V. CONCLUSIONS

High-frequency magnetoacoustic data have been obtained for both indium and lead using an automatic recording technique. For both metals reasonable agreement is obtained between the extremal dimensions of the Fermi surface and those obtained from the free-electron model. The OPW model of Anderson gives an even better fit to the data for lead.

ACKNOWLEDGMENTS

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Theory of the Intrinsic Electronic Thermal Conductivity of Superconductors*

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The analog to the Bloch equation for the case of thermal conduction in a superconductor limited by phonon scattering is derived by introducing an appropriate general form for the nonequilibrium part of the distribution function into the corresponding Boltzmann equation. This integral equation for the deviation function is solved numerically for different temperatures T by replacing it by sets of simultaneous linear equations with dimensions up to 39. The limiting curve for the deviation function when T approaches the transition temperature T_c from below turns out to be identical to the curve which has been reported by Klemens for the normal state. With T decreasing below T_c the maximum of the deviation function rises and shifts to higher energies. The ratio of the thermal conductivity in the superconducting state to that in the normal state, κ_s/κ_n, plotted against T/T_c is found to increase monotonically and to have a limiting slope of about 1.62 at T_c. Consideration of the energy dependence of the energy gap in the case of lead yields a sizable effect on the plot of κ_s/κ_n vs T/T_c.

I. INTRODUCTION

An outstanding feature of the experimental results for the electronic thermal conductivity of superconductors is the qualitatively different behavior of the 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, κ_s/κ_n, plotted against the reduced temperature, T/T_c, is found to have a zero slope at the transition temperature T_c if the scattering is predominantly by the impurities, but it is found to have a finite limiting slope, of about 1.6 for tin and of about 5 for lead and mercury, if the scattering is predominantly by phonons.

Bardeen, Rickayzen, and the author[1] have derived an expression for κ_s/κ_n on the basis of the Bardeen-Cooper-Schrieffer microscopic theory of superconductivity,[2] valid when the impurity scattering limits the heat flux. They find excellent agreement between their theoretical curve and the various experimental data; in particular, this theory yields a zero slope of κ_s/κ_n at T_c. So far, the electronic thermal conductivity limited by the phonons has not been understood as well. This problem has been treated first in BRT by setting up the full Boltzmann equation for the deviation in the distribution function of the quasi-particles from the equilibrium distribution. This Boltzmann equation takes into account the occurrence of the energy gap in a superconductor, the modified group velocity of the quasi-particle excitations, and the coherence factors in the matrix elements for the particle-phonon interaction. Lower bounds on the thermal conductivity were obtained by making use of Kohler's variational principle. One of the trial solutions which were used for the deviation function gave a negative slope of κ_s/κ_n versus T/T_c at T_c.

Kadanoff and Martin[3] derived an approximate expression for κ_s/κ_n by using thermodynamic Green's functions and introducing a finite lifetime for the excitations as a parameter into the theory. Their basic approximation consists in the replacement of the transport cross section by the scattering cross section. In evaluating their expression for κ_s/κ_n they further assumed that the lifetimes of a quasi-particle and a normal state excitation are the same and do not depend on the excitation energy. Under these assumptions the two (unknown) lifetimes drop out from the expression for κ_s/κ_n, and the temperature dependence of this ratio

* This work was supported in part by the National Science Foundation.

[1] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959), hereafter referred to as BRT.

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957), hereafter referred to as BCS.

[3] L. P. Kadanoff and P. Martin, Phys. Rev. **124**, 670 (1961).

can easily be calculated. The author[4] has rederived Kadanoff and Martin's general expression for κ_s/κ_n by starting from the Boltzmann equation given in BRT and by neglecting that part of the scattering term in this equation which constitutes the difference between the transport and the scattering cross section. This procedure yields immediately an expression for the lifetime due to the interaction of the quasi-particles with the phonons. The same expression for the quasi-particle lifetime has been derived also from first principles by employing thermodynamic Green's functions. The energy and temperature dependence of the lifetime have been calculated explicitly and have been considered when evaluating the integrals in the expression for κ_s/κ_n which contain the lifetimes. The theory of Kadanoff and Martin, as well as the refined one of the author, gives fair agreement with the experimental data on tin reported by Guénault.[5]

The assumption that in the case of thermal conduction a relaxation time approximation of the Boltzmann equation does not lead to a significant error appears to be plausible but is difficult to justify. In order to clarify the situation beyond any doubts we present here a calculation of the thermal conductivity limited by phonons within the framework of the BCS theory and the Boltzmann equation but which does not rest on further assumptions. In particular, we replace the relaxation time approximation by an exact numerical solution of the resulting integral equation for different temperatures. The main question we are interested in is whether or not the complete theory then will yield a positive slope of about 1.6 for the plot of κ_s/κ_n versus T/T_c at T_c. A positive answer to this question would definitely remove the puzzle which has been created by the use of variational solutions in BRT. It would mean another important confirmation of the BCS theory, since the exact temperature dependence of the thermal conductivity depends on the details of the microscopic theory of superconductivity which we use.

