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PHYSICAL REVIEW B VOLUME 3, NUMBER 2 15 JANUARY 1971

Electron-Phonon Effects in the Infrared Properties of Metals

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(Received 1 September 1970)

Electron-phonon contributions to the infrared absorption in metals are examined from two points of view. First, "golden-rule" calculations are given for normal metals and superconductors which reproduce the phenomenological theory used by Joyce and Richards to analyze their data in lead. This theory is expected to be valid for weak electron-phonon coupling. Second, the Holstein transport theory for normal metals is used to examine the corrections arising from strong coupling. Solutions are found for the response function at general frequencies and wave vectors. The results are similar in form to the golden-rule theory, and provide a simple correction factor to this theory. It is suggested that optical measurements on both normal and superconducting materials may provide a valuable tool for analyzing the coupled electron-phonon system.

In a recent letter, Joyce and Richards[1] (JR) have reported the observation of phonon contributions to the far-infrared absorptivity in lead. The experiments were done at 1.2 °K both for the superconducting and the normal state (by the application of a 1200-G magnetic field). The important feature of the JR experiment is an additional absorption above what is expected for a collisionless electron gas. This extra absorption is ascribed by JR to the Holstein mechanism[2] in which the incident photon is absorbed in a second-order process involving creation of both a phonon and an electron-hole pair. Evidence for this mechanism is the fact that the onset of the extra absorption occurs in the frequency range of abundant phonons, 30–70 cm^{-1}, in normal lead, while in superconducting lead the onset appears to be shifted up by 22 cm^{-1}, which is 2Δ, or the minimum energy required to create an electron-hole pair in the superconducting state.

To further substantiate their identification of the Holstein mechanism, JR presented a semiquantitative theory in which they assume the absorption scales as the density of final states for the combined electron, hole, and phonon with energy conservation the only constraint. This theory seemed to give a fairly satisfactory explanation of the structure that was observed in the ratio of superconducting-to-normal-state absorption. However, the theory had a number of deficiencies. The absolute magnitude of the effect was not predicted. The role of momentum conservation was unclear. The electron-phonon coupling strength was taken into account by the use of the superconducting tunneling data of McMillan and Rowell.[3] However, the electron-light matrix element was omitted.

There already exists in the literature a number of discussions of the Holstein mechanism. Pippard[4] has given an elegant qualitative description and Holstein[5] an elegant formalism for the normal-metal problem. Scher[6] has made numerical calculations based on Holstein's formalism in the local limit where the anomalous skin effect is ignored. In this paper we present calculations of the infrared absorption for lead in the normal state, based on a solution of Holstein's equation[5] for the response function at all $\vec{q}$ and ω. We also give a derivation of the JR phenomenological theory.

The plan of the paper is as follows. Section I contains a review of the theory of optical absorption. The standard solutions for pure metals, both normal and superconducting, without electron-phonon interactions, are derived from a golden-rule argument. In Sec. II we go to second order in the golden rule in order to include the lowest-order effect of electron-phonon interactions on the optical properties in the local approximation. The resulting theory is identical in form to the JR phenomenological theory. This theory is formally valid only for weak electron-phonon coupling and for frequencies high enough that the anomalous skin regime is avoided. However, the theory is interesting for three reasons. First, it gives in a simple form a good qualitative picture. Second, it illuminates the somewhat obscure results of more exact theories. In fact, for normal metals the solution of the Holstein equation can be almost constructed completely by intuitive extensions of the simple theory. Third, it turns out for normal metals that the simple theory is not a bad approximation to the full theory in spite of nonlocal and strong coupling effects. Calculations based on the simple theory are presented in Sec. III.

In Sec. IV, the Holstein theory[5] for normal metals is presented and solved formally. Some of the consequences of this theory discussed by Holstein[5] are rederived in an elementary way. Calculations based on the Holstein theory are given in Sec. V. In Sec. VI the results are summarized, and new experiments are suggested. In the Appendix the weighted phonon density of states α^2F and its relatives are discussed.

I. GENERAL THEORY OF INFRARED ABSORPTION

Owing to the presence of free carriers, the light incident on a metal is largely reflected at low frequencies. The absorption is given by

$$A = (c/\pi)\,\mathrm{Re}(Z), \tag{1}$$

where Z is the surface impedance of the metal, and is several orders of magnitude smaller (in the infrared) than the free-space impedance $4\pi/c$. In the far-infrared frequencies at low temperatures, the penetration depth of light is usually smaller than the mean free path. Under these circumstances the surface impedance depends on the nature of the interaction of the electrons with the surface.[7] Another way of saying this is to note that in order for energy to be dissipated in the metal there must be some momentum sink to balance the extra momentum of an electron-hole pair (which has nonzero momentum, while the light quantum which created it has nearly zero momentum in vacuum). A mean free path shorter than the penetration depth means that the momentum balance may be taken up in collisions; this type of process is called "volume" absorption. However, a collisionless electron gas still has a dissipative mechanism because the presence of a surface breaks down translational invariance; momentum conservation normal to the surface is no longer strictly required. When the electronic mean free path exceeds the penetration depth, "surface" absorption is the dominant mechanism for absorption. This is the situation in the JR experiment at low frequencies (below ~ 30 cm^{-1}) because their lead sample was very pure and the mean free path effectively infinite. However, above 30 cm^{-1} there is a finite amplitude for scattering electrons by phonons. In this regime volume absorption begins to compete with surface absorption.

General expressions for the surface impedance have been derived by Reuter and Sondheimer[8] for two cases: Z_s corresponding to the case where the electron surface scattering is specular, and Z_d corresponding to the case where the surface scattering is diffuse:

$$Z_s = -\frac{8i\omega}{c^2}\int_0^\infty \frac{dq}{q^2-(\omega^2/c^2)\epsilon(q,\omega)}\ , \tag{2}$$

$$Z_d = \frac{4\pi^2 i\omega}{c^2}\left[\int_0^\infty dq\,\ln\left(1-\frac{\omega^2}{c^2q^2}\epsilon(q,\omega)\right)\right]^{-1}\ . \tag{3}$$

In these expressions, $\epsilon(\vec{q},\omega)$ is the wave-vector and frequency-dependent transverse dielectric function which is related to the conductivity $\sigma(\vec{q},\omega)$ by

$$\epsilon(\vec{q},\omega) = 1 + 4\pi i\sigma(\vec{q},\omega)/\omega\ . \tag{4}$$

It is assumed that the metal has cubic or higher symmetry with the light incident along a cube axis so that the transverse conductivity is a scalar.

The imaginary part of ϵ contains information about decay processes for electromagnetic excitations of frequency ω and wave vector $\vec{q}$. For a collisionless gas, energy and momentum conservation will allow decay by electron-hole pair creation only if $qv_F > \omega$, where v_F is the Fermi velocity. Thus, the "surface absorption" is identical with the large q contributions to the integrals (2) and (3). When collisions are added, decays become possible for all $\vec{q}$ and ω. Roughly speaking, the "volume absorption" is associated with the small q contribution to (2) and (3). A skin depth δ is roughly defined as q_m^{-1}, where q_m is the minimum q above which contributions to Z in (2) or (3) are negligible. If this depth δ is greater than the distance v_F/ω which an electron travels in a period of the radiation field, the surface absorption is negligible. In this case, a local conductivity is adequate (i.e., q can be neglected in ϵ and σ), and Eq. (2) and (3) can be integrated. The result in both cases is an ordinary classical wave impedance[4] for the surface impedance:

$$Z_w = (4\pi/c)[\epsilon(\omega)]^{-1/2}. \tag{5}$$

This formula will be valid in the near infrared and higher frequencies, and gives the classical expression for the (volume) absorption,

$$A_{\text{cl}} = 2/\omega_p\tau \;. \tag{6}$$

This equation results from the Drude formula for $\epsilon(\omega)$, with a transport lifetime τ and a plasma frequency ω_p, under the assumptions $\omega\tau \gg 1$ and $\omega \ll \omega_p$.

A complete program for calculating the far-infrared absorption involves first a calculation of the response function $\sigma(\vec{q}, \omega)$ and then the use of Eqs. (1) and (2) or (3). For normal metals a semiclassical Boltzmann equation yields good results for $\sigma(q\omega)$ for low frequencies, but breaks down when the frequency becomes comparable to phonon frequencies. Holstein[5] has derived a generalization of the Boltzmann equation valid in the phonon frequency range by using diagrammatic perturbation theory to calculate the thermodynamic current-current correlation function in normal metals. An analogous formalism unfortunately has not yet been worked out for superconductors. Nam[9] has partially carried through this program for superconductors by including electron-phonon self-energy corrections in the conductivity. However, he erroneously assumed that the ladder diagrams were negligible. [The Migdal theorem does not hold for $\sigma(\vec{q}, \omega)$ unless $\vec{q}$ is comparable to k_F, the Fermi wave vector of the metal.] In principle, integral equations analogous to Holstein's and valid for strong coupling superconductors could be derived. The algebraic problem would be difficult but not prohibitive. However, we shall see in Sec. IV that for normal metals, the effect of the ladder diagrams is relatively minor. It would not be surprising if the same were true of the superconducting state; then the Nam theory could be expected to be quite adequate.

In the first part of this paper, we will study the structure of the weak coupling solutions. A simple unified procedure for this problem is to use the golden-rule formula for the real part of the conductivity. Then the imaginary part may be found by Kramers-Kronig transforms, and the errors may be estimated by appealing to the f sum rule. As an introduction we now derive the conductivity for a collisionless electron gas. In this case the golden rule gives the same answers as the Boltzmann equation.

