PHYSICAL REVIEW B VOLUME 25, NUMBER 2 15 JANUARY 1982

Frequency dependence of the optical relaxation time in metals

Jeffrey B. Smith*
Department of Physics, Harvard University, Cambridge, Massachusetts 02138

H. Ehrenreich
Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

(Received 9 March 1981)

The optical relaxation times for electron-phonon and for impurity scattering are shown to have the form $\tau^{-1}(\omega)=\tau_0^{-1}+b\omega^2$, and values of b for impurity and electron-phonon effects (including umklapp processes) are calculated. The values of b for electron-phonon scattering are compared with estimates for electron-electron scattering and with experiment for the alkali and noble metals. It appears that the observed frequency dependence in these materials at room temperature derives from correction terms of higher order in $\hbar\omega/E_F$ to the electron-phonon interaction. For impurity scattering b is predicted to be negative.

I. INTRODUCTION

Present knowledge of the effect of temperature on optical properties is still very limited. This is particularly unfortunate, since a better understanding of the optical properties of metals at high temperatures could play a significant role in the development of new technologies such as solar—thermal-energy conversion.[1] The intraband absorption in the alkali and noble metals for $\omega\tau >> 1$ is described empirically by the Drude formula with a frequency dependent relaxation time given by[2,3]

$$\tau^{-1}(\omega)=\tau_0^{-1}+b\omega^2 \ . \tag{1}$$

We seek to identify the origin of the ω^2 frequency dependence. An understanding of the mechanism could help to clarify the behavior of the intraband absorption at high temperatures.

A survey of some mechanisms that could contribute to the frequency dependence of $\tau(\omega)$ has been given by Hopfield.[4] In the alkali and noble metals, electron-phonon scattering and electron-electron scattering are the major possibilities. In transition metals a two-carrier mechanism is also conceivable. A two-carrier model involving crystalline defects has been proposed by Nagel and Schatterly.[5] As discussed below, impurity scattering also yields a frequency-dependent $\tau^{-1}(\omega)$ of the form (1).

The electron-phonon mechanism is known to be responsible for the frequency-independent term τ_0^{-1} of Eq. (1).[6] However, there has been no quantitative estimate of its contribution to the frequency dependence of $\tau^{-1}(\omega)$. In this paper, we derive an expression of the form (1) for the $\tau^{-1}(\omega)$ due to electron-phonon scattering, and calculate the values of b using a free-electron band model and the Debye approximation for phonons. In this model normal phonon scattering gives no contribution to the ω^2 term of $\tau^{-1}(\omega)$; b is entirely due to umklapp scattering. The calculated values of b for umklapp scattering are in good general agreement with experiment at room temperature.

We also derive an expression for b due to impurity scattering. The origin of the frequency dependence is similar to the electron-phonon case, but is simpler to analyze. The frequency dependence is basically a phase-space effect, but its sign and magnitude are strongly influenced by the scattering mechanism. Surprisingly, the result of the phase-space effect by itself is a decrease in $\tau^{-1}(\omega)$ with frequency, that is, a negative b. If the scattering increases sufficiently rapidly with momentum transfer, however, b can be positive. This is the case for electron-phonon scattering, provided umklapp processes are taken into account. For impurity scattering, b is negative.

Umklapp processes also play a crucial role in the electron-electron scattering mechanism. It is well known that there is no absorption of light by a uniform electron gas. Taking umklapp processes into account, Gurzhi calculated an absorption rate having the form (1).[7] The frequency-independent term is very small and can be neglected in comparison with the frequency-independent term due to electron-phonon scattering, but the ω^2 term is comparable to the experimental values for the alkali and noble metals. A better estimate is obtained by combining the Gurzhi formula with recent detailed calculations of the frequency-independent scattering rate. The resulting values for b are an order of magnitude smaller in most cases.

These estimates imply that electron-phonon scattering is responsible for both terms of $\tau^{-1}(\omega)$ in the alkali and noble metals at room temperature. This conclusion could be tested by an examination of the temperature dependence of b. According to our model, the electron-phonon scattering b is constant at low temperature and increases linearly with T at high temperature. In the Gurzhi model the electron-electron scattering b is independent of temperature. Unfortunately, there is no information on the temperature dependence of b in the alkali metals, where both models apply. The data available for the noble metals do not fit the prediction of either model. However, we suggest that the noble metal data can be explained by electron-phonon scattering if the anisotropy of the Fermi surface is taken into account.

