2\frac{\partial F}{\partial\epsilon_0^2}\right],$$

where one has to take the principal part of the integral that has a singularity at $\epsilon=0$. The first term of η is just the value one has for the normal metal. Now

$$\int_{-\infty}^{\infty} d\epsilon'\, F(\epsilon,\epsilon',0)$$

$$=f(\epsilon)\int_{-\infty}^{\infty} dx\frac{x^4}{|e^{-x}-1|(1+e^{x-\epsilon})}$$

$$=f(\epsilon)f(-\epsilon)\int_0^{\infty} dx\, x^4\left[\frac{2}{e^x-1}+\frac{1}{(1+e^{x-\epsilon})}+\frac{1}{(1+e^{x+\epsilon})}\right]$$

$$=f(\epsilon)f(-\epsilon)\int_0^{\infty} dx\,\frac{x^5}{5}\left[\frac{2e^x}{(e^x-1)^2}+\frac{e^{x-\epsilon}}{(1+e^{x-\epsilon})^2}+\frac{e^{x+\epsilon}}{(1+e^{x+\epsilon})^2}\right]$$

$$=\tfrac{1}{5}f(\epsilon)f(-\epsilon)\left\{2\mathcal{J}_5+2\int_0^{\infty}\frac{x^5+10x^3\epsilon^2+5x\epsilon^4}{(1+e^x)(1+e^{-x})}dx+2\int_0^{|\epsilon|}\frac{(|\epsilon|-x)^5dx}{(1+e^x)(1+e^{-x})}\right.$$

$$=\tfrac{1}{5}f(\epsilon)f(-\epsilon)\left\{2\mathcal{J}_5+2c_5+20\epsilon^2c_3+10\epsilon^4c_1+2\int_0^{|\epsilon|}\frac{(|\epsilon|-x)^5dx}{(1+e^x)(1+e^{-x})}\right\},$$

where

$$\mathcal{J}_n=\int_0^\infty \frac{x^n dx}{(e^x-1)(1-e^{-x})}$$

$$c_n=\int_0^\infty \frac{x^n dx}{(e^x+1)(1+e^{-x})}=\left(1-\frac{1}{2^{n-1}}\right)\mathcal{J}_n.$$

Therefore

$$\int\int_{-\infty}^{\infty} d\epsilon d\epsilon'[F(\epsilon,\epsilon',0)-F(0,\epsilon',0)]\epsilon^{-2}$$

$$=\tfrac{2}{5}(\mathcal{J}_5+c_5)\int_{-\infty}^{\infty}\frac{d\epsilon}{e^2}[f(\epsilon)f(-\epsilon)-\tfrac{1}{4}] +8c_0c_3+4c_2c_1+2R$$

$$=-\frac{8}{5\pi^2}(\mathcal{J}_5+c_5)\sum_{n=0}^{\infty}\frac{1}{(2n+1)^3}+8c_0c_3+4c_1c_2+2R,$$

where

$$R=\tfrac{2}{5}\int_0^\infty\frac{d\epsilon}{\epsilon^2}f(\epsilon)f(-\epsilon)\int_0^\epsilon(\epsilon-x)^5 f(x)f(-x)dx.$$

Similarly

$$\int\int_{-\infty}^{\infty} d\epsilon d\epsilon'\frac{\partial F}{\partial\epsilon_0^2}(\epsilon,\epsilon',\epsilon_0)\bigg|_{\epsilon_0=0}$$

$$=-P\int\int\frac{d\epsilon d\epsilon'}{\epsilon\epsilon'}\frac{(\epsilon+\epsilon')^4}{|e^{-\epsilon-\epsilon'}-1|}f(\epsilon)f(\epsilon')$$

$$=-2\int_{-\infty}^{\infty}\frac{d\epsilon\, f(\epsilon)\, f(-\epsilon)}{\epsilon}\int_0^\infty dx\, x^3\left[\frac{1}{1+e^{x-\epsilon}}-\frac{1}{1+e^{x+\epsilon}}\right]$$

$$=-2\int_{-\infty}^{\infty}\frac{d\epsilon\, f(\epsilon)\, f(-\epsilon)}{\epsilon}\int_0^\infty\frac{dx\, x^4}{4}\times\left[\frac{e^{x-\epsilon}}{(1+e^{x-\epsilon})^2}-\frac{e^{x+\epsilon}}{(1+e^{x+\epsilon})^2}\right]$$

$$=-\int_{-\infty}^{\infty}\frac{d\epsilon}{\epsilon}f(\epsilon)\, f(-\epsilon)\times\left\{4\epsilon c_3+4\epsilon^3c_1+\int_0^\epsilon(\epsilon-x)^4 f(x)\, f(-x)dx\right\}$$

$$=-8(c_0c_3+c_2c_1)-2S,$$

where

$$S=\int_0^\infty\frac{d\epsilon}{\epsilon}f(\epsilon)\, f(-\epsilon)\int_0^\epsilon(\epsilon-x)^4 f(x)\, f(-x)dx.$$