The golden-rule formula for the conductivity at zero temperature is

$$\sigma(q\omega) = \tfrac{1}{2}\hbar\omega\,(\omega/c\,A_x)^{-2}\textstyle\sum_f (2\pi/\hbar)\left|\langle f|H'|0\rangle\right|^2 \times\delta(E_0+\hbar\omega-E_f) \tag{7}$$

where $|0\rangle$ is the ground state of energy E_0, and the sum runs over final states $|f\rangle$ of energy E_f. The perturbation Hamiltonian H' has two parts, the radiation field part H_{ext} and the electron-phonon part H_{ep}. Let us first consider the conductivity in the absence of electron-phonon interactions. We are neglecting Coulomb interactions between electrons throughout this paper. In a normal metal the perturbation is

$$H_{\text{ext}} = \textstyle\sum_{\vec{k}}(e/c)(\text{v}_{\vec{k}+\vec{q}/2})_x A_x\, c^\dagger_{\vec{k}+\vec{q}}c_{\vec{k}}\;, \tag{8}$$

where $c^\dagger_{\vec{k}}$ is the creation operator for a Bloch electron of wave vector $\vec{k}$, energy $\epsilon_{\vec{k}}$, and velocity $\vec{\text{v}}_{\vec{k}} = (\nabla_{\vec{k}}\epsilon_{\vec{k}})/\hbar$, and $\vec{A}$ is the vector potential of the radiation field, chosen to be in the x direction. We use Hartree-Fock states for the system, with the ground state represented by an unperturbed Fermi sea and an excited state represented by an electron-hole pair. Then Eqs. (7) and (8) yield

$$\sigma^1_{N,0}(\vec{q}, \omega) = (\pi e^2/\omega)\textstyle\sum_k v^2_{\vec{k}x} f_{\vec{k}}(1-f_{\vec{k}+\vec{q}})\delta(\hbar\omega - \hbar\vec{\text{v}}_{\vec{k}}\cdot\vec{q}), \tag{9}$$

where $f_{\vec{k}}$ is the Fermi function $[\exp(\beta\epsilon_{\vec{k}})-1]^{-1}$, β is the inverse temperature, and the wave vector $\vec{q}$ of the light is assumed small compared with $\vec{k}$. The superscripts 1 or 2 will be used to denote real or imaginary parts, the subscripts N or S will denote normal or superconducting, and the subscripts 0 or i or ph will denote the collisionless part of σ, or the part of σ arising from impurities, or the part of σ arising from phonons, respectively. Equation (9) can be readily integrated and Kramers-Kronig transformed to yield precisely the $\tau=\infty$ limit of the familiar transverse conductivity from the Boltzmann equation.[10] Furthermore, it is easily shown that (9) exhausts the f sum rule[11,12]:

$$\int_0^\infty \sigma^1_{\text{tot}}(\vec{q}, \omega)\,d\omega = \tfrac{1}{8}\omega_p^2\;. \tag{10}$$

In order to integrate Eq. (9), it is convenient to use the assumption of cubic symmetry to replace $v^2_{\vec{k}x}$ by $\frac{1}{2}[v^2_{\vec{k}} - (\vec{\text{v}}_{\vec{k}}\cdot\vec{q})^2/q^2]$. We quote the result to lowest order in ω/qv_f [which is equivalent to neglecting the part $(\vec{\text{v}}\cdot\vec{q})^2/q^2$]:

$$\sigma^1_{N,0} \cong \tfrac{3}{16}(\omega_p^2/qv_f)\,\theta(qv_f-\omega). \tag{11}$$

The θ function shows that there is no dissipation if $qv_f < \omega$. At low frequencies and temperatures, the surface impedance (2) or (3) is dominated by values of $q \gg \omega/v_f$ (in other words, the skin effect is highly anomalous). In this limit (which we shall call the Pippard limit), Eq. (11) is a good approximation to the total conductivity, and the θ function can be omitted. If this approximation is used in Eqs.

(1)–(4) the absorption is

$$A_{N,p}=\sqrt{3}\left[\frac{4}{3\pi}\left(\frac{v_f}{c}\right)\left(\frac{\omega}{\omega_p}\right)^2\right]^{1/3} \tag{12}$$

for diffuse scattering, valid when

$$\gamma\equiv\left[\left(\frac{v_f}{c}\right)\left(\frac{\omega_p}{\omega}\right)\right]^{2/3}\gg 1$$

and $\omega\tau\gg 1$.

The results for specular reflection in this regime differ by a factor $\frac{8}{9}$. Dingle[13] has presented series expansions in powers of $(1-i/\omega\tau)/\gamma$ for Z_s and Z_d^{-1}, using the complete Boltzmann equation solution for σ_N rather than the approximation (11). His results [Equation (6.4)] in the limit $\omega\tau\gg 1$, $\gamma\gg 1$ agree with (12). The code for subscripts on A is "N or S" stands for "normal or superconducting," while "cl, p, or d" stand for "classical, Pippard limit, or Dingle's series expansion." Only diffuse surface scattering will be considered from here on.

The analysis for a superconductor is completely parallel, but numerically more complicated. In order to have tractable expressions for the absorption, we choose at this point to use the Bardeen-Cooper-Schrieffer[14] (BCS) representation rather than the more accurate extension of this theory due to Nambu, Gor'kov, and Eliashberg.[15] Furthermore, we use a very simple model of the theory where the gap Δ is taken to be independent of both $\vec{k}$ and ω. These approximations are reasonable for weak coupling materials. However, for strong coupling materials such as lead, this introduces significant errors of order Δ/ω_D, where ω_D is the Debye frequency.

Within the BCS model, the perturbation Hamiltonian is

$$\begin{aligned}H_{\text{ext}}=&\textstyle\sum_k e/c(\vec{v}_{\vec{k}+\vec{q}/2})_x A_x\\&\times[l(\vec{k},\vec{k}+\vec{q})(\gamma^\dagger_{\vec{k}+\vec{q}\uparrow}\gamma_{\vec{k}\uparrow}-\gamma^\dagger_{-\vec{k}\downarrow}\gamma_{-\vec{k}-\vec{q}\downarrow})\\&-p(\vec{k},\vec{k}+\vec{q})(\gamma^\dagger_{\vec{k}+\vec{q}\uparrow}\gamma^\dagger_{-\vec{k}\downarrow}+\gamma_{\vec{k}\uparrow}\gamma_{-\vec{k}-\vec{q}\downarrow})],\end{aligned} \tag{13}$$

where $\gamma^\dagger_{k\uparrow}$ is the creation operator for a single-particle excitation of energy $E_{\vec{k}}=(\epsilon_{\vec{k}}^2+\Delta^2)^{1/2}$. The functions l and p are the "coherence factors" of BCS. At $T=0$, only the term with two quasiparticle creation operators enters in lowest order. The function p^2 is given by

$$p^2(\vec{k},\vec{k}')=\frac{1}{2}\left(1-\frac{\epsilon_{\vec{k}}\epsilon'_{\vec{k}}+\Delta_{\vec{k}}\Delta'_{\vec{k}}}{E_{\vec{k}}E'_{\vec{k}}}\right)\ . \tag{14}$$

The expression for the conductivity analogous to (9) is

$$\sigma^1_{s,0}=(\pi e^2/\omega)\textstyle\sum_{\vec{k}} v^2_{\vec{k}x}\,p^2(\vec{k},\vec{k}+\vec{q})\,\delta(E_{\vec{k}}+E_{\vec{k}+\vec{q}}-\hbar\omega). \tag{15}$$

The integration can be explicitly carried out to lowest order in ω/qv_f analogous to (11), and yields

$$\sigma^1_{S,0}+i\sigma^2_{S,0}=\sigma^1_{N,0}\,[r_1(\omega)-ir_2(\omega)], \tag{16}$$

$$r_1(\omega)=\begin{cases}0 & \text{if } \hbar\omega<2\Delta\\ \left(1+\dfrac{2\Delta}{\hbar\omega}\right)E(\eta)-\dfrac{4\Delta}{\hbar\omega}\,K(\eta) & \text{otherwise}\end{cases} \tag{17a}$$

$$r_2(\omega)=\frac{1}{2}\left(1+\frac{2\Delta}{\hbar\omega}\right)E(\eta')-\frac{1}{2}\left(1-\frac{2\Delta}{\hbar\omega}\right)K(\eta'), \tag{17b}$$

where K and E are complete elliptic integrals of the first and second kinds, respectively, and η and η' are defined by

$$\begin{aligned}\eta&=\frac{\hbar\omega-2\Delta}{\hbar\omega+2\Delta}\ ,\\ \eta'&=(1-\eta^2)^{1/2}.\end{aligned} \tag{18}$$

These results have the same range of validity as (11), and yield an absorption in the Pippard limit,

$$A_{s,p}=A_{N,p}\,\text{Re}[2e^{i\pi/3}/r(\omega)^{1/3}]. \tag{19}$$

This shows a vanishing absorption for $\omega<2\Delta$, and an absorption rapidly approaching the normal-metal value (12) when $\omega>2\Delta$. These results were first derived by Mattis and Bardeen.[16]

No integrated expressions analogous to Dingle's series expansion exist to take the superconducting absorption beyond the Pippard limit. Partial solutions to this problem have been presented by Miller.[17] However, the algebra appears prohibitively difficult, and the corrections are no more important than corrections for strong electron-phonon coupling which have been ignored in this analysis.

II. PHONON-ASSISTED ABSORPTION WITHIN THE GOLDEN RULE

In the collisionless case, the golden rule in first order gave results identical to the collisionless Boltzmann equation and satisfying the sum rule (10). To take account of collisions, we will go to second order in the golden rule. This is equivalent to a first iteration of the collision term in the Holstein-type Boltzmann equation, and will no longer be as accurate as the full solution of the Boltzmann equation. However, the loss in accuracy is partly compensated by the simplicity of the derivation and of the results. The technique works equally well for normal metals and superconductors. In Sec. IV it is shown how the golden-rule results for the normal metal follow from the weak coupling limit of the Holstein theory.

The second-order golden-rule formula consists of replacing $\langle f|H'|0\rangle$ in Eq. (7) by

$$\sum_n\frac{\langle f|H'|n\rangle\langle n|H'|0\rangle}{E_0-E_n}\,. \tag{20}$$

We are interested in final states where the electron-hole pair has a nonzero momentum, the balance of momentum being taken up by phonon creation. Elastic collisions with impurities can balance momentum in a precisely analogous way; this will be demonstrated by making a parallel calculation of the impurity conductivity. In both problems the final state in (20) can be reached from the ground state by operating once with the external field Hamiltonian [Eq. (8) for normal metals] and once with the collision Hamiltonian. The collisions will be electron-phonon interactions (H_{ep}) or electron-impurity interactions (H_{imp}), and take the form (for normal metals)

$$H_{\mathrm{ep}} = \sum_{\vec{k}\vec{k}'} M_{\vec{k}\vec{k}'} c^{\dagger}_{\vec{k}'} c_{\vec{k}} \left(a_{\vec{Q}} + a^{\dagger}_{-\vec{Q}}\right), \tag{21}$$

$$H_{\mathrm{imp}} = \sum_{\vec{k}\vec{k}'} V_{\vec{k}\vec{k}'} c^{\dagger}_{\vec{k}'} c_{\vec{k}} \;, \tag{22}$$

where $M_{\vec{k}\vec{k}'}$ ($V_{\vec{k}\vec{k}'}$) is the matrix element for scattering an electron from a Bloch state $\vec{k}$ to $\vec{k}'$ by electron-phonon (impurity) scattering, and $a^{\dagger}_{\vec{Q}}$ is the creation operator for a phonon of wave vector $\vec{Q} = \vec{k}' - \vec{k}$ and energy $\hbar\Omega_{\vec{Q}}$. Phonon-polarization indexes are suppressed, as are electron band and spin indexes.