II. OPTICAL RELAXATION TIME

The classical Drude formula for the optical conductivity is

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

where ω_p is the plasma frequency and τ is a phenomenological relaxation time. A rigorous definition of τ is obtained from a comparison of Eq. (2) with the linear response formula for the conductivity, which can be written in the form[8]

$$\sigma(\omega)=(i/4\pi)\omega_p^2/[\omega=M(\omega)] , \tag{3}$$

where $M(\omega)=M'(\omega)+iM''(\omega)$ is the damping or memory function. [Equations (2)–(5) summarize some relevant results of the memory function formalism developed in Ref. 8.] The inverse of the optical relaxation time $\tau(\omega)$ is simply equal to the imaginary part of M,

$$\tau^{-1}(\omega)=M''(\omega) , \tag{4}$$

because for optical frequencies the real part gives a frequency shift which is negligible compared to ω. $M''(\omega)$ and therefore $\tau^{-1}(\omega)$ are even functions of ω. Equation (4) must be contrasted with the result for the dc relaxation time,[8]

$$\tau_{\mathrm{dc}}^{-1}=M''(0)\left[1+\left[\frac{\partial}{\partial\omega}M'(\omega)\right]_{\omega=0}\right]^{-1} , \tag{5}$$

which includes a renormalization factor arising from the real part of M. One obtains the representation $\tau^{-1}=\tau_0^{-1}+b(\hbar\omega)^2$ by evaluating $M''(\omega)$ in the optical frequency region and then expanding the resulting expression in powers of $\hbar\omega/E_F$. Because $\omega\tau>>1$, it is clear that τ_0^{-1} is not the same as τ_{dc}^{-1} [nor, in general, is it necessarily equal to the physical zero-frequency values of $M''(\omega)$]. This point can be confusing, because in some cases τ_0^{-1} and τ_{dc}^{-1} do have the same value: Examples are impurity scattering[9] and phonon scattering at high temperatures.[6] For phonon scattering at low temperatures, however, τ_0^{-1} approaches a constant value while τ_{dc}^{-1} vanishes as T^5.

As discussed below, the inverse relaxation time τ_i^{-1} for impurity scattering and τ_ϕ^{-1} for phonon scattering can be written in the form

$$\tau_{i,\phi}^{-1}(\omega)=(\hbar\omega)^{-1}\sum_{kk'}F_{i,\phi}(\vec{k}\vec{k}')f(\vec{k})[1-f(\vec{k}')]\delta(\mathscr{E}_{\vec{k}'}-\mathscr{E}_{\vec{k}}-\hbar\omega) , \tag{6}$$

where $F_{i,\phi}(\vec{k},\vec{k}')$ is a factor characterizing the transition rate for the given scattering mechanism. For impurity scattering,

$$F_i(\vec{k},\vec{k}')=(2\pi m^* n_i/3n\hbar)\,|\vec{v}_{\vec{k}}-\vec{v}_{\vec{k}'}|^2\,|\mathscr{U}_{\vec{k}\vec{k}'}|^2 , \tag{7}$$

while for normal phonon scattering,

$$F_\phi(\vec{k},\vec{k}')=(2\pi m^*/3MN_n)\,|\vec{v}_{\vec{k}}-\vec{v}_{\vec{k}'}|^2\,|\vec{k}-\vec{k}'|^2\,|V_{\vec{k}\vec{k}'}|^2[2N(q)+1]/2\Omega(q) . \tag{8}$$

In these equations, m, $\vec{v}_{\vec{k}}$, and $\mathscr{E}_{\vec{k}}$ are the mass, velocity, and energy of an electron in a Bloch state of wave vector $\vec{k}$, $f(\vec{k})$ is the Fermi distribution, n and n_i are the electron and impurity densities, $\mathscr{U}_{\vec{k}\vec{k}'}=\mathscr{U}(|\vec{k}-\vec{k}'|)$ is the impurity potential, $V_{\vec{k}\vec{k}'}$ is the screened electron-ion potential between single plane waves $\vec{k}$ and $\vec{k}'$ and is assumed to be frequency independent, and $N(q)$ and $\Omega(q)$ are the density and frequency of phonons of wave vector $\vec{q}=\vec{k}'-\vec{k}$. An isotropic Debye spectrum is assumed, and $\vec{q}$ is restricted to the Debye sphere $q \leq q_D$. (Umklapp scattering is treated explicitly in Sec. III.)