The thermal current is

$$W\propto\int_{-\infty}^{\infty}\epsilon^2\, d\epsilon\, f(E)\, f(-E)$$

$$=\int_{-\infty}^{\infty}\epsilon^2\, d\epsilon\, f(\epsilon)\, f(-\epsilon)+\int_{-\infty}^{\infty}\epsilon^2\, d\epsilon(E-\epsilon)\frac{\partial}{\partial\epsilon}[f(\epsilon)\, f(-\epsilon)]$$

$$=2c_2-\tfrac{1}{2}\epsilon_0^2\int_{-\infty}^{\infty}d\epsilon\, f(\epsilon)\, f(-\epsilon)$$

$$=2c_2-\tfrac{1}{2}\epsilon_0^2.$$

Hence

$$\frac{\kappa_{es}}{\kappa_{en}}=\frac{\mathcal{J}_5(1-\epsilon_0^2/2c_2)}{\mathcal{J}_5-\epsilon_0^2[(14/15\pi^2)(\mathcal{J}_5+c_5)(c_2/6)+2c_2c_1-R+S]}.$$

The integrals R and S have been evaluated numerically and lead to

$$\kappa_{es}/\kappa_{en}=1-0.13\epsilon_0^2.$$

Case (b)

η can still be written in the form (A1) but in this case

$$F(E,E',\epsilon_0)=\frac{(E+E')^2 f(E)\, f(E')}{|e^{-E-E'}-1|}\left\{(E^2+E'^2)\left(1+\frac{\epsilon_0^2}{EE'}\right)\times\left(1+\frac{\epsilon_0^4}{E^2E'^2}\right)-4\epsilon_0^2+2\left[1-\epsilon_0^2\frac{(E^2+E'^2)}{E^2E'^2}+\frac{\epsilon_0^4}{E^2E'^2}\right]\times(E^2-\epsilon_0^2)^{\frac{1}{2}}(E'^2-\epsilon_0^2)^{\frac{1}{2}}\right\}.$$

The only term of N different from that in case (a) is the one involving $\partial F/\partial\epsilon_0^2$. Now

$$\int\int_{-\infty}^{\infty} d\epsilon\, d\epsilon'\frac{\partial F}{\partial\epsilon_0^2}(\epsilon,\epsilon',\epsilon_0)\bigg|_{\epsilon_0=0}=-2\int\int\frac{(\epsilon+\epsilon')^4 ff'\, d\epsilon d\epsilon'}{\epsilon\epsilon'|e^{-\epsilon-\epsilon'}-1|}$$

$$=-16(c_0c_3+c_2c_1)-4S.$$

The thermal current is

$$W\propto 2\int_0^\infty d\epsilon\frac{\epsilon^3}{E}f(E)\, f(-E)$$

$$=2\int_0^\infty d\epsilon\,\epsilon^2 f(\epsilon)\, f(-\epsilon)+\int_0^\infty d\epsilon\,\epsilon^2\epsilon_0^2\frac{\partial}{\partial\epsilon}\left[\frac{f(\epsilon)\, f(-\epsilon)}{\epsilon}\right]$$

$$=2c_2-\epsilon_0^2.$$

Therefore

$$\kappa_{es}/\kappa_{en}=1-0.29\,\epsilon_0^2.$$

Case (c)

Again η can be written in the form (A1) but in this case

$$F(E,E',\epsilon_0)=\frac{(E+E')^2 f(E)\,f(E')}{e^{-E-E'}-1}\left[(E^2+E'^2)\left(1+\frac{\epsilon_0^2}{EE'}\right)+2(E^2-\epsilon_0^2)^{\frac{1}{2}}(E'^2-\epsilon_0^2)^{\frac{1}{2}}\right].$$

The only term different from case (*a*) is that involving $\partial F/\partial\epsilon_0^2$, which in this case is zero.