When the summation over intermediate states in (20) is performed, using the Hamiltonians (21) and (22) in (20) and (7), we obtain for the conductivity

$$\sigma^{1}_{N,\mathrm{ph}} = \frac{2\pi e^2}{3\hbar^2\omega^3} \sum_{kk'} |M_{\vec{k}\vec{k}'}|^2 (\vec{v} - \vec{v}')^2 f(1 - f') \times \delta(\epsilon' - \epsilon + \hbar\Omega_{\vec{Q}} - \hbar\omega), \tag{23}$$

$$\sigma^{1}_{N,i} = \frac{2\pi e^2}{3\hbar^2\omega^3} \sum_{kk'} |V_{\vec{k}\vec{k}'}|^2 (\vec{v} - \vec{v}')^2 f(1 - f') \times \delta(\epsilon' - \epsilon - \hbar\omega), \tag{24}$$

where the sums go over states of single spin orientation, and subscripts $\vec{k}$ or $\vec{k}'$ are implied on the unprimed and primed variables. In deriving these expressions, energy denominators of the type $\omega - \vec{q} \cdot v_{\vec{k}}$ have been approximated by ω. This is the local approximation which together with the weak coupling approximation underlies the simple theory of the present section. The local approximation is intuitively justified for the collision terms in $\sigma(q\omega)$ by the fact that when we calculate Z using Eq. (2) or (3), the collision terms contribute mainly for small q, while at large q the results are dominated by the collisionless (surface) terms.

The summations in Eqs. (23) and (24) are most conveniently performed by integrating over constant-energy shells:

$$\sum_{kk'} G(\vec{k}, \vec{k}') \cong \left(\frac{N(0)}{2}\right)^2 \int_{-\infty}^{\infty} d\epsilon \int_{-\infty}^{\infty} d\epsilon' \langle\langle G(\epsilon, \hat{k}, \epsilon', \hat{k}')\rangle\rangle , \tag{25}$$

where $N(0)$ is the unrenormalized density of states for both spin orientations at the Fermi energy (which is taken as the zero of energy). The angular brackets denote averages over the Fermi surface (FS):

$$\langle\langle G(\hat{k}, \hat{k}')\rangle\rangle \equiv \int_{\mathrm{FS}} \frac{dS}{|\vec{v}|} \int_{\mathrm{FS}} \frac{dS'}{|\vec{v}'|} G(\hat{k}, \hat{k}') \left(\int_{\mathrm{FS}} \frac{dS}{|\vec{v}|} \int_{\mathrm{FS}} \frac{dS'}{|\vec{v}'|} \right)^{-1} . \tag{26}$$

In writing (25) we use the fact that the integrand G is rapidly varying in ϵ and ϵ' only very near the Fermi surface, and falls to zero elsewhere; we have also assumed that very close to the Fermi surface the angular variation in $\hat{k}$ and $\hat{k}'$ is independent of ϵ and ϵ'. Now we define

$$\alpha^2_{\mathrm{tr}}(\Omega) F(\Omega) = \frac{N(0)}{4v^2_{F,0}} \langle\langle |M_{\vec{k}\vec{k}'}|^2 (\vec{v} - \vec{v}')^2 \delta(\hbar\Omega_Q - \hbar\Omega)\rangle\rangle , \tag{27}$$

$$\frac{1}{\tau_{N,i}} = \frac{\pi N(0)}{2v^2_{F,0}\hbar} \langle\langle |V_{\vec{k}\vec{k}'}|^2 (\vec{v} - \vec{v}')^2 \rangle\rangle ,$$

where $\alpha^2_{\mathrm{tr}}F$ is a phonon density of states weighted by the amplitude for large-angle scattering on the Fermi surface. It is closely related to the phonon density of states F, the dc electrical resistivity, and among other properties, the function $\alpha^2_0 F$ which is measured by superconducting tunneling.[3] This function and its relatives and their properties are more fully discussed in the Appendix. Using these definitions, the conductivities (23) and (24) can be written in the form

$$\sigma^1 = (\omega_p^2/4\pi\omega)(1/\omega\tau), \tag{29}$$

where $\tau_{N,i}$ is given by Eq. (28) and $\tau_{N,\mathrm{ph}}$ is given by

$$\frac{1}{\tau_{N,\mathrm{ph}}} = \frac{2\pi}{\omega} \int_0^{\omega} d\Omega\, (\omega - \Omega)\, \alpha^2_{\mathrm{tr}} F(\Omega). \tag{30}$$

The form (29) is the Drude formula to lowest order in $(\omega\tau)^{-1}$, which is the effective expansion parameter of our perturbation-theory approach. Equation (28) is the standard expression for the impurity-limited transport scattering time in lowest-order perturbation theory. Equation (30) is the analogous expression for the phonon-limited transport scattering time. This scattering time is frequency dependent, going to infinity as ω^{-5} for frequencies low compared with typical phonon frequencies, and approaching a constant value first found by Holstein[2] for frequencies above the phonon frequencies. In the notation of (A12), this limiting value is

$$1/\tau_{N,\mathrm{ph}} \rightarrow \pi\lambda_{\mathrm{tr}} \langle\omega\rangle_{\mathrm{tr}} , \tag{31}$$

where $\langle\omega\rangle_{\mathrm{tr}}$ is an average phonon frequency calculated using $\alpha^2_{\mathrm{tr}}F(\omega)/\omega$ as a weight function, and λ_{tr} is an effective coupling constant, defined as twice the normalization of the weight function,

$$\lambda_{\mathrm{tr}} = 2 \int \frac{d\omega}{\omega}\, \alpha^2_{\mathrm{tr}} F(\omega). \tag{32}$$

By use of Eq. (A11), this limiting relaxation time can be related to the high-temperature dc conductivity $\sigma = ne^2\tau_\sigma/m$:

$$1/\tau_{N,\mathrm{ph}} \to (1/\tau_\sigma)(\hbar\langle\omega\rangle_{\mathrm{tr}}/2k_BT), \tag{33}$$

where T is the temperature at which the resistivity τ_σ is measured. In the model of a Debye spectrum and a constant matrix element for electron-phonon coupling, $\alpha^2_{\mathrm{tr}}F$ scales as ω^4 and $\langle\omega\rangle_{\mathrm{tr}} = \frac{4}{5}\omega_D$. Using this model, Eq. (33) reduces to the result given by Holstein.[2]

The formula (30) for the transport relaxation time can be contrasted with the random-phase-approximation (RPA) results for the lifetime τ_0 for a quasiparticle of energy ω to decay by phonon emission [see Eq. (56)]:

$$\frac{1}{\tau_0} \equiv \frac{2|\Gamma(\omega)|}{\hbar} = 2\pi\int_0^\omega d\Omega\, \alpha_0^2 F(\Omega), \tag{34}$$

where α_0^2F is the isotropically weighted phonon density of states defined by Eq. (A2). At low frequencies α_0^2F scales as ω^2 and τ_0 goes to infinity as ω^3. If the difference between α^2_{tr} and α_0^2 is neglected, the transport lifetime $\tau^{-1}_{N,\mathrm{ph}}$ is an *average* of τ_0^{-1} over the frequency range 0 to ω. Thus, $\tau_{N,\mathrm{ph}}$ has less structure than τ_0. The difference between α^2_{tr} and α_0^2 causes $\tau_{N,\mathrm{ph}}$ to exceed τ_0, especially at low frequencies. This reflects the well-known fact that small-angle scatterings are inefficient in relaxing a current-carrying electron distribution.

It is interesting to ask how well the conductivities derived in second order [Eqs. (29) and (30)] satisfy the sum rule (10). In the impurity case, Eq. (29) diverges when used in the sum rule (10). This divergence is easily understood. Our perturbation theory is an expansion in powers of $(\omega\tau)^{-1}$, which fails to be small at very small ω. The use of a Boltzmann equation (or a T matrix) rectifies the situation, yielding the familiar transverse conductivity which does satisfy (10).

In the case of phonons, there is no divergence at small ω; $(\omega\tau_{\mathrm{ph}})^{-1}$ is small and low-order perturbation theory is valid both at low frequencies and at high frequencies. At frequencies near ω_D, however, $(\omega\tau_{\mathrm{ph}})^{-1}$ approaches unity and low-order perturbation theory is suspect. The use of Eq. (30) in the sum rule (10) yields

$$\int_0^\infty d\omega\, \sigma^1_{N,\mathrm{ph}}(\omega) = \tfrac{1}{8}\omega_p^2\lambda_{\mathrm{tr}}. \tag{35}$$

Thus, if the coupling constant λ_{tr} is small, the sum rule is not badly violated. For large λ_{tr}, one might expect that the effect of higher-order corrections would be to reduce the contribution (35) by a renormalization factor $(1+\lambda_{\mathrm{tr}})^{-1}$. An argument for the plausibility of this approach is provided by the fact, first pointed out by Holstein[5] (and rederived in Sec. IV), that in the low-frequency limit the optical mass is renormalized by the factor $(1+\lambda_{\mathrm{tr}})$. Thus, the sum rule (10) can be exactly satisfied if the total conductivity is considered as a sum of the collisionless conductivity and the phonon term (30), with the effective plasma frequency in each case reduced by $(1+\lambda_{\mathrm{tr}})^{-1}$. This is really only an *ad hoc* procedure. A more accurate scheme for including higher-order corrections, discussed in Sec. IV, is not quite equivalent.