We obtain Eqs. (6)–(8) by evaluating $M''(\omega)$ from Ref. 8 in the limits $\hbar\omega >> kT$ and $\omega >> \Omega(q_0)$. They can also be obtained by a golden rule calculation for the second-order process in which an electron absorbs a photon and scatters from an impurity or a phonon.[6,10] No backscattering (photon-emission) term appears in Eq. (6) because $\hbar\omega >> kT$ and $\omega >> \Omega_D$. The latter condition also allows the phonon scattering to be treated as elastic.

Converting the wave-vector sums in Eq. (6) to integrals and using the zero-temperature approximation for the Fermi distribution, we obtain

$$\tau_{i,\phi}^{-1}(\omega)=\frac{1}{\hbar\omega}\int_{E_F-\hbar\omega}^{E_F} d\mathscr{E}'\left\{\frac{1}{(2\pi\hbar)^6}\int\frac{d\vec{k}}{\hbar v_{\vec{k}}}\int\frac{d\vec{k}'}{\hbar v_{\vec{k}'}}F_{i,\phi}(\vec{k},\vec{k}')\right\}, \tag{9}$$

where the initial states $\vec{k}$ lie on the surface of energy $\mathscr{E}'$, which ranges from $E_F-\hbar\omega$ to E_F, while the final states $\vec{k}'$ lie on the surface of energy $\mathscr{E}+\hbar\omega$ [Fig. 1(a)]. Holstein approximated Eq. (9) by taking $\vec{k}$ and $\vec{k}'$ to lie on the Fermi surface.[6] This gives a frequency-independent relaxation time. In this paper, we retain the energy dependence of the initial and final state surfaces and investigate the frequency dependence of $\tau^{-1}(\omega)$ by expanding Eq. (9) in powers of $\hbar\omega/E_F$.

Before proceeding in the following sections to the detailed treatment of Eq. (9), we discuss some features of the frequency dependence in a more general way.[11] First, we change to an integration variable $\mathscr{E}=\mathscr{E}'-E_F+\hbar\omega$ so that Eq. (9) takes the form

$$\tau^{-1}(\omega)=(\hbar\omega)^{-1}\int_0^{\hbar\omega} d\mathscr{E}\{\ \} . \tag{10}$$

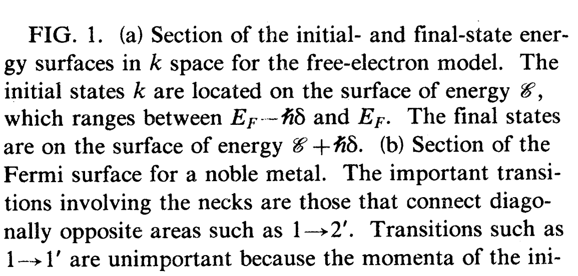

FIG. 1. (a) Section of the initial- and final-state energy surfaces in k space for the free-electron model. The initial states k are located on the surface of energy $\mathscr{E}$, which ranges between $E_F-\hbar\delta$ and E_F. The final states are on the surface of energy $\mathscr{E}+\hbar\delta$. (b) Section of the Fermi surface for a noble metal. The important transitions involving the necks are those that connect diagonally opposite areas such as 1→2′. Transitions such as 1→1′ are unimportant because the momenta of the initial and final states are nearly identical in that case.