In Sec. II of this work we derive the analog to the Bloch equation for the case of thermal conduction in a superconductor by introducing into the Boltzmann equation of BRT a general form for the nonequilibrium part of the quasi-particle distribution function which corresponds to that used for the normal state. In Sec. III we discuss the numerical procedure used to solve the integral equation for the deviation function, and we discuss the results for the deviation as a function of the energy and its dependence on the temperature. In Sec. IV we compare the calculated temperature dependence of κ_s/κ_n with the data on the superconductor tin characterized by weak electron-phonon interaction. Further, we discuss some modifications of the simple theory which we have carried out in order to solve the puzzle of the very large limiting slopes of κ_s/κ_n which have been observed for the superconductors mercury and lead[6] characterized by strong electron-phonon interaction.

[4] L. Tewordt, Phys. Rev. **128**, 12 (1962), hereafter referred to as I.

[5] A. M. Guénault, Proc. Roy. Soc. (London) **A262**, 420 (1961).

II. THE ANALOG OF THE BLOCH EQUATION

The Boltzmann equation for the distribution function of quasi-particles in a temperature gradient has been set up in BRT. We briefly recapitulate the essential equations. For simplicity it is assumed here that the energy of a quasi-particle with momentum **p** is given by $E_p=+(\epsilon_p^2+\Delta^2)^{1/2}$, where $\epsilon_p=(p^2/2m)-\mu$, and where $\Delta=\Delta(T)$ is the energy gap parameter of BCS which is a constant for the temperature T considered. The group velocity of a wave packet of quasi-particles $(\mathbf{p},\uparrow)$, that is particles having momenta around **p** and a spin component parallel to the axis of quantization, is

$$\mathbf{v}_p=\nabla_p E_p=(\mathbf{p}/m)(\epsilon_p/E_p). \tag{2.1}$$

Notice that **v** changes the direction when **p** crosses the Fermi sphere. The rate of change of the distribution function f_p of particles $(\mathbf{p},\uparrow)$ due to their drift into and out of a considered volume element in coordinate space is found to be

$$\left(\frac{\partial f_p}{\partial t}\right)_{\text{drift}}=-v_{pz}\left(\frac{\partial f_p}{\partial T}\right)_{E\ \text{const}}\frac{dT}{dz}$$
$$=\left(\frac{p_z}{m}\frac{\epsilon_p}{E_p}\right)\left(\frac{E_p}{T}\frac{\partial f_p}{\partial E_p}\right)\frac{dT}{dz}. \tag{2.2}$$

The z axis is taken along the direction of the temperature gradient ∇T. The distribution function f_p is taken to be the equilibrium distribution, $f_p=f(\beta E_p)=[\exp(\beta E_p)+1]^{-1}$.

The rate of change of the deviation Δf_p of particles $(\mathbf{p},\uparrow)$ from the equilibrium distribution due to the scattering of particles $(\mathbf{p},\uparrow)$ and the destruction or creation of pairs of particles $(\mathbf{p},\uparrow)$, $(\mathbf{p}',\downarrow)$ by the interaction with the phonons can be written as

$$\left(\frac{\partial\Delta f_p}{\partial t}\right)_{\text{phonon}}=-\left(-\frac{\partial f_p}{\partial E_p}\right)\int d^3p'$$
$$\times W(\mathbf{p},\mathbf{p}')(\chi_p-\chi_{p'}). \tag{2.3}$$

Here instead of Δf_p a new function χ_p has been used which is defined by

$$\Delta f_p=(-\partial f_p/\partial E_p)\chi_p. \tag{2.4}$$

The kernel of the integral operator on the right-hand

[6] J. K. Hulm, Proc. Roy. Soc. (London) **A204**, 98 (1950).

side of Eq. (2.3) is found to be

$$W(\mathbf{p},\mathbf{p}')=(2\pi)^{-2}|V_q|^2(1-f)^{-1}\Big\{\tfrac{1}{2}\Big(1+\frac{\epsilon\epsilon'-\Delta^2}{EE'}\Big)\times[(1+N)(1-f')\delta(E'+\Omega-E)+N(1-f')\delta(E'-\Omega-E)]+\tfrac{1}{2}\Big(1-\frac{\epsilon\epsilon'-\Delta^2}{EE'}\Big)(1+N)f'\delta(E'+E-\Omega)\Big\}. \quad (2.5)$$

In this equation the following notation has been used: The unprimed and primed quantities ϵ, E, and f refer to arguments $\mathbf{p}$ and $\mathbf{p}'$, respectively; Ω is the phonon frequency for momentum $\mathbf{q}=\mathbf{p}'-\mathbf{p}$; N denotes the distribution function of the phonons which is taken according to Bloch's approximation to be the equilibrium distribution, i.e., $N=N_q=[\exp(\beta\Omega_q)-1]^{-1}$. The matrix element for the electron-phonon interaction is set equal to V_q.