We now fill in an analogous derivation of the effect of collisions on the conductivity in superconductors. The Hamiltonians analogous to (21) and (22) are

$$H_{\mathrm{ep}} = \sum_{\vec{k}\vec{k}'} M_{\vec{k}\vec{k}'}(a_{\vec{Q}} + a^\dagger_{-\vec{Q}})[n(\vec{k},\vec{k}')(\gamma^\dagger_{\vec{k}'\uparrow}\gamma_{\vec{k}\uparrow} + \gamma^\dagger_{-\vec{k}\downarrow}\gamma_{-\vec{k}'\downarrow})$$
$$+ m(\vec{k},\vec{k}')(\gamma^\dagger_{\vec{k}'\uparrow}\gamma^\dagger_{-\vec{k}\downarrow} - \gamma_{\vec{k}\uparrow}\gamma_{-\vec{k}'\downarrow})], \tag{36}$$

$$H_{\mathrm{imp}} = \sum_{kk'} V_{\vec{k}\vec{k}'}\,[\quad], \tag{37}$$

where the quantity in brackets in (37) is identical to that in (36), and n and m are coherence factors similar to l and p in Eq. (13). The calculation will be carried out only in the local limit $(\vec{q}\cdot\vec{v}_{\vec{k}} \ll \omega)$ and at $T=0$. In these limits, the coherence factors can be written

$$l(\vec{k},\vec{k}+\vec{q}) \approx 1, \quad p(\vec{k},\vec{k}+\vec{q}) \approx 0,$$
$$m(\vec{k},\vec{k}') = \left[\frac{1}{2}\left(1 - \frac{\epsilon\epsilon' - \Delta\Delta'}{EE'}\right)\right]^{1/2}. \tag{38}$$

Note that in this approximation the factor p, which was responsible for the collisionless absorption, now vanishes. This corresponds to the fact that in the local limit, light cannot create excitations in a Fermi gas, normal or superconducting. The effect of the light is through the factor l which governs the scattering of light by excitations already present. At $T=0$ the only excitations present are those created by the collision terms (36) or (37), and this is governed by the term proportional to m. The factor n thus cannot enter the conductivity in lowest order. The expressions for the conductivity are

$$\sigma^1_{S,\mathrm{ph}} = \frac{\pi e^2}{3\hbar^2\omega^3}\sum_{\vec{k}\vec{k}'} |M_{\vec{k}\vec{k}'}|^2(\vec{v}-\vec{v}')^2\,\frac{1}{2}\left(1 - \frac{\epsilon\epsilon'-\Delta\Delta'}{EE'}\right)$$
$$\times\,\delta(E+E'+\hbar\Omega_{\vec{Q}}-\hbar\omega), \tag{39}$$

$$\sigma^1_{S,i} = \frac{\pi e^2}{3\hbar^2\omega^3}\sum_{\vec{k}\vec{k}'} |V_{\vec{k}\vec{k}'}|^2(\vec{v}-\vec{v}')^2\,\frac{1}{2}\left(1 - \frac{\epsilon\epsilon'-\Delta\Delta'}{EE'}\right)$$
$$\times\,\delta(E+E'-\hbar\omega). \tag{40}$$

These are analogous to (23) and (24), with the coherence factor m^2 now playing the role of the Fermi factors.

The integrations can now be carried out by analogy with the normal-state calculation to yield

$$\sigma^1_S = (\omega_p^2/4\pi\omega)(1/\omega\tau_s), \tag{41}$$

$$\frac{1}{\tau_{S,\mathrm{ph}}}=\frac{2\pi}{\omega}\int_0^{\omega-2\Delta}d\Omega\,(\omega-\Omega)E\left[\left(1-\frac{4\Delta^2}{(\omega-\Omega)^2}\right)^{1/2}\right]\times\alpha_{\mathrm{tr}}^2F(\Omega), \tag{42}$$

$$\frac{1}{\tau_{S,i}}=\frac{1}{\tau_{N,i}}\,E\left[\left(1-\frac{4\Delta^2}{\omega^2}\right)^{1/2}\right], \tag{43}$$

where E is the complete elliptic integral of the second kind. Both relaxation times (42) and (43) are infinite when the frequency is less than 2Δ. These results reduce to the normal-metal results at large frequencies.

The results (30) and (42) are precisely equivalent to the semiquantitative expressions of JR, with three modifications: (a) It is now possible to fix the over-all magnitude. (b) The effect of the electron-light matrix element which was left out by JR is to convert the isotropic density of states α_0^2F to the anisotropic form α_{tr}^2F. (c) The introduction of coherence factors in the superconducting case serves to simplify the JR theory by eliminating a term proportional to the elliptic integral K which occurs in their Eq. (3). This also has the effect of sharpening the threshold of Holstein volume absorption.

III. CALCULATION BASED ON THE GOLDEN-RULE THEORY

In Sec. I we presented nonlocal conductivities for normal and superconducting metals in the absence of collisions. In Sec. II the contribution to the local conductivities arising from collisions was calculated in lowest order. We now present a simple approximate scheme for calculating the total absorption, and compare the results with the measurements of JR on lead. The scheme consists of taking the absorption to be the sum of the Pippard-limit absorption for the collisionless gas and the classical absorption for the collision terms. This is essentially the procedure used by JR to analyze their data. The scheme has obvious defects, the worst of them being that it is a poor approximation for the superconducting absorption in the case of a strong coupling material like lead. The scheme does have virtues, namely, it provides a simple analytical form for analyzing experimental data. Furthermore, it provides a faithful representation of the structure to be expected in the normal-state data, and is quantitatively not far wrong. In the case where it fails badly, namely, the superconducting state with strong coupling, the only recourse is a complicated theory based on numerical solutions of the Nambu-Gor'kov-Eliashberg[15] integral equations.

The first step in calculating the phonon-assisted absorption is the determination of the function $\alpha_{\mathrm{tr}}^2F(\omega)$. Calculations of the related function $\alpha_0^2F(\omega)$ have been discussed previously.[18] For Pb, $\alpha_0^2F(\omega)$ is known from experiment. For the purpose of calculating the ratio $\alpha_{\mathrm{tr}}^2/\alpha_0^2$ we have used a "spherical model"[19] characterized as follows:

(i) The phonon spectrum $\Omega_{\vec{Q}}$ is approximated by spherically symmetric functions.

(ii) The phonon-polarization vectors are taken to be purely longitudinal or purely transverse.

(iii) The Fermi surface is represented by the free-electron sphere, with an isotropic mass m_b/m given by the ratio of the band-structure density of states to the free-electron value.

(iv) The wave functions on the Fermi surface are approximated by single orthogonalized plane waves (OPW's).

(v) The electron-ion matrix element is represented by a pseudopotential. For Pb we have found[19] the model potential of Animalu and Heine[20] to be adequate.

(vi) Umklapps are explicitly included. This leads to errors at small ω where the single OPW model allows unphysical umklapps to occur. However, in this region α_{tr}^2F is very small and errors are unimportant.

The spherical model is probably quite good[19] for calculating the coupling constant λ; it is less good for α_0^2F, and certainly still less good for α_{tr}^2F. However, it is probably reasonably fair when used to calculate the ratio $\alpha_{\mathrm{tr}}^2/\alpha_0^2$. Using the techniques described in Ref. 19, we have calculated this ratio, which turns out to be a decreasing function of ω in the important part of the phonon spectrum. The most important feature of the ratio is that is is half as large in the region of the longitudinal-phonon peak (ω_l) as it is in the region of the transverse peak (ω_t). This is because the factor $(\vec{v}-\vec{v}\,')^2$ in α_{tr}^2 tends to eliminate most of the normal (N) scattering contribution which occurs in α_0^2, while leaving the umklapp (U) part less altered. This results in a bigger reduction in the longitudinal-phonon contribution than in the transverse contribution. This matter is discussed further in the Appendix. Accordingly, in our calculations we have taken the empirical α_0^2F of McMillan and Rowell[3] and scaled it by a linear function of ω which is twice as large at ω_t as it is at ω_l . The over-all magnitude was adjusted to give $\lambda_{\mathrm{tr}}=0.9$, a value calculated in the spherical model.[21]

As a partial justification of our simple scheme for the absorption, we have made a more complicated calculation for the normal metal. This consists of taking the familiar transverse conductivity from the Boltzmann equation in the collision-time approximation, using the frequency-dependent collision time (30). In Sec. IV it is shown that this is the correct form for the weak coupling theory. The resulting absorption is shown in Fig. 1, based on Dingle's series expansion[13] for diffuse boundary conditions. The over-all shape is in fairly good agreement with the experimental data, in contrast with the absorption predicted when the collision time is infinite. The absolute magnitude of the data has been scaled by JR to agree with the Dingle theory at around 30 cm^{-1}. The extra absorption due to phonons appears as increases in the slope of absorption vs frequency occurring at the transverse- and longitudinal-phonon frequencies. A precise comparison between theory and experiment is not possible, because the noise level in the experimental data is quite high.

The results of our simple approximate scheme for normal lead are shown in Fig. 2. In this figure the inverse lifetime $\tau_{N,\mathrm{ph}}^{-1}$ has been scaled by the semiphenomenological factor $(1+\lambda_{\mathrm{tr}})^{-1}$. The agreement with experiment is fortuitously good. By comparison with Fig. 1, it is clear that the Pippard limit overestimates the collisionless absorption at higher frequencies, although it is asymptotically correct at lower frequencies. However, the classical limit scaled down by $(1+\lambda_{\mathrm{tr}})^{-1}$ agrees very well with the extra phonon-induced absorption. This can be understood as follows: The extra absorption can be written as a power series in $(\omega\tau)^{-1}$, with the first term adequate everywhere except possibly near ω_D. The coefficient of this term is such that the extra absorption can be written

$$A_{\mathrm{tot}}-A_s=\Phi(\omega)(2/\omega_p\tau_{\mathrm{ph}}), \qquad (44)$$

where $\Phi(\omega)$ is weakly varying with frequency. In the wave-number range 50–150 cm^{-1}, Φ is close to 0.5 [and not very different from $(1+\lambda_{\mathrm{tr}})^{-1}$]. At high wave numbers (near 1000 cm^{-1}), Φ approaches the classical value of 1.

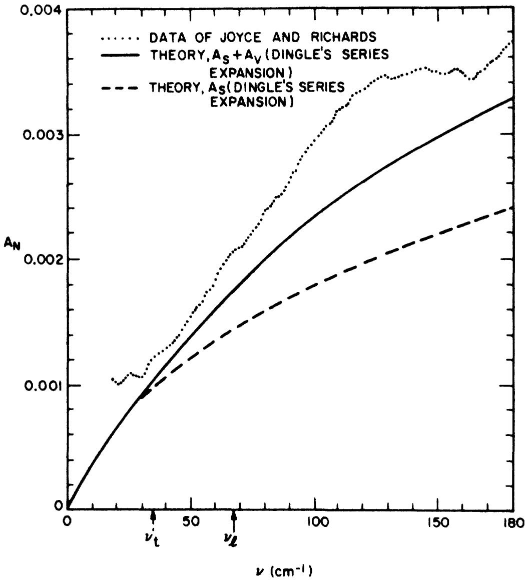

FIG. 1. Absorption vs frequency for normal lead. The surface absorption (A_s) is calculated from Dingle's series expansions (Ref. 13) for diffuse boundary conditions, using free-electron parameters for lead and $\tau=\infty$. The total absorption (A_s+A_v) is calculated in the same way, using the frequency-dependent phonon-limited lifetime τ as explained in the text. The experimental data is from Joyce and Richards (Ref. 1). The structure near 150 cm^{-1} is instrumental in origin.