The quantity in curly brackets may be regarded as the partial relaxation rate for electrons in initial states of energy $E_F-\hbar\omega+\mathscr{E}$ going to final states of energy $E_F+\mathscr{E}$. Because of the overall factor of $(\hbar\omega)^{-1}$, the total inverse relaxation time $\tau^{-1}(\omega)$ is given not by the sum of these partial rates, but by their *average.*

The simplest estimate of the frequency dependence of $\tau^{-1}(\omega)$ is obtained with $F(\vec{k},\vec{k}')$ constant and with free-electron energy surfaces, so that $\int d\mathscr{S}_{\vec{k}}/v_{\vec{k}} \sim \sqrt{2m\mathscr{E}_k}=k$ and

$$\tau^{-1}(\omega)\sim(\hbar\omega)^{-1}\int_0^{\hbar\omega} d\mathscr{E}\, k_i k_f , \tag{11}$$

where $k_i \sim \sqrt{E_F-\hbar\omega+\mathscr{E}}$ and $k_f \sim \sqrt{E_F+\mathscr{E}}$ are the magnitudes of the initial and final state wave vectors of a transition. The integral can be evaluated exactly, or estimated (correctly to order ω^2) using the "average" value of $\mathscr{E}$, $\mathscr{E}=\hbar\omega/2$. This gives

$$\tau^{-1}(\omega)\sim 1-\tfrac{1}{8}(\hbar\omega/E_F)^2+\cdots . \tag{12}$$

The negative sign of the ω^2 term can be understood as follows. Since $k\sim\sqrt{E}$ for free electrons, the range of initial-state wave vectors k_i in Eq. (11) is larger than the range of the final-state wave vectors k_f. Therefore, the average of the product $k_i \times k_f$ is smaller than the $\omega=0$ value k_F^2.

The preceding argument may be generalized. We define a surface-average matrix element $F(\mathscr{E},\omega)$ by

$$f(\mathscr{E},\omega)=\frac{\displaystyle\int\frac{d\mathscr{S}_{\vec{k}}}{\bar{h}v_{\vec{k}}}\int\frac{d\mathscr{S}_{\vec{k}'}}{\hbar v_{\vec{k}'}}F(\vec{k},\vec{k}')}{\displaystyle\int\frac{d\mathscr{S}_{\vec{k}}}{\hbar v_{\vec{k}}}\int\frac{d\mathscr{S}_{\vec{k}'}}{\hbar v_{\vec{k}'}}} . \tag{13}$$

The inverse relaxation time is then given by

$$\tau^{-1}(\omega)=(\hbar\omega)^{-1}\int_0^{\hbar\omega}d\mathscr{E}\,D(E_F-\hbar\omega+\mathscr{E})\times D(E_F+\mathscr{E})F(\mathscr{E},\omega)\;, \tag{14}$$

where $D(E)=(2\pi\hbar)^{-3}\int d\mathscr{S}_{\vec{k}}/\hbar v_{\vec{k}}$ is the single spin density of states. Note that $F(\mathscr{E},\omega)$ has the property $F(\mathscr{E}-\hbar\omega,-\omega)=F(\mathscr{E},\omega)$, which guarantees that $\tau^{-1}(\omega)$ is even in ω.

The overall frequency dependence of τ^{-1} is determined by both the density of states and the transition rate factor F. To investigate the phase space or density of states effect, we set F equal to a constant and expand Eq. (14) in powers of $\hbar\omega$. This gives

$$\tau^{-1}(\omega)\sim[D(E_F)]^2\;+(\hbar\omega)^2[\,2D(E_F)D''(E_F) \tag{15}$$

where D' and D'' are the first and second derivatives of $D(E)$. If $D(E)$ follows the power law $D(E)\sim E^n$, then for $n>1$ the ω^2 term is positive while for $n<1$ it is negative. Since $D\sim E^{1/2}$ for free electrons, the ω^2 term is negative in this case, as shown above.

In general, the sign of b is determined by a balance between the initial and final densities of state, weighted by the matrix-element factors. In the next section it is shown that b becomes positive if F increases rapidly enough with energy.