The thermal current is

$$W\propto 2\int_0^\infty d\epsilon\,\epsilon E f(E)\,f(-E)=2c_2+O(\epsilon_0^3).$$

Therefore

$$\kappa_{es}/\kappa_{en}=1+0.05\,\epsilon_0^2.$$

APPENDIX B

We have to evaluate

$$g(u)=\frac{1-e^{-u}}{u}(2J_1+J_2),$$

where

$$J_1=\int_{\epsilon_0}^\infty dE\left(\frac{\epsilon^2+Eu}{\epsilon\epsilon'}\right)f(E)\,f(-E'),$$

$$J_2=\int_{-u+\epsilon_0}^{-\epsilon_0} dE\left|\frac{EE'}{\epsilon\epsilon'}\right|\left(1-\frac{\epsilon_0^2}{EE'}\right)f(E)\,f(-E'),$$

$$E'=E+u.$$

At low temperatures

$$\int_{\epsilon_0}^\infty dE\frac{\epsilon}{\epsilon'}f(E)\,f(-E')\simeq\int_{\epsilon_0}^\infty e^{-E}\left(\frac{E^2-\epsilon_0^2}{E'^2-\epsilon_0^2}\right)^{\frac{1}{2}}dE.$$

If we put $y=(E-\epsilon_0)$ this integral becomes approximately

$$e^{-\epsilon_0}\int_0^\infty dy\,e^{-y}\left(\frac{y}{y+u}\right)^{\frac{1}{2}}\left(\frac{2\epsilon_0}{u+2\epsilon_0}\right)^{\frac{1}{2}}\left[1+\frac{y}{4\epsilon_0}-\frac{y}{2(u+2\epsilon_0)}\right].$$

Similarly

$$\int_0^\infty\frac{Eu}{\epsilon\epsilon'}f(E)\,f(-E')\,dE\simeq\frac{u}{2}e^{-\epsilon_0}\left[\frac{2\epsilon_0}{(u+2\epsilon_0)}\right]^{\frac{1}{2}}\times\int_0^\infty\frac{dy\,e^{-y}}{y^{\frac{1}{2}}(y+u)^{\frac{1}{2}}}\left[1+\frac{3y}{4\epsilon_0}-\frac{y}{2(u+2\epsilon_0)}\right].$$

Hence

$$J_1=e^{-\epsilon_0}\left(\frac{2\epsilon_0}{u+2\epsilon_0}\right)^{\frac{1}{2}}\int_0^\infty\frac{dy\,e^{-y}}{y^{\frac{1}{2}}(y+u)^{\frac{1}{2}}}\left[y+\frac{u}{2}+\frac{(3u+4\epsilon_0)\,uy}{8\epsilon_0(u+2\epsilon_0)}\right]$$

$$=e^{-\epsilon_0}\left(\frac{2\epsilon_0}{u+2\epsilon_0}\right)^{\frac{1}{2}}\frac{u}{2}e^{u/2}\left\{K_1(u/2)+\frac{(3u+4\epsilon_0)u}{8\epsilon_0(u+2\epsilon_0)}\times[K_1(u/2)-K_0(u/2)]\right\},$$

where K_0 and K_1 are Bessel functions of imaginary argument.

J_2 is nonzero only if $u>2\epsilon_0$. The exponentials are less than $e^{-\epsilon_0}$ throughout the interval, so that at low temperatures the integral is

$$J_2\simeq\int_{-u+\epsilon_0}^{-\epsilon_0}\left|\frac{EE'}{\epsilon\epsilon'}\right|\left(1-\frac{\epsilon_0^2}{EE'}\right)dE.$$

This integral can be evaluated exactly in terms of complete elliptic integrals and one finds

$$J_2=2[(\tfrac{1}{2}u+\epsilon_0)E(k)-u\epsilon_0(\tfrac{1}{2}u+\epsilon_0)^{-1}K(k)],$$

where

$$k=(u-2\epsilon_0)/(u+2\epsilon_0).$$

For small k, one has

$$J_2\simeq\pi(\tfrac{1}{4}u^2+\epsilon_0^2)/(\tfrac{1}{2}u+\epsilon_0).$$

When $u>2\epsilon_0$ and $\epsilon_0>2$, one has $J_2\gg 2J_1$. If one takes J_2 to be infinitely large when $u>2\epsilon_0$, one obtains a result which is accurate to within 10% when $\epsilon_0=2$, and more accurate than this for larger values of ϵ_0.