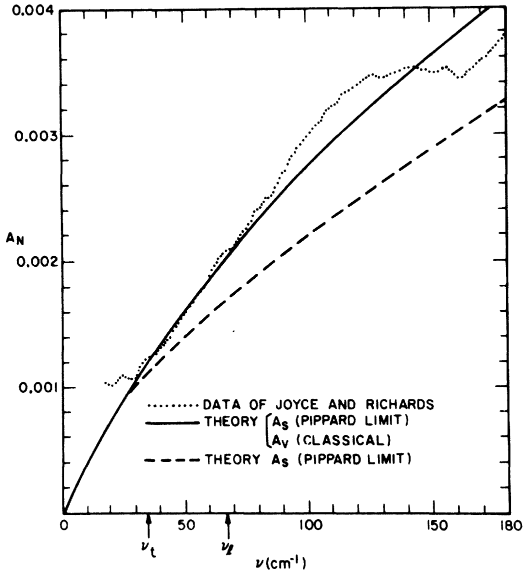

FIG. 2. Absorption vs frequency for normal lead. The surface absorption (A_s) is calculated in the Pippard limit for diffuse boundary conditions and scales as $\omega^{2/3}$. (This corresponds to the first term of Dingle's series expansions, Ref. 13.) The volume absorption (A_v) is calculated in the classical limit, and equals $(2/\omega_p\tau)(1+\lambda_{\mathrm{tr}})^{-1}$. The experimental structure near 150 cm^{-1} is instrumental in origin.

A similar series expansion undoubtedly holds for superconductors, although no one has derived it yet. Thus, it is reasonable to try the same approximation. This is illustrated in Fig. 3. The Pippard limit has again been used for the collisionless absorption, and is expected to be an overestimate at high frequencies. The structure in the phonon-assisted absorption is somewhat more visible in both the theory and experiment than it was in the normal-metal case. This is a consequence of the peak in the electronic density of states of the superconductor. There are real discrepancies between theory and experiment in Fig. 3. The most serious discrepancy is the failure to reproduce the observed sharpness in the onset of absorption above the energy gap. This discrepancy is well known, and has been resolved by Swihart and Shaw,[22] using the strong coupling theory of Nam.[9] They found that the strong coupling effects and departures from

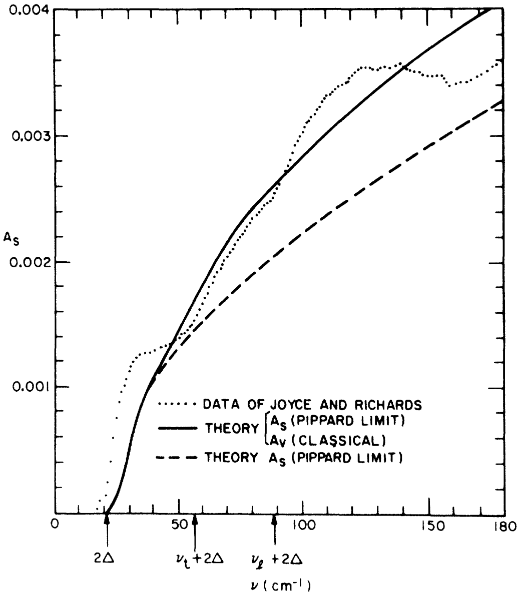

FIG. 3. Absorption vs frequency for superconducting lead. The surface absorption (A_s) is calculated in the Pippard limit for diffuse boundary conditions. The volume absorption (A_v) is calculated in the classical limit and equals $(2/\omega_p\tau)(1+\lambda_{tr})^{-1}$. The experimental structure near 150 cm^{-1} is instrumental in origin.

the Pippard limit were of roughly equal importance in explaining the extra steepness of the absorption onset. However, even away from the onset, the experiment shows sharper structure than the simple theory.

Figure 4 shows the ratio of the absorption in the superconducting state to that in the normal state. When plotted this way, the data show strong structure associated with the phonons, and the noise level is expected to be smaller than in the previous figures because spurious structure associated with cavity modes is eliminated. The structure in the theoretical curve is not as dramatic as in the measured curve; three sources contribute to this discrepancy. The first source is the local approximation for the collisions and the Pippard limit (nonlocal) for the surface absorption. The truth for lead lies between these two extremes. Hopefully, the extremes give qualitatively correct answers. The second source is the breakdown near $\omega=\omega_D$ of the expansion in powers of $(\omega\tau)^{-1}$, which we will call strong coupling of the first kind. The third source is a more fundamental limitation of our theory. This is the structure of the superconducting gap function $\Delta(\omega)$ (strong coupling of the second kind) which was eliminated by our use of the BCS theory. For a strong coupling superconductor, there is in fact no separation between collisionless and interacting cases. When phonon collisions are eliminated, the superconductor goes normal. If a correct treatment of the strongly coupled superconductor is used to calculate optical properties, as in Nam's formulation,[9] strong images of the phonon spectrum may be expected.[22,23] This occurs even though real collisions are not entirely accounted for in a theory like Nam's which omits ladder diagrams. Much of the effect of real phonons is automatically included through the imaginary part of the self-energy corrections, which must necessarily be present in a correct treatment of the superconducting state. In addition, there are strong dispersive effects in the real part of the superconducting self-energy. It is these strong coupling effects of the second kind which are probably responsible for much of the discrepancy between theory and experiment in Fig. 4, including the noticeable shift of the experimental absorption onsets to higher frequencies.[1,24] Strong coupling of the first kind also is important, but gives results not very different from the weak coupling theory, as shown in Sec. IV.

It must be concluded that the golden-rule theory has serious limitations when applied to strong coupling superconductors. The limitations should be less important for the normal state, although the data are not good enough yet to confirm this. However, the theory does give a good qualitative explanation of the features observed, and should be quantitatively correct for weak coupling metals.

IV. HOLSTEIN THEORY FOR NORMAL METALS

In Sec. II we showed that a weak coupling theory of the local conductivity reproduces the semiphe-

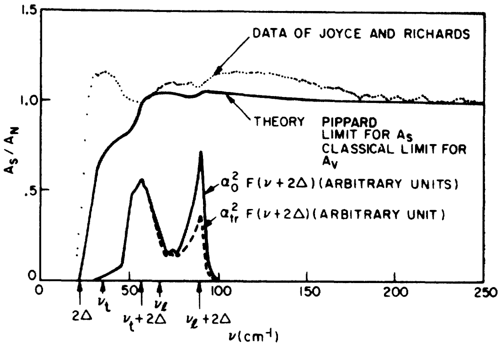

FIG. 4. Ratio of superconducting-to-normal absorption vs frequency in lead. The theory uses the Pippard limit with diffuse boundary conditions for the surface absorption (A_s) and the classical limit for the volume absorption (A_v). The *ad hoc* factor $(1+\lambda_{tr})$ is not included in the volume absorption. Also shown is the isotropically weighted electron-phonon density of states α_0^2F deduced from superconducting tunneling experiments by McMillan and Rowell (Ref. 3) and the anisotropically weighted version α_{tr}^2F appropriate for the conductivity as defined in the text.

nomenological theory used by JR to analyze their data on Pb. However, numerical calculations presented in Sec. III show that the discrepancies between this theory and experiment are more severe than was believed by JR. This is not surprising, since neither weak coupling nor a local approximation are particularly valid for lead.

In this section we analyze the infrared absorption from the point of view of the most complete theory available, the Holstein theory[5] for normal metals. This theory is parallel to but more complete than Nam's theory[9] for superconductors. In both theories, the conductivity is calculated by a diagrammatic analysis of the current-current correlation function using thermal Green's functions. Both theories include phonon self-energy corrections exactly to first order in $(m/M)^{1/2}$, where m/M is the electron-to-ion mass ratio. The Holstein theory then includes ladder diagrams exactly to the same order by writing an integral equation (the Bethe-Salpeter equation). The theory obeys local charge conservation. The Nam theory leaves out the ladder diagrams, contains no additional integral equations [beyond those necessary to calculate the superconduction energy gap $\Delta(\omega)$], and can be expected to violate local charge conservation. In spite of the shortcomings of Nam's theory, we shall see that the formal solution of the Holstein theory is very similar to the normal limit of Nam's theory. This partially justifies the Nam theory and explains the success of calculations based on it.[22-24]

The Bethe-Salpeter equation of Holstein's theory yields an integral equation for the conductivity, which has the form of a generalized Boltzmann equation,

$$\sigma(q,\omega)=2e^2\sum_{\vec{k}} v_{\vec{k}x}\Phi_{\vec{k}}\left(\frac{f(\epsilon_{\vec{k}})-f(\epsilon_{\vec{k}}+\hbar\omega)}{\hbar\omega}\right) , \tag{45}$$

$$i(\vec{q}\cdot\vec{v}_{\vec{k}}-\omega)\Phi_{\vec{k}}=v_{\vec{k}x}+\frac{i}{\hbar}\sum_{k'}|M_{\vec{k}\vec{k}'}|^2(\Phi_{\vec{k}}-\Phi_{\vec{k}'})\left\{\quad\right\} , \tag{46}$$

where

$$\left\{\quad\right\}=\frac{f(\epsilon')+N(\omega_{\vec{q}})}{\epsilon-\epsilon'+\hbar\omega_{\vec{q}}-i\delta}+\frac{1-f(\epsilon')+N(\omega_{\vec{q}})}{\epsilon-\epsilon'-\hbar\omega_{\vec{q}}-i\delta}$$
$$-\frac{f(\epsilon'+\hbar\omega)+N(\omega_{\vec{q}})}{\epsilon-\epsilon'+\hbar\omega_{\vec{q}}+i\delta}-\frac{1-f(\epsilon'+\hbar\omega)+N(\omega_{\vec{q}})}{\epsilon-\epsilon'-\hbar\omega_{\vec{q}}+i\delta} \tag{47}$$

and where δ is a positive infinitesimal, $N(\omega)$ is the Bose function $(e^{\beta\omega}-1)^{-1}$, and ϕ plays role of the distribution function. Holstein[5] has also derived coupled equations for the electron- and phonon-distribution functions for the case where both distributions deviate from equilibrium. However, we shall assume that the phonons are in equilibrium.