The Boltzmann equation, which results from the condition that Δf_p is stationary in the presence of the temperature gradient, becomes, according to Eqs. (2.2) and (2.3),

$$\frac{p_z}{m}\frac{\epsilon_p}{T}\Big(-\frac{dT}{dz}\Big)=2\Gamma_p\chi_p-\int d^3p'\,W(\mathbf{p},\mathbf{p}')\chi_{p'}. \quad (2.6)$$

The quantity $2\Gamma_p$, defined by

$$2\Gamma_p=\int d^3p'\,W(\mathbf{p},\mathbf{p}'), \quad (2.7)$$

is just the decay rate of a quasi-particle as has been shown in I. One recognizes from the Eq. (2.5) for W that the first two terms in this expression, having different delta functions, correspond to the scattering of a particle from $\mathbf{p}$ to $\mathbf{p}'$ with the emission or the absorption of a phonon $\mp\mathbf{q}$, and that the third term corresponds to the destruction of a pair of particles $(\mathbf{p},\uparrow)$ and $(\mathbf{p}',\downarrow)$ with the emission of a phonon $-\mathbf{q}$.

In I we have carried through a kind of relaxation time approximation of the Boltzmann equation, that is more exactly, we have neglected the second term on the right-hand side of Eq. (2.6) which, as can be seen from Eq. (2.3), tends to decrease the effect of the forward scattering. Then we were able to write down immediately the solution for χ_p. Now we make a corresponding Ansatz for χ_p which contains an unknown function $g(E_p)$

$$\chi_p=(p_z/m)(\epsilon_p/T)(-dT/dz)g(E_p). \quad (2.8)$$

Then the sign of χ_p is determined by the factor $p_z\epsilon_p$ in this expression. Thus, for positive values of p_z, for instance, χ_p will be positive above and negative below the Fermi surface. In Fig. 1 we illustrate the sign of

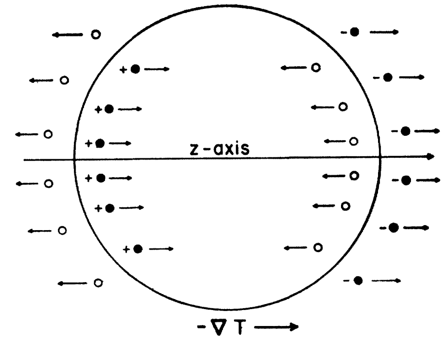

FIG. 1. Schematic representation of the nonequilibrium part of the distribution of quasi-particles with respect to the Fermi sphere in the presence of a temperature gradient ∇T. The filled-in and the empty circles designate particle excess and deficiency, respectively. The arrows denote the direction of the group velocity of quasi-particles in that region, and the sign stands for the sign of the charge which is located in a wave packet of particles.

χ_p, and thus of Δf_p, with respect to the Fermi surface and the z direction by filled-in circles (excess) or empty circles (deficiency). We indicate the directions of v_z for particles $(\mathbf{p},\uparrow)$ for $\mathbf{p}$ above and below the Fermi surface in the positive as well as the negative z direction. One recognizes from this figure that this kind of deviation Δf_p gives rise to a net flow of energy in the positive z direction, while it makes the electric current equal to zero. The vanishing of the electric current can be verified from the fact that the electric charge which is located in a wave packet of quasi-particles $(\mathbf{p},\uparrow)$ is equal to $e(\epsilon_p/E_p)$, as has been shown in BRT. This form for χ_p given in Eq. (2.8) corresponds also to the one which one takes for the normal state.