III. IMPURITY SCATTERING

In this section the expansion of Eq. (9) in powers of $\hbar\omega$ is carried out for impurity scattering. In the free-electron model the surface integrals in Eq. (9) can be reduced to a single integral over the magnitude of the momentum transfer $\vec{K}=\vec{k}'-\vec{k}$. The result is

$$\tau_i^{-1}(\omega)=\frac{A_i/k_F^4}{\hbar\omega}\int_{E_F-\hbar\omega}^{E_F}d\mathscr{E}\int_{k_{\min}(\mathscr{E},\omega)}^{K_{\max}(\mathscr{E},\omega)}dK\,I_i(K) \tag{16}$$

where $A_i=16\pi^3mn_i[3n\hbar^3(2\pi\hbar)^6]^{-1}k_F^4$ and $I_i(K)=K^3\,|\,\mathscr{U}(K)\,|^2$, and the limits of integration are $K_{\max},K_{\min}=(k(\mathscr{E}+\hbar\omega)\pm k(\mathscr{E})$, with $k(E)=(2mE)^{1/2}/\hbar$. The significant feature of Eq. (16) is that the ω and $\mathscr{E}$ dependence of the surface integrals now appears only in the limits of the K integral, so the expansion in powers of ω can proceed without prior specification of the form of the matrix element.

When Eq. (16) is rewritten in terms of dimensionless variables $\alpha=\hbar\omega/E_F$, $x=\mathscr{E}/E_F$, and $y=K/k_F$,

$$\tau_i^{-1}(\omega)=\frac{A_i}{\alpha}\int_{1-\alpha}^{1}dx\int_{\sqrt{x+\alpha}-\sqrt{x}}^{\sqrt{x+\alpha}+\sqrt{x}}dy\,I(y)\;, \tag{17}$$

where $I(y)=I_i(k_Fy)$. Expansion in powers of α yields

$$\tau_i^{-1}(\omega)=A_i\left[\int_0^2 dy\,I(y)-\alpha^2[2I(2)-I'(2)+3I'(0)]/24\right]+O(\alpha^4)\;. \tag{18}$$

The frequency-independent term involves the integral of $I(y)$, while the term proportional to ω^2 involves I and its first derivatives evaluated at the upper and lower limits of the momentum transfer range. The lower limit usually makes no contribution because $I'(0)$ vanishes for reasonable models of the scattering potential.

If $I(y)$ is taken to be constant, Eq. (18) predicts a negative ω term, as expected from the discussion in the last section. If I increases rapidly enough near $y=2$, however, the derivative term will predominate and b will be positive. Supposing that $I(y)\sim y^n$, with $n>1$, we find that b is negative for $n<4$ and positive for $n>4$. Thus b will be positive if $|\,\mathscr{U}(K)\,|^2$ increases faster than K.

A reasonable model for impurity scattering is the screened Coulomb potential. This gives $I(y)=(4\pi)^2y^3[(k_Fy)^2+k_s^2]^{-2}$ and a negative b. The resulting tendency of $\tau_i^{-1}(\omega)$ to decrease with increasing frequency has been obtained previously [in the coherent potential approximation (CPA) calculations of Velicky and Levin for binary alloys,[12] for example] but a simple explanation for it has not been suggested before.

IV. PHONON SCATTERING

For normal phonon scattering (treated as an elastic process) Eq. (9) becomes

$$\tau_N^{-1}(\omega)=A_N\frac{1}{\hbar\omega}\int_{E_F-\hbar\omega}^{E_F}d\mathscr{E}\int_{K_{\min}(\omega)}^{q_D}dK\,I_N(K)\;, \tag{19}$$

where $A_N = 16\pi^3/[3MNn(2\pi\hbar)^6]$ and $I_N(K) = K^5 \mid V(K) \mid^2 [2N(K)+1]/2\Omega(K)$. We have again assumed free-electron energy surfaces. The structure of the integrals is the same as in Eq. (16), except that the upper limit of the momentum transfer integral is cut off at the Debye wave vector. The upper limit therefore plays no role in the frequency expansion. The lower limit contributes an ω^2 term involving the derivative of $I_N(K)$, but since $V(0)$ is finite and $\Omega(K)$ is proportional to K, this term vanishes also. Thus normal phonon scattering makes no contribution to the ω^2 term of the total inverse relaxation time: $\tau_N^{-1}(\omega) = \tau_{0N}^{-1} + O(\omega^4)$. In a more general model, the normal scattering contribution would not be strictly zero. It would be small, however, because the momentum transfers are small compared to those possible with umklapp scattering.