The kernel of the integral equation (46) bears a striking resemblance to the equation for the electronic self-energy arising from phonons:

$$\Sigma(\omega\pm i\delta)=M(\omega)\mp i\Gamma(\omega)=\int_0^{\omega_D}d\omega'\int_{-\infty}^{\infty}d\epsilon'\,\alpha_0^2F(\omega')$$
$$\times\left(\frac{f(\epsilon')+N(\omega')}{\omega-\epsilon'+\omega'\pm i\delta}+\frac{1-f(\epsilon')+N(\omega')}{\omega-\epsilon'-\omega'\pm i\delta}\right) . \tag{48}$$

We have assumed isotropy of the electron-phonon system in neglecting the $\vec{k}$ dependence of Σ in (48). We can exploit this resemblance and obtain a formal solution of the integral equation. The technique is similar to the method of Scher,[6] who found solutions in the local $(q=0)$ limit. We make the *ansatz*

$$\Phi_k=v_{kx}/i[\vec{q}\cdot\vec{v}_{\vec{k}}-\omega-W_{\vec{k}}(\vec{q},\omega)]. \tag{49}$$

Then the integral equation (46) becomes an equation for W which can be written

$$W_{\mathbf{k}}=\left(\frac{\Sigma_{1r}(\epsilon-i\delta)-\Sigma_{1r}(\epsilon+\omega+i\delta)}{\hbar}\right) , \tag{50}$$

where Σ_{1r} is the same as Σ in Eq. (48) except that α_0^2 is replaced by α_{1r}^2 defined as

$$\alpha_{1r}^2F(\omega)\equiv\frac{N(0)}{2}\left\langle\left\langle|M_{\vec{k}\vec{k}'}|^2\left(1-\frac{v_x'}{v_x}\frac{\vec{q}\cdot\vec{v}-\omega-W}{\vec{q}\cdot\vec{v}'-\omega-W'}\right)\right.\right.$$
$$\left.\left.\times\,\delta(\hbar\omega-\hbar\omega_{\vec{q}})\right\rangle\right\rangle . \tag{51}$$

Note that Eq. (50) is still implicitly an integral equation for W. However, the integrand depends on W only through the function (51) which can be seen to be independent of W in a number of limits. These limits are (i) $\vec{q}\cdot\vec{v}\gg\omega$; (ii) $\vec{q}\cdot\vec{v}\ll\omega$, and either (a) $\omega\gg\omega_D$, or (b) $\omega\ll\omega_D$. In fact, in the frequencies of interest for the infrared absorption problem, there is only the region $qv_F\lesssim\omega$, $\omega\sim\omega_D$, where α_{1r}^2F depends significantly on W. It is precisely this region which Scher[6] has solved by an iterative method for the case of an Einstein phonon spectrum. He found that even in this region W' could be approximated by W, causing an error of less than 2%. Equations (50) and (51) then determine W in terms of a weighted density of states α_{1r}^2F which is effectively independent of W. Thus, the transport problem is formally solved. The angular weighting factor of α_{1r}^2,

$$1-\frac{v_x'}{v_x}\frac{\vec{q}\cdot\vec{v}-\omega-W}{\vec{q}\cdot\vec{v}'-\omega-W} ,$$

is more complicated than the factor $(\vec{v}-\vec{v}')^2/v^2$ of the function α_{tr}^2 of the simple theory. However, in the local limit, in cubic symmetry, and neglecting umklapps, they are the same.

One region of phase space where Eq. (50) remains an integral equation is the dc limit

$$(\vec{q}\cdot\vec{v},\ \omega) \ll k_B T \ll k_B \Theta_D\ ,$$

where Θ_D is the Debye temperature. In this limit, the dc conductivity has been solved by variational techniques which give the result (A5). Nam's theory gives an incorrect expression for the dc conductivity. However, if the temperature is of the order of the Debye temperature or higher, Eq. (50) is no longer an integral equation and the result (A10) is obtained.

It is convenient to rewrite Eq. (50) as

$$W = \omega\lambda_{1r}(\epsilon,\ \omega) + i/\tau_{1r}(\epsilon,\ \omega), \tag{52}$$

$$\lambda_{1r} = [M_{1r}(\epsilon+\omega) - M_{1r}(\epsilon)]/\hbar\omega\ , \tag{53}$$

$$1/\tau_{1r} = [\Gamma_{1r}(\epsilon+\omega) + \Gamma_{1r}(\epsilon)]/\hbar\ , \tag{54}$$

where λ_{1r} and τ_{1r} play the roles of effective renormalization and scattering-time parameters. Explicit equations for M_{1r} and Γ_{1r} at zero degrees are

$$M_{1r}(\epsilon) = \int_0^{\omega_D} d\omega'\ \alpha_{1r}^2 F(\omega')\ \ln\left|\frac{\epsilon-\omega'}{\epsilon+\omega'}\right|\ , \tag{55}$$

$$\Gamma_{1r}(\epsilon) = \pi\textstyle\int_0^{|\epsilon|} d\omega'\ \alpha_{1r}^2 F(\omega')\ . \tag{56}$$

The formal solution for the conductivity has the form [from Eqs. (45), (49), and (50)]

$$\sigma(q,\ \omega) = -ie^2 N(0)\int_{-\hbar\omega}^{0}\frac{d\epsilon}{\omega} \times\left\langle\frac{v_x^2}{\vec{q}\cdot\vec{v}_{\vec{k}} - \omega[1+\lambda_{1r}(\epsilon,\ \omega)] - i/\tau_{1r}(\epsilon,\ \omega)}\right\rangle, \tag{57}$$

where the angular brackets denote averaging over the Fermi surface in the manner of Eq. (26). This formula is similar to the usual solution of the semiclassical Boltzmann equation. Arguing intuitively, Scher[6] proposed essentially the result (57) as a semiphenomenological method of including nonlocal effects into his local theory.

In the weak coupling limit, defined by $\lambda_{1r} \ll 1$ and $1/\omega\tau_{1r} \ll 1$, Eq. (57) can be simplified

$$\sigma(q,\ \omega) \cong -ie^2 N(0)\left\langle\frac{v_x^2}{\vec{q}\circ\vec{v}_{\vec{k}} - \omega[1+\bar{\lambda}(\omega)] - i/\bar{\tau}(\omega)}\right\rangle, \tag{58}$$

where $\bar{\lambda}$ and $\bar{\tau}$ are defined by

$$\bar{\lambda}(\omega) = \int_{-\hbar\omega}^{0}\frac{d\epsilon}{\hbar\omega}\ \lambda_{1r}(\epsilon,\ \omega)$$

$$= -\frac{2}{\omega}\int_0^{\omega_D} d\omega'\ \alpha_{1r}^2 F(\omega') \times\left[\ln\left|\frac{\omega-\omega'}{\omega+\omega'}\right| - \frac{\omega'}{\omega}\ln\left|\frac{\omega^2-\omega'^2}{\omega'^2}\right|\right]\ , \tag{59}$$

$$\frac{1}{\bar{\tau}(\omega)} = \int_{-\hbar\omega}^{0}\frac{d\epsilon}{\hbar\omega}\ \frac{1}{\tau_{1r}(\epsilon,\ \omega)}$$

$$= \frac{2\pi}{\omega}\int_0^{\omega} d\omega'\ (\omega-\omega')\ \alpha_{1r}^2 F(\omega')\ . \tag{60}$$

Note that if α_{1r}^2 is replaced by α_{tr}^2 (which is a good approximation when $qv_F < \omega$) then $1/\bar{\tau}(\omega)$ is identical to $1/\tau_{N,\mathrm{ph}}(\omega)$ derived in Eq. (30). Moreover, the renormalization parameter $\bar{\lambda}(\omega)$ is intimately related to the Kramers-Kronig transform of $1/\tau_{N,\mathrm{ph}} \times(\omega)$. In the limit of small frequencies $\bar{\lambda}(\omega)$ becomes a constant, equal to λ_{tr} if α_{1r}^2 equals α_{tr}^2. The weak coupling equation (58) can be rewritten as

$$\sigma(\vec{q},\ \omega) = -ie^2 N^*(0)\left\langle\frac{v_x^{*2}}{\vec{q}\cdot\vec{v}_{\vec{k}} - \omega - i/\tau^*(\omega)}\right\rangle. \tag{61}$$

This is identical to the solution of the usual semiclassical Boltzmann equation in the scattering-time approximation, with a renormalized velocity, density of states, and scattering time defined by

$$\vec{v}^* \equiv \vec{v}/[1+\bar{\lambda}(\omega)]\ ,$$
$$N^*(0) \equiv N(0)[1+\bar{\lambda}(\omega)]\ , \tag{62}$$
$$1/\tau^*(\omega) = 1/\bar{\tau}(\omega)[1+\bar{\lambda}(\omega)]\ .$$

For a spherical Fermi surface, (61) leads to the well-known expressions

$$\sigma = \frac{3}{16\pi i}\ \frac{\omega_p^{*2}}{\omega + i/\tau^*}\ g\!\left(\frac{qv_F^*}{\omega + i/\tau^*}\right)\ , \tag{63}$$

$$g(x) = \frac{1}{x^3}\left[(x^2-1)\ln\!\left(\frac{1-x}{1+x}\right) + 2x\right]\ , \tag{64}$$

$$\omega_p^* = \omega_p^2/[1+\bar{\lambda}(\omega)]\ . \tag{65}$$

Equation (65) shows the result, first proved by Holstein,[5] that the optical mass at low frequencies is renormalized by the phonons. However, at low frequencies, for a good metal at low temperatures the Pippard limit determines the optical properties. In this limit, $g(x) = i\pi/x$ and renormalization effects do not appear in the conductivity (63) or the absorption (12). This was first shown by Nakajima and Watabe.[25]

V. CALCULATION BASED ON HOLSTEIN THEORY

Scher[6] has presented solutions of the Holstein-Boltzmann equation (46) in the local limit. His method is equivalent to the use of Eqs. (57) and (51) with $\vec{q}$ set equal to zero. The weighting factor

$$\left(1 - \frac{v_x'}{v_x}\ \frac{\vec{q}\cdot\vec{v} - \omega - W_{\vec{k}}(q,\ \omega)}{\vec{q}\cdot\vec{v}' - \omega - W_{\vec{k}'}(q,\ \omega)}\right) \tag{66}$$

then becomes equal to the usual transport weighting factor

$$\left(1-\frac{\vec{v}\cdot\vec{v}'}{\vec{v}\cdot\vec{v}}\right)\sim\left(1-\frac{v_x'}{v_x}\right) \tag{67}$$

in the two extreme limits $\omega \ll \omega_D$ (where W is a constant) and $\omega \gg \omega_D$ (where $W \ll \omega$). In the region $\omega \sim \omega_D$, an integral equation needs to be solved. He found that for an Einstein model, the solutions of the integral equation were very similar to the simple integral obtained using (67) in place of (66). He then replaced (67) by a constant factor 0.56, obtained from the Animalu-Heine pseudopotential. He finally used the classical approximation (5) to obtain the absorption. In this context the classical approximation has roughly the same validity as the calculations of Sec. III, i.e., it can be viewed as the leading contribution from collisions in the Dingle series expansion. Scher's work goes beyond the approximate theory of Secs. II and III by including dispersive effects as well as dissipative effects, which is necessary when the coupling is strong. In the present section we present calculations which take the nonlocality into account as well.