The thermal conductivity κ_s in the superconducting state is determined by the general formula

$$\kappa_s=\Big(-\frac{dT}{dz}\Big)^{-1}2\int d^3p\,v_{pz}E_p\Delta f_p. \quad (2.9)$$

By using the Eqs. (2.1), (2.4), and (2.8), we obtain from Eq. (2.9) the following expression for κ_s

$$\kappa_s=\frac{1}{2}\frac{n}{m}k_B\beta^2\int_\Delta^\infty dE(E^2-\Delta^2)^{1/2}E\,\mathrm{sech}^2(\tfrac{1}{2}\beta E)g(E). \quad (2.10)$$

If we insert the expression for χ_p given in Eq. (2.8) into the Boltzmann equation [Eq. (2.6)], this goes over into the following integral equation for $g(E_p)$:

$$2\Gamma_p g(E_p)=1+\int d^3p'\,W(\mathbf{p},\mathbf{p}')\frac{p_z'}{p_z}\frac{\epsilon_{p'}}{\epsilon_p}g(E_{p'}). \quad (2.11)$$

The integration over $\mathbf{p}'$ on the right-hand side of Eq. (2.11) is transformed into an integration over $\mathbf{q}=\mathbf{p}'-\mathbf{p}$. We introduce polar coordinates q, ϑ, φ, in q space where the polar axis is taken along the direction of $\mathbf{p}$. If θ and θ_1 are the angles between the z axis and $\mathbf{p}$ or

q, respectively, we have

$$q_z = q\cos\theta_1 = q(\cos\theta\cos\vartheta + \sin\theta\sin\vartheta\cos\varphi). \quad (2.12)$$

Since q_z is the only quantity in the integrand of Eq. (2.11) which depends on the azimuth φ, the second term on the right-hand side of Eq. (2.12) gives no contribution to this integral. Hence, the factor (p_z'/p_z) in the integrand of Eq. (2.11) gives rise to a factor $[1+(q/p)\cos\vartheta]$ which can be written

$$1+(q/p)\cos\vartheta = 1+(\epsilon_{p'}-\epsilon_p)(p^2/2m)^{-1}-(q^2/2p^2). \quad (2.13)$$

Since the second term on the right-hand side of this last equality is of the order k_BT/ϵ_F, where ϵ_F is the Fermi energy, it can be neglected in comparison to one. For temperatures which are much lower than the Debye temperature also, the third term on the right of Eq. (2.13) can be neglected in comparison to one. In this approximation the Eq. (2.11) goes over into

$$2\Gamma_p g(E_p) = 1+\int d^3q\, W(\mathbf{p},\mathbf{p}+\mathbf{q})\frac{\epsilon_{p+q}}{\epsilon_p}g(E_{p+q}). \quad (2.14)$$

The integration over the q space in the integral on the right of Eq. (2.13) can be handled in complete analogy to the integration for $2\Gamma_p$ [Eq. (2.7)]. The latter integration has been carried out in I. First the integration over $\sin\vartheta d\vartheta$ is transformed into an integration over $E'=E_{p+q}$ which yields, beside other factors, the density-of-states factor $E'|\epsilon'|$. The integration over q is transformed into an integration over $\Omega=\Omega_q$ by assuming a Debye spectrum for the phonon frequencies. For a fixed Ω the integration over E' can be carried out by making use of the delta functions in the expression for $W(\mathbf{p},\mathbf{p}+\mathbf{q})$ from Eq. (2.5). The limits of the remaining Ω integrations, which depend on the arguments of these delta functions, have been determined in I.

One important result of the investigations made in I is that the integration over E' for a fixed Ω yields both signs of $\epsilon'=\epsilon_{p+q}$. Therefore, all the terms in the integrand of Eq. (2.14) which are linear in ϵ' vanish. If we consider now the combination of the density-of-states factor $E'/|\epsilon'|$, the factor ϵ'/ϵ in the integrand of Eq. (2.14), and the coherence factors in W given in Eq. (2.5), we see that the only terms in these combinations which contribute to the integral in question are the following:

$$(E'/|\epsilon'|)(\epsilon'/\epsilon)(\pm\epsilon'\epsilon/E'E) = \pm|\epsilon'|/E. \quad (2.15)$$

Thus, the expressions obtained for the integral on the right of Eq. (2.14) will be identical to those which we have obtained in I for $2\Gamma_p$, except that the terms $(E'/|\epsilon'|)[1\mp(\Delta^2/E'E)]$ are now replaced by $\pm(|\epsilon'|/E)g(E')$. Here the upper sign corresponds to the scattering and the lower sign to the destruction of pairs of particles. If we introduce, as in the case of $2\Gamma_p$, the new integration variable t and the parameters x and y by

$$t=\Omega/\Delta,\quad x=E_p/\Delta,\quad y=\Delta/k_BT, \quad (2.16)$$

and further introduce new functions $\Gamma(x)$ and $G(x)$ by

$$2\Gamma_p = A\Gamma(x),\quad g(E_p)=A^{-1}G(x), \quad (2.17)$$

where A is a certain constant which has been written down in I, then we find from Eq. (2.14) the following integral equation for $G(x)$:

$$\begin{aligned}\Gamma(x)G(x) = 1+(1+e^{-yx})x^{-1}\\ \times\Big\{\int_0^{x-1} dt\, t^2[(x-t)^2-1]^{1/2}[1-e^{-yt}]^{-1}\\ \times[1+e^{-y(x-t)}]^{-1}G(x-t)\\ +\int_0^{\infty} dt\, t^2[(x+t)^2-1]^{1/2}[e^{yt}-1]^{-1}\\ \times[1+e^{-y(x+t)}]^{-1}G(x+t)\\ -\int_{x+1}^{\infty} dt\, t^2[(t-x)^2-1]^{1/2}[1-e^{-yt}]^{-1}\\ \times[1+e^{y(t-x)}]^{-1}G(t-x)\Big\}. \quad (2.18)\end{aligned}$$