With umklapp processes, the matrix-element factor $F_\phi(k,k')$, Eq. (8), takes the form

$$F_\phi(\vec{k},\vec{k}') = \frac{2\pi m^*}{3MNn} \sum_{G_i} \mid \vec{v}_{\vec{k}} - \vec{v}_{\vec{k}'} \mid^2 \mid \vec{k} - \vec{k}' \mid^2 \times \mid V_{\vec{k}\vec{k}'} \mid^2 \frac{2N(q)+1}{2\Omega(q)} , \tag{20}$$

where G_i is a reciprocal-lattice vector and $\vec{q} = \vec{k}' - \vec{k} - \vec{G}_i$, with the restriction $q \leq q_D$. All phonons are assumed to have the same spectrum independent of polarization. Because F in the presence of umklapp processes is no longer independent of the orientation of $\vec{k}$ and $\vec{k}'$ with respect to the lattice, the k and k' surface integrals in Eq. (9) cannot be reduced to a single integral over the momentum transfer. It is possible, however, to obtain a qualitative estimate of the unklapp scattering contribution by extending the range of the K integration in Eq. (19) for normal scattering to the $K_{\max}$ determined by energy and momentum conservation. This assumes that the main effect of umklapp scattering is simply to eliminate the restrictions on allowed transitions imposed by the Debye cutoff. The ω^2 terms involving the integrand and its derivative at $K = 2k_F$ now reappear as in Eq. (18). With umklapp scattering, the factor $[2N(K)+1]/\Omega(K)$ in Eq. (19) must be replaced by $[2N(q)+1]/\Omega(q)$. For K near $K_{\max}$, where $q \approx G - 2k_F$, this factor is approximately constant. Provided that $V(K)$ is not rapidly varying, the integrand goes as K^5 near $2k_F$. The discussion following Eq. (18), therefore, indicates that b for umklapp scattering should be positive.

To obtain a more quantitative estimate for the umklapp scattering contribution, we use an approximation of Ziman,[13] which involves averaging Eq. (9) over directions of $\vec{K}$ with respect to the lattice. The result is

$$\tau_u^{-1}(\omega) = \frac{16\pi^3 m}{3nNM\hbar^2} \frac{1}{(2\pi\hbar)^6} \sum_i \frac{Z_i}{2G_i} \frac{1}{\hbar\omega} \int_{E_F-\hbar\omega}^{E_F} d\mathscr{E} \int_{G_i-K_{\max}(\omega)}^{q_D} dq\, q \frac{2N(q)+1}{2\Omega(q)} \int_{G_i-q}^{K_{\max}(\omega)} dK\, K^4 \mid V(K) \mid^2 . \tag{21}$$

Here the sum extends over classes of equivalent reciprocal-lattice vectors with Z_i vectors of length G_i in a class. For typical lattices, only the first few smallest-length classes contribute, because of the restriction $0 \leq G_i - K_{\max}(\omega) \leq q_D$. Except for the frequency-dependent limits of integration Eq. (21) has precisely the same structure as Ziman's result for the dc resistivity.

Equation (21) can now be expanded in powers of $\alpha = \hbar\omega/E_F$ as before. In terms of the dimensionless variables $y = q/k_F'$, $z = K/k_F$, $\bar{q}_0 = q_0/k_F$, and $\bar{G}_i = G_i/k_F$, the result is

$$\tau_u^{-1}(\omega) = \frac{3\pi m}{4M\hbar} \sum_i \frac{Z_i}{2\bar{G}_i} \left[\int_{\bar{G}_i-2}^{\bar{q}_D} dy\, J(y) \int_{\bar{G}_i-y}^{2} dy\, K(z) + \frac{\alpha^2}{24} \left[J(\bar{G}_i-2)K(2) + [K'(2) - 2K(2)] \int_{\bar{G}_i-2}^{\bar{q}_D} dy\, J(y) \right] \right] + O(\alpha^4) , \tag{22}$$

where $J(y) = y[2N(k_F y)+1]/2\hbar\Omega(k_F y)$ and $K(z) = z^4 \mid V(k_F z) \mid^2$. The first term in Eq. (22) is to be added to the frequency-independent term for normal scattering to give the total τ_0^{-1} for phonon scattering. In the