A completely thorough calculation of the nonlocal conductivity would require taking explicit account of the angular factor (66). Roughly speaking, however, the influence of the factor (66) should be intermediate between a factor like (67) and a factor of 1. For values of q greater than v_F/ω, the factor differs from 1 by a term varying almost randomly with angle. For the sake of simplicity, the calculations of this section are carried through with (66) replaced by 1. Then $\alpha_{tr}^2 F$ is identical to $\alpha_0^2 F$, which is known from tunneling measurements.[3] The theory is then exactly the normal limit of Nam's theory.[9] The remaining integrations are tedious but straightforward. As a first step, the self-energy $\Sigma = M - i\Gamma$ was calculated from (55) and (56). The results are shown in Fig. 5. The coupling constant $\lambda = \lambda_0$ was normalized to 1.5. The effective-renormalization and scattering-time parameters were then calculated from (59) and (60). These are shown in Fig. 6.

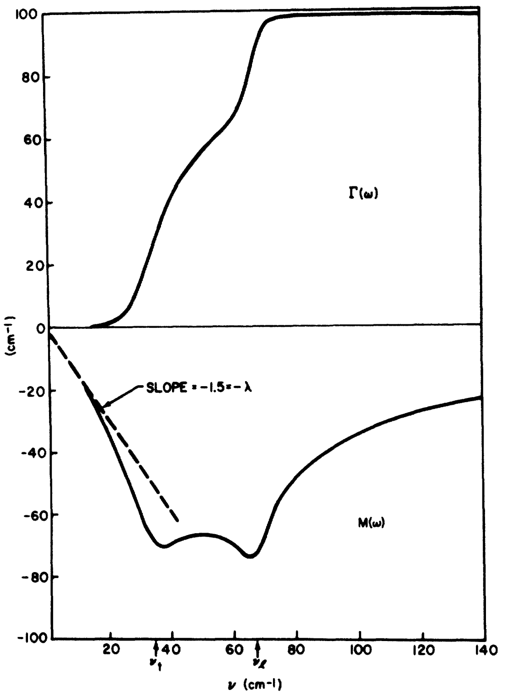

FIG. 5. Real [$M(\omega)$] and imaginary [$\Gamma(\omega)$] parts of the phonon-induced electronic self-energy calculated from the tunneling data of McMillan and Rowell (Ref. 3) for lead. The results are plotted vs energy in cm^{-1} measured from the Fermi energy. A graph of the related function $Z \equiv 1 - \Sigma/\omega$ is given by W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969).

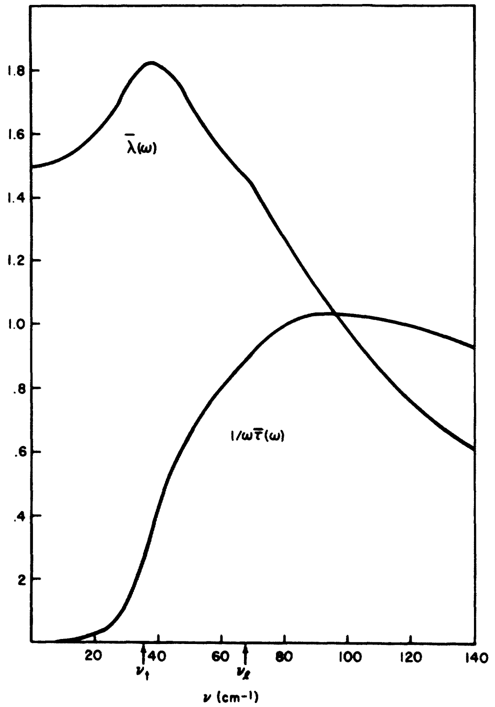

FIG. 6. Effective renormalization parameter $\bar{\lambda}(\omega)$ and scattering time $1/\omega\bar{\tau}(\omega)$ vs frequency for lead. These parameters enter the approximate form of the Holstein theory. They are calculated from Eqs. (59) and (60) using the tunneling data of McMillan and Rowell (Ref. 3). The scattering-time parameter also enters the golden-rule theory in Eq. (30).

Using these quantities, the conductivity was calculated from Eq. (57), assuming a spherical Fermi surface. The result was compared with the approximate conductivity (63) at 170 points in the $(\vec{q}\omega)$ plane. The real parts were found to agree typically to better than 5%, with a maximum discrepancy un-

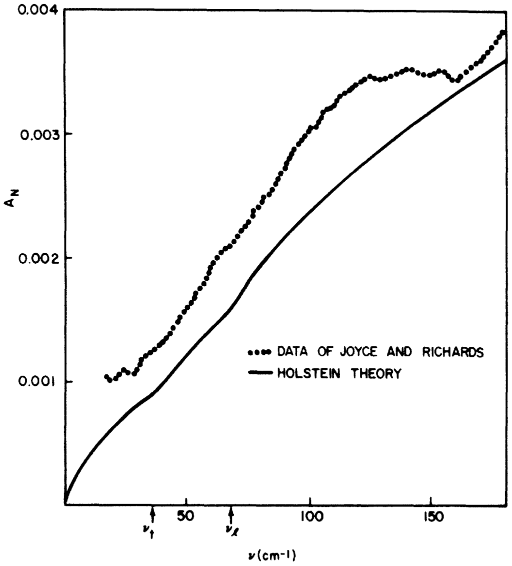

FIG. 7. Absorption vs frequency for normal lead. The Holstein theory is basically Eq. (57), with the surface impedance determined by numerical integration using Eq. (3) for diffuse boundary conditions. The approximate Holstein theory [Eqs. (61) through (65)] gives almost identical results, using the Dingle series expansion. The free-electron Fermi velocity is used. The experimental data of Joyce and Richards contain an arbitrary normalizing factor. The structure near 150 cm^{-1} is instrumental in origin.

der 9%. The imaginary parts typically agreed to better than 2%, with a maximum discrepancy under 3%. Thus, in spite of the large coupling constant in lead, the weak coupling approximation (63) appears quite good. However, the approximations of Sec. II are not so good for Pb because of the neglect of the dispersive effects contained in $\bar{\lambda}(\omega)$.

Finally, the conductivity was used to calculate the surface impedance from Eq. (3). The results are shown in Fig. 7, and agree to within 1% with the Dingle expansion of the approximate theory based on (63). The structure at the phonon frequencies ω_t and ω_l is more dramatic than the structure predicted by the simple theory in Sec. III. This is partly because of the inclusion of dispersive effects, and partly because of the use of α_0^2 (and a coupling constant $\lambda_0 = 1.5$) in place of α_{tr} (with a coupling constant $\lambda_{tr} = 0.9$).

The results presented here serve to justify the approximate theory in the weak coupling limit. In particular, the Dingle expansion has been found adequate even for strong coupling. The leading term for strong coupling must be modified from Eq. (44) to read

$$A_{tot} - A_S = \Phi(\omega)\, \frac{2}{\omega_p \tau_{ph}[1+\bar{\lambda}(\omega)]^{1/2}}\, . \tag{68}$$

For weak coupling materials, Eq. (44) should be quite adequate.

VI. SUMMARY, CONCLUSIONS, AND SUGGESTIONS

In Secs. I–III we have presented a theory of the phonon-assisted infrared absorption which should be valid for weak coupling metals. The absorption is expressed in terms of the phonon density of states and has the same structure of the semiquantitative theory of Joyce and Richards.[1] The results are written

$$A_{N,\mathrm{ph}} = \Phi_N(\omega)\, \frac{4\pi}{\omega\omega_p} \int_0^{\omega} d\Omega\, (\omega-\Omega)\, \alpha_{tr}^2 F(\Omega), \tag{69}$$

$$A_{S,\mathrm{ph}} = \Phi_S(\omega)\, \frac{4\pi}{\omega\omega_p} \int_0^{\omega-2\Delta} d\Omega\, (\omega-\Omega)\, E \times \left(1 - \frac{4\Delta^2}{(\omega-\Omega)^2}\right)^{1/2} \alpha_{tr}^2 F(\Omega)\, , \tag{70}$$

where Φ_N and Φ_S are weakly varying functions of ω which approach the classical value 1 at high frequencies.

This theory incorporates several improvements over the JR theory. The use of correct matrix elements has altered some factors in the density of states $\alpha_{tr}^2 F$, which is discussed in the Appendix. Coherence factors have been included in the superconducting case and have lead to a simpler equation than was found by JR. An estimate of the over-all magnitude of the effect is available.

In Secs. IV and V the strong coupling theory of normal metals is analyzed using the theory of Holstein.[5] The results justify the use of (69) for the normal state, with the inclusion of a correction factor $[1+\bar{\lambda}(\omega)]^{-1/2}$, where $\bar{\lambda}$ is given in Eq. (59). This modified version should be valid to nearly 10% accuracy. The strong coupling theory of superconductivity as contained in Nam's formalism[9] does not provide similar justification for (70) unless the electron-phonon coupling is quite weak.

For a weak coupling material, Eqs. (69) and (70) suggest that derivative measurements of the absorption would be extremely valuable. For a normal metal, Eq. (69) shows that the *second* derivative of the absorption will contain a term proportional to $\alpha_{tr}^2 F(\omega)$ in addition to a more slowly varying background. For a truly weak coupling material, the absorption in the superconducting state will not differ much from that in the normal state; however, there is a new term in the *first* derivative proportional to $\alpha_{tr}^2 F$, premultiplied by the small factor Δ. If these derivatives could be measured with precision, a very powerful spectroscopic tool would be available. In a sense this is the content of the JR experiment: The ratio of superconducting to normal absorption is roughly equivalent to a first derivative measurement.[26] The derivative is replaced by the finite difference 2Δ.

Improved experimental techniques would open up the possibility of detailed experimental investigation of the coupled electron-phonon system in a range of materials previously inaccessible to experiment.[27] These include some of the most interesting superconductors presently known, such as the semiconductors $SrTiO_3$, SnTe, and GeTe (the present theory should be applicable to these materials only for high carrier densities), layer compounds such as $TaSe_2$ and $NbSe_2$, and β-tungsten structure materials. In these last materials, particularly the high T_c compounds like Nb_3Sn, it is not clear how badly the weak coupling limit is violated; this depends on whether low-lying phonon modes are found and how important they are. Furthermore, if anomalous peaks in the electronic density of states exist,[28] of width comparable to the phonon frequencies, then strong coupling of another kind arises (associated with the new parameter $2\Delta/E_B$, where E_B is the width of the peak). In this case the assumption of Eqs. (25) and (26) breaks down; the Drude absorption in such a material should be quite anomalous.