The expression for $\Gamma(x)$ can be obtained from the second term on the right of Eq. (2.18) by replacing $x^{-1}[(x\mp t)^2-1]^{1/2}G(|x-t|)$ by $[(x\mp t)^2-1]^{-1/2}(x\mp t-x^{-1})$. In deriving Eq. (2.18) we have assumed that the matrix element V_q is proportional to $q^{1/2}$, and we have neglected Umklapp processes. Thus, the integral equation in Eq. (2.18) constitutes the analog to the Bloch equation for the case of thermal conduction in a superconductor.

The integral equation which corresponds to the normal state is obtained from Eq. (2.14) by letting Δ tend to zero. If we introduce, instead of the deviation function for the normal state, say, $g_0(\epsilon_p)$ (which is even in ϵ_p), a new function $G_0(z)$, by the relation

$$g_0(\epsilon_p)=A^{-1}y^3G_0(z),\quad\text{with}\quad z=\epsilon_p/k_BT, \quad (2.19)$$

then we obtain the following integral equation for $G_0(z)$

$$\begin{aligned}\int_0^\infty \frac{ds\, s^2}{(e^s-1)}\Big\{[zG_0(z)-(z-s)G_0(z-s)]\frac{(1+e^{-z})}{(e^{-s}+e^{-z})}\\ +[zG_0(z)-(z+s)G_0(z+s)]\frac{(1+e^z)}{(e^z+e^{-s})}\Big\} = z. \quad (2.20)\end{aligned}$$

This integral equation can also be obtained immediately from the Eq. (2.18) by dropping the ones in all the integrals, by replacing the integration variable t by $y^{-1}s$ and the parameter x by $y^{-1}z$, and further by replacing $G(x)$ by $y^3G_0(z)$ and $G(|x\mp t|)$ by $y^3G_0(|z\mp s|)$. If we introduce instead of $G_0(z)$ the new function $c(z) = -zG_0(z)$ into the Eq. (2.20), then we obtain an integral equation for $c(z)$ which is seen to be identical to the one presented for instance by Klemens[7] for the normal metal at temperatures $T \ll \theta$.

The ratio of the thermal conductivity in the superconducting state, κ_s, to that in the normal state, κ_n, is obtained from Eq. (2.10) and the corresponding equation for the normal state which arises if one lets the Δ tend to zero in Eq. (2.10). If we introduce new integration variables x and z instead of E_p and ϵ_p, respectively, and further the functions $G(x)$ and $G_0(z)$ instead of $g(E_p)$ and $g_0(\epsilon_p)$, respectively, we find the following final formula for the ratio κ_s/κ_n:

$$\frac{\kappa_s}{\kappa_n} = \frac{\int_1^\infty dx\, x(x^2-1)^{1/2}\,\mathrm{sech}^2(\tfrac{1}{2}yx)G(x)}{\int_0^\infty dz\, z^2\,\mathrm{sech}^2(\tfrac{1}{2}z)G_0(z)}. \tag{2.21}$$

The aim is to determine the function $G(x)$ for a given temperature, that is a given value of the parameter $y = \Delta(T)/k_BT$, from its integral equation in Eq. (2.18), and also to determine the single function $G_0(z)$ from its integral equation Eq. (2.20), and finally to evaluate the expression given in Eq. (2.21). Then the ratio κ_s/κ_n is obtained as a function of y. Since y can be written as

$$y = [\Delta(T)/\Delta(0)](T_c/T)[\Delta(0)/k_BT_c], \tag{2.22}$$

one recognizes that the plot of the ratio κ_s/κ_n versus the reduced temperature T/T_c depends on the value of the ratio $\Delta(0)/k_BT_c$ and the dependence of the ratio $\Delta(T)/\Delta(0)$ on the reduced temperature.