In all the materials mentioned so far, except lead, an additional complication arises from the presence of optical phonons which in principle give rise to a direct absorption. This problem has been recently considered by Ipatova, Maradudin, and Mills,[29] who find the effect is quite small. This can be seen physically as follows. The light couples to phonons of the proper symmetry by the direct electromagnetic coupling of the radiation field to the charged ions. If the phonons are not coupled to electrons (which is not a bad approximation for infrared-active phonon modes), the resulting conductivity obeys the f-sum rule [Eq. (10)] with the ionic-plasma frequency replacing the electronic-plasma frequency. Then assuming equal numbers of carriers and ions, the conductivity for direct phonon absorption is smaller than that for electronic absorption by the electron-to-ion mass ratio. Thus, the phonon-assisted electronic absorption should be much stronger than the direct phonon absorption.

In all these cases, infrared experiments should be extremely interesting, and should help to resolve important questions about the mechanisms for superconductivity in these materials.

ACKNOWLEDGMENTS

I would like to thank R. R. Joyce and P. L. Richards for communicating their results prior to publication, for many discussions, and especially R. R. Joyce for help with preliminary calculations. I am indebted to H. Scher and to J. C. Swihart for discussions of their work prior to publication, to E. I. Blount and P. M. Platzman for helpful discussions, and to S. J. Allen and W. F. Brinkman for constructive suggestions on the manuscript.

APPENDIX: WEIGHTED DENSITIES OF STATES

In problems where electrons in metals are probed at frequencies ω which are commensurate with a Bose-type excitation of the system (i.e., phonons, magnons), the response function of the metal generally shows structure which reflects the density of states of the Bose excitations that are coupled to the electrons. This structure is directly evident in tunneling experiments, and promises to be evident in optical experiments as sources and detectors in the infrared are improved. For analysis of such experiments it is convenient to have a theory formulated in terms of the density of states. Usually this amounts to a boundary condition on the order in which integrations are to be performed.

First, we define an ordinary density of states. In a quasiparticle picture, this is

$$F(\omega) \equiv \Sigma_{\vec{q}}\, \delta(\omega - \omega_{\vec{q}}), \tag{A1}$$

where the sum runs over the first Brillouin zone, and $\omega_{\vec{q}}$ is the energy of the quasiparticle (phonon, magnon) of wave vector $\vec{q}$. The picture can be given broader validity by using a spectral-weight function $B(\vec{q}, \omega)$ in place of the δ function. The weighted density of states appears somewhat different. The outstanding example is

$$\alpha_0^2 F(\omega) \equiv [N(0)/2\hbar]\, \langle\langle |M_{\vec{k}\vec{k}'}|^2\, \delta(\omega - \omega_{\vec{k}-\vec{k}'})\rangle\rangle, \tag{A2}$$

where $M_{\vec{k}\vec{k}'}$ is the matrix element for scattering an electron from $\vec{k}$ to $\vec{k}'$ by emission of a phonon of energy $\hbar\omega_{\vec{k}-\vec{k}'}$, and $N(0)$ is the density of states at the Fermi surface. The angular brackets indicate that both $\vec{k}$ and $\vec{k}'$ are to be averaged over the Fermi surface, in the manner of Eq. (26). As in the ordinary density of states, the δ function can be replaced by the spectral-weight function, and phonons can be interchanged with magnons. The remaining discussion will be limited to phonons.

The particular weighted density of states (A2) is the one that is measured in superconducting tunneling.[3] It is known empirically that in the strong coupling superconductors $\alpha_0^2 F$ resembles quite closely F, which is the ordinary phonon density of states. Van Hove singularities are unaltered in going from (A1) to (A2). The reason for the resemblance is that the Fermi surface is large. Almost any given phonon will couple some set of states on the Fermi surface to some other set of states, and usually several such sets of states can be found, some of them normal or N transitions and some of them umklapps or U's. In general, there will be selection rules on some phonons (at symmetry points, or alternately the partially valid rule that electrons do not couple to transverse phonons by N processes). However, for a large Fermi surface the effects of these selection rules cannot be seen, *except* at small ω where transverse phonons are almost rigorously excluded from coupling.[30] Furthermore, if the Fermi surface is large, the relative weights of peaks in F should roughly be preserved in α_0^2F. These conclusions should be valid for weak coupling superconductors as well as strong coupling ones. However, for monovalent metals the Fermi surface is small enough that the transverse-phonon peaks are likely to couple less strongly that the longitudinal, and the relative weights in α_0^2F will be distorted.

We now introduce a series of functions

$$\alpha_l^2F(\omega) \equiv [N(0)/2\hbar] \langle\langle | M_{\vec{k}\vec{k}'} |^2 P_l(\cos\theta)\delta(\omega - \omega_q)\rangle\rangle, \tag{A3}$$

$$\alpha_{\mathrm{tr}}^2F(\omega) \equiv [N(0)/4\hbar v_F^2] \langle\langle | M_{\vec{k}\vec{k}'} |^2 (\vec{\mathrm{v}} - \vec{\mathrm{v}}')^2 \delta(\omega - \omega_{\vec{q}})\rangle\rangle \tag{A4}$$

where $P_l(\cos\theta)$ is the Legendre polynomial of the cosine of the angle between $\hat{k}$ and $\hat{k}'$, and v_F is the Fermi velocity.

The $l = 0$ case is just the function defined above in (A2). The $l \neq 0$ functions are distorted versions of F, with Van Hove singularities still present, but shapes which are highly dependent on the matrix elements and the Legendre polynomials. The function α_{tr}^2F is the density of states which occurs in transport properties such as the optical conductivity. It is weighted not only by the electron-phonon coupling $M_{\vec{k}\vec{k}'}$ but also by the electron-field coupling $\vec{\mathrm{v}}_{\vec{k}}$. The weighting factor is positive, so α_{tr}^2F should be less distorted than $\alpha_l^2F(l > 0)$, but more distorted than α_0^2F. For spherical Fermi surfaces, $\alpha_{\mathrm{tr}}^2 = \alpha_0^2 - \alpha_1^2$, and we see the familiar $(1 - \cos\theta)$ which weights the scattering processes in favor of large angles. For very small frequencies where only longitudinal phonons coupling by N processes contribute, α_0^2F scales as ω^2, but α_{tr}^2F scales as ω^4. At higher frequencies α_{tr}^2F can be expected to be quite similar in shape to α_0^2F, except that the transverse peak will be more heavily weighted than the longitudinal peak. The reason for this is that the umklapps tend to come from large angles where $\alpha_{\mathrm{tr}}^2 \approx \alpha_0^2$, whereas normal processes came from smaller angles where $\alpha_{\mathrm{tr}}^2 < \alpha_0^2$. The transverse peak arises mainly from U's, and is largely unaltered in going from α_0^2 to α_{tr}^2, whereas the longitudinal peak arises from both N's and U's, and only the U's survive strongly in α_{tr}^2.

The function α_{tr}^2F is directly related not only to the optical conductivity, but also to the dc conductivity as a function of temperature. The standard expressions[31] for the resistivity can be written in the form

$$\rho(T) = \frac{4\pi\beta\hbar}{ne^2}\int_0^{\omega_D} d\omega\, \omega\, \alpha_{\mathrm{tr}}^2F(\omega) N(\omega) [N(\omega) + 1], \tag{A5}$$

where n is the density of conduction electrons, N is the Bose occupation function, and $\beta = (k_BT)^{-1}$.

Various moments of the weighted densities of state have direct uses or interpretations. Of these the most important are the dimensionless moments λ_l which play the role of dimensionless coupling constants:

$$\lambda_l = 2\int \frac{d\omega}{\omega}\, \alpha_l^2F(\omega). \tag{A6}$$

The $l = 0$ constant λ_0, better known as λ, is the important coupling constant of superconductivity and is also the mass-enhancement parameter which occurs in low-temperature specific heat, cyclotron resonance, and the temperature dependence of de Hass – van Alphen signals:

$$m^* = m_b(1 + \lambda), \tag{A7}$$

where m_b is the unrenormalized (band-structure) mass. The $l > 0$ constants are of importance in Fermi-liquid theory, where they play the role of the phonon contributions to the Fermi-liquid parameters. For example, Rice[32] has discussed parameters g_l^{ep} which are related to λ_l by

$$g_l^{ep} = \lambda_l/(1 + \lambda_0). \tag{A8}$$

It also is useful to define an analogous parameter for α_{tr}^2F,

$$\lambda_{\mathrm{tr}} = 2\int \frac{d\omega}{\omega}\, \alpha_{\mathrm{tr}}^2F(\omega). \tag{A9}$$

This parameter measures the renormalization of the optical mass at low frequencies, as is discussed in Sec. IV. It is also related to the high-temperature resistivity within the harmonic approximations of Eq. (5) by

$$\rho = (ne^2\tau_p/m)^{-1}, \tag{A10}$$

$$\hbar/\tau_p = 2\pi\lambda_{\mathrm{tr}}k_BT. \tag{A11}$$

These relations have been exploited recently by several authors[33] to estimate Fermi-liquid parameters.

Higher moments of these functions are also of some use. A convenient notation for these moments is

$$\langle\omega^n\rangle_l = (2/\lambda_l)\int d\omega\, \omega^{n-1}\, \alpha_l^2F(\omega). \tag{A12}$$

An example of the occurrence of such moments is the high-frequency limit of the phonon-induced optical conductivity [Eq. (30)] which scales as the first moment of $\alpha_{\mathrm{tr}}^2F/\omega$.

The second moments are useful because they are independent of the phonon spectrum, as was pointed out by McMillan[34]:

$$\begin{aligned}(\tfrac{1}{2}\lambda_l)\, \langle\omega\rangle_l &\equiv \int d\omega\, \omega\, \alpha_l^2F(\omega)\\ &= [N(0)/2M]\, \langle\langle |\langle\vec{\mathrm{k}}'|\, \vec{\nabla}V|\vec{\mathrm{k}}\rangle|^2\, P_l(\cos\theta)\rangle\rangle.\end{aligned}$$

Here $\vec{\nabla} V$ is the gradient of the effective screened electron-ion potential. In simple metals the average on the right-hand side of (A12) can be readily computed using a pseudopotential and a single orthogonalized plane-wave band structure. The results are in good agreement with the empirically determined moments for $l = 0$.

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PHYSICAL REVIEW B VOLUME 3, NUMBER 2 15 JANUARY 1971

Spin Relaxation Time of Conduction Electrons in Bulk Sodium Metal*

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(Received 13 July 1970)

A remeasurement of the temperature dependence of the conduction-electron spin relaxation time in sodium is reported. These experiments were made using high-purity bulk sodium. They agree with previous data using dispersions of small particles but extend the results to much lower temperatures.

I. INTRODUCTION

The first measurements of the temperature dependence of the electron spin relaxation time T_1 in sodium metal were made by Feher and Kip.[1] They concluded from their data that T_1 was proportional to $1/T$ over the entire temperature range from 300 to 4 °K. At that time, theoretical calculations of