III. SOLUTION OF THE INTEGRAL EQUATION

The integral equation in Eq. (2.18) which has been set up for the function $G(x)$ determining the deviation of the quasi-particles from the equilibrium distribution at $x = E_p/\Delta(T)$, is easily transformed into the standard form of a Fredholm integral equation of the third kind. We obtain from Eq. (2.18)

$$\Gamma(x)G(x) + \int_1^\infty dt\, K(x|t)G(t) = 1, \tag{3.1}$$

where the kernel $K(x|t)$ is given by

$$K(x|t) = K_1(x|t) + K_1(-x|t), \tag{3.2}$$

and

$$K_1(x|t) = x^{-1}(1+e^{-yx})\frac{(t^2-1)^{1/2}}{(1+e^{-yt})}\frac{(x+t)^2}{|e^{yt}-e^{-yx}|}, \tag{3.3}$$

and the integral $\Gamma(x)$ by

$$\Gamma(x) = \int_1^\infty dt\,[I_1(x|t) + I_1(-x|t)], \tag{3.4}$$

with

$$I_1(x|t) = \frac{(1+e^{-yx})}{(t^2-1)^{1/2}(1+e^{-yt})}\frac{(x+t)^2(t+x^{-1})}{|e^{yt}-e^{-yx}|}. \tag{3.5}$$

Since the kernel $K(x|t)$ and the integrand of $\Gamma(x)$ are even functions in x, one recognizes from Eq. (3.1) that $G(x)$ becomes an even function in x, as it should.

For later purposes it is useful to write down a relation for $G(x)$ which is valid for large values of x and is obtained by means of asymptotic expansions from the Eq. (3.1)

$$G(x) \underset{x\to\infty}{=} x^{-1}\frac{\int_1^x dt\, G(t)\dfrac{(t^2-1)^{1/2}(x-t)^2}{(1+e^{-yt})(1-e^{-y(x-t)})}}{\int_1^x dt\dfrac{t(x-t)^2}{(t^2-1)^{1/2}(1+e^{-yt})(1-e^{-y(x-t)})}} + \cdots. \tag{3.6}$$

The dots in Eq. (3.6) denote terms which are smaller by factors $x^{-n}\exp(-xym)(n\geq 1, m\geq 0)$ than the first term. One recognizes from this asymptotic formula that the exponent of the leading term in the asymptotic expansion of $G(x)$, say x^λ, must be greater than -2, since for $\lambda \leq -2$ the right-hand side of Eq. (3.6) would bear out a different asymptotic behavior of $G(x)$ than x^λ.

The analog to Eq. (3.1) which applies for the normal state and corresponds to the limit $y = \Delta(T)/k_BT \to 0$ can be obtained from Eq. (2.20). Klemens[7] has solved this latter integral equation numerically by replacing it by a set of 10 simultaneous linear equations. Klemens result for the deviation function $c(z) = -zG_0(z)$ (with $z = \epsilon_p/k_BT$) turned out to be radically different from previously determined trial solutions, for instance, Sondheimers solution, and the resultant thermal conductivity exceeds the value derived from Sondheimers trial solution by 11%.

Since obviously the variational method does not yield the desired accuracy which we need for our purposes, we have decided to solve Eq. (3.1) by a numerical procedure. Another reason for using a numerical method is that the integrand of $\Gamma(x)$ and the kernel $K(x|t)$ are much more complicated than the corresponding expressions for the normal state and do not allow for analytic integrations.

Since in a numerical procedure the integral in Eq. (3.1) which contains the unknown function $G(t)$ under the integral is evaluated by means of a finite sum, for instance, by Simpson's rule, it seems natural to follow Klemens method. Thus, we replace the integral equation by a set of simultaneous linear equations where the unknowns are the discrete values of $G(t)$ at the chosen equidistant points in the integration interval. A serious

[7] P. G. Klemens, Australian J. Phys. 7, 64 (1954).

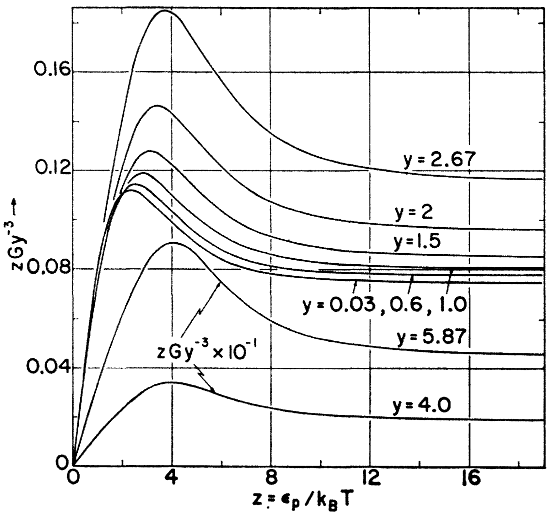

FIG. 2. The nonequilibrium part of the quasi-particle distribution as a function of the energy for different temperatures. Plotted is $zG[(z^2y^{-2}+1)^{1/2}]y^{-3}$ vs $z=\epsilon_p/k_BT$ for different values of the parameter $y=\Delta(T)/k_BT$. G is the solution of the integral equation, ϵ_p is the normal-state excitation energy, and $\Delta(T)$ is the energy gap valid for the temperature T considered.

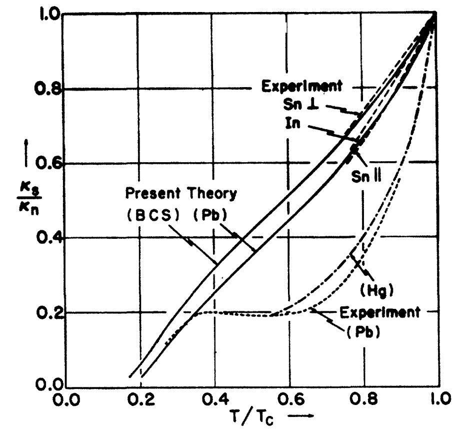

FIG. 3. Theoretical curves for the ratio of the thermal conductivity in the superconducting state, κ_s, to that in the normal state, κ_n, vs the reduced temperature, T/T_c. The curves designated by BCS and Pb are calculated with a value of the ratio $2\Delta(0)/k_BT_c$ equal to 3.52 and 4.1, respectively. For comparison, experimental results on tin and indium (Guénault), mercury (Hulm), and lead are included.

difficulty arises from the fact that the upper limit of the integral containing $G(t)$ is infinite. If we introduce a cutoff, say $t=\alpha$, instead of this upper limit ∞, then we can derive easily the following upper bound for the absolute value of the remainder $R=R(\alpha)$ of the integral in question, provided that $|G(t)|\leq|G(\alpha)|$ for $t\geq\alpha$

$$|R(\alpha)|<|G(\alpha)|\{8(1-e^{-y\alpha})^{-1}e^{-y\alpha}[(\alpha y)^3+3(\alpha y)^2+6(\alpha y)+6]y^{-4}+[4\zeta(3)+12\zeta(4)(y\alpha)^{-1}]y^{-3}\},\quad(3.7)$$

where the symbol ζ denotes Riemann's ζ function. The aim is then to find for an assumed $\delta\ll1$ a cutoff α which makes this upper bound for $|R(\alpha)|$ smaller than δ.

The validity of the assumption that $|G(x)|\leq|G(\alpha)|$ for $x\geq\alpha$ has to be verified from the numerical solution. Indeed we find that $G(x)$ decreases monotonically with x and behaves like x^{-1} for large values of x. One recognizes that such an asymptotic behavior of $G(x)$ is consistent with the asymptotic relation for $G(x)$ which is given in Eq. (3.6).

There are two kinds of errors which are introduced by our numerical procedure. They correspond either to the truncation of the integral in Eq. (3.1) at $t=\alpha$ or to the use of Simpson's rule in evaluating this integral. Since the dimension of the set of linear equations which we can use is restricted by the size of the available computer, we have to make an appropriate compromise between the requirements that α should be made as large as possible and that the spacing between the equidistant points which we use in Simpson's rule should be made as small as possible. In order to obtain estimates of the corresponding errors we have carried out three runs for each value of y. In the first run we have chosen $\alpha=\alpha_1\approx20y^{-1}$ and 29 equations, and we find that $G(x)$ is positive and decreases monotonically from $x=1$ to $x=\alpha_1$, and that it behaves very nearly to x^{-1} for $x>\frac{1}{2}\alpha_1$. From the Eq. (3.7) we calculate with the help of the numerical value for $G(\alpha_1)$ an upper bound for $|R(\alpha_1)|$ equal to $\delta=0.01$ for all values of y. In the second run we have chosen once more $\alpha=\alpha_1$ but 39 equations in order to estimate the error which is introduced by using Simpson's rule. In the third run we have chosen $\alpha=\alpha_2\approx\frac{1}{2}\alpha_1$ and 29 equations in order to obtain another estimate of the error which arises from the cutoff in the integral. It turns out that the results for $G(x)$ differ at the most by 1% for all the three runs.

In Fig. 2 part of the results of runs 2 for the solutions $G(x)$ which were computed for a number of different parameter values of $y=\Delta(T)/k_BT$ are shown. In order to obtain a better comparison between these solutions and the normal-state solution we have not plotted the $G(x)$'s vs $x=E_p/\Delta(T)=(z^2y^{-2}+1)^{1/2}$ but the functions $zG[(z^2y^{-2}+1)^{1/2}]y^{-3}$ vs $z=\epsilon_p/k_BT=y(x^2-1)^{1/2}$. The curve for zGy^{-3} with $y=0.03$ is found on the scale of Fig. 2 to be the same as the one shown by Klemens for $|c(z)|=zG_0(z)$. The curve for zGy^{-3} with $y=0.3$ is found to lie very close to the one with $y=0.03$; this curve has been omitted for clarity. One sees from the Fig. 2 that the maximum of the deviation function zGy^{-3} increases and shifts to higher values of z with increasing y.

In evaluating the ratio of the thermal conductivities, κ_s/κ_n, with the help of the Eq. (2.21), we have calculated the numerator integral numerically by using Simpson's rule and by introducing a cutoff. We have taken the cutoffs α_1 and α_2 and the discrete values of $G(x)$ which were obtained in the runs 1, 2, and 3, respectively. It turns out that the resulting three values of the numerator integral agree within the limit of 1%.

The value of the denominator integral in Eq. (2.21) has been determined by extrapolation from the values of the numerator integral at $y=0.3$ and $y=0.03$ to $y=0$. In Fig. 3 we show the plots of κ_s/κ_n vs the reduced temperature T/T_c for the two cases where the value of the ratio $2\Delta(0)/k_BT_c$ is taken to be the BCS value 3.52 (upper solid curve) and 4.1 (lower solid curve); the value of 4.1 lies close to most experimental values for this ratio which have been reported for lead. The dependence of $\Delta(T)/\Delta(0)$ on T/T_c was taken to be the one given by the BCS theory in both cases. For comparison we have included in this figure also experimental values of κ_s/κ_n measured for tin,[5] mercury, and lead.[6]

IV. CONCLUSION

One recognizes from Fig. 3 that our theoretical curve for κ_s/κ_n, which is exact within the framework of the BCS model and the Boltzmann equation, agrees fairly well with the data of Guénault for very pure tin. Comparison of this curve with the one obtained in I with the help of the relaxation time approximation shows that this approximation, in fact, does not lead to a great error. Special care has been taken in our numerical procedure to obtain the right behavior of κ_s/κ_n for values of T/T_c close to one. No evidence of a negative limiting slope of κ_s/κ_n vs T/T_c could be detected, but the limiting slope turns out to be about $+1.62$.

From Fig. 3 one recognizes also that the theoretical curve for κ_s/κ_n calculated with a value of the ratio $2\Delta(0)/k_BT_c$ equal to 4.1, which is roughly appropriate to lead, lies appreciably below the curve calculated with the BCS value 3.52 for this ratio. But this curve lies still far above the experimental curves for mercury and lead. Two other attempts have been made to explain the data on lead.

In the first attempt we have determined a somewhat more realistic form of the matrix element V_q for the electron-phonon interaction. The largest corrections to the Bloch form we used before, i.e., $V_q \propto q^{1/2}$, are found to come from the Umklapp processes and the interference factor.[8] The effective matrix element for the Umklapp processes has been calculated by using the approximation method of Ziman.[8] But we find that in the case of lead the additive effect of the Umklapp processes is largely compensated for by the reduction of the matrix element for the normal processes due to the interference factor. The effect of any finer details in the behavior of V_q on κ_s/κ_n is expected to be small since V_q occurs in both expressions for κ_s and κ_n.

Schrieffer and co-work rs[9] have suggested that the maximum they find in the energy gap when considered as a function of the energy might affect transport properties of superconductors. Accordingly, in our second investigation we have introduced in all the relevant expressions of above work the modifications which result from an energy dependence of the gap. First, the density-of-states functions occurring in all the integrals are modified. Second, the terms with Δ^2/EE' in the coherence factors of the particle-phonon interaction matrix element [see Eq. (2.5)] are modified. We have calculated κ_s/κ_n for various temperatures by taking into account the corresponding corrections due to those $\Delta(E)$ curves, in the work of Schrieffer *et al.*, which are roughly appropriate to the case of lead. It turns out that the correction for $C=0.5$ (see reference 9) lowers the Pb curve in Fig. 3 by approximately the same amount as the difference between the BCS curve and the Pb curve.

Thus, it seems that the large limiting slopes of κ_s/κ_n measured for lead and mercury cannot be explained completely within the scope of the BCS model and the conventional Boltzmann equation approach. Since the Boltzmann equation is limited to weak interaction, while the electron-phonon interaction in lead and mercury is very strong, we try to solve the problem by means of the more general method of thermodynamic Green's functions.[10]

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[8] See J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960).

[9] G. J. Culler, B. D. Fried, R. W. Huff, and J. R. Schrieffer, Phys. Rev. Letters **8**, 399 (1962).

[10] Compare also V. Z. Kresin, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 1947 (1959) [translation: Soviet Phys.—JETP **9**, 1385 (1959)].