Debye approximation, the coefficient of the $(\hbar\omega)^2$ term is

$$b = b_0 \sum_i \frac{Z_i}{2\bar{G}_i} \left\{ \tfrac{1}{2} \coth\left[\frac{\Theta}{2T} \frac{\bar{G}_i - 2}{\bar{q}_D} \right] + \frac{C'(2)}{C(2)} \frac{2\bar{q}_D T}{\Theta} \left[\ln\sinh\frac{\Theta}{2T} - \ln\sinh\frac{\Theta}{2T}\left[\frac{\bar{G}_i - 2}{\bar{q}_D}\right]\right]\right\} , \tag{23}$$

where $b_0 = 2\pi m \bar{q}_D C^2(2)/9Mk_B\hbar\Theta$, Θ is the Debye temperature, k_B is Boltzmann's constant, and $C(y)$, the ion potential normalized to 1 at $y=0$, is $(-2E_F/3)^{-1}V(k_F y)$. $C'(2)$ is the derivative of the potential at $y=2$, taken with initial and final k states at a constant scattering angle of 180°.

For temperatures large compared to Θ, b becomes proportional to T, while for $T << \Theta$, b approaches the constant value

$$b(T << \Theta) = b_0 \sum_i \frac{Z_i}{2\bar{G}_i} \left[\frac{1}{2} + \frac{C'(2)}{C(2)} \times [\bar{q}_D - (\bar{G}_i - 2)] \right] , \tag{24}$$

For the alkali and noble metals, this limiting value is approximately 20% of the value of b at the Debye temperature.

Using Eq. (23) we have calculated $b_{e\phi}$, the electron-phonon scattering contribution to b, for the alkali and noble metals at room temperature. For both the bcc and fcc lattices, there are two sets of reciprocal-lattice vectors that enter the sum. For the fcc lattice, for example, these are the [111] and [100] vectors with $Z_i/2\bar{K}_i = 1.805$ and 1.172 and $(\bar{K}_i - 2)/\bar{q}_D = 0.171$ and 0.444, respectively. For the alkali metals, values of $C(y)$ and its derivative were obtained from the pseudopotential calculations of Animalu and Heine[14]; for the noble metals, the values were estimated from the pseudopotential curves given by Cohen and Heine.[15] The results are given in Table I, together with the room-temperature experimental data and with two estimates (discussed below) for the electron-electron scattering contribution b_{ee}. Table II is a summary of the available experimental information. For the alkali metals, the results for b listed here were calculated by us from the published data. The data for Li in the range 0.7 – 2 eV were fitted very well by $\tau^{-1}(\omega) = \tau_0 + b(\hbar\omega)^2$, but the results given for Na and K are estimates correct to perhaps a factor of 2. The agreement between $b_{e\phi}$ and the experimental b is comparable to the accuracy of the experimental values.

V. ELECTRON-ELECTRON SCATTERING

Gurzhi's result for the inverse relaxation time due to electron-electron scattering with umklapp processes is[7]

$$\tau_{ee}^{-1}(\omega) = \nu_{ee}^0(T)[1 + (\hbar\omega/2\pi k_B T)^2] , \tag{25}$$

where $\nu_{ee}^0(T)$ is a scattering rate for free electrons, given by

$$\nu_{ee}^0(T) = \omega_p (k_B T/\hbar\omega_p)^2 . \tag{26}$$

The first estimate for b_{ee} in Table I is obtained from Eqs. (25) and (26) with values of the plasma

TABLE I. Comparison of the room-temperature experimental b (from Table II) for the alkali and noble metals with the calculated values for the electron-phonon and electron-electron scattering mechanism. m^* is the optical mass and Θ is the Debye temperature. $b_{ee}^{(1)}$ is based on the free-electron scattering rate, while $b_{ee}^{(2)}$ uses a scattering rate derived from the calculations of Refs. 16 and 17.

	Electron-phonon estimate			Experimental		Electron-electron estimates	
	m^*	Θ (K)	$b_{e\phi}$ (10^{14} sec^{-1}eV^{-2})	τ_0^{-1} (10^{14} sec^{-1})	b (10^{14} sec^{-1}eV^{-2})	$b_{ee}^{(1)}$ (10^{14} sec^{-1}eV^{-2})	$b_{ee}^{(2)}$ (10^{14} sec^{-1}eV^{-2})
Li	1.33	400	0.13	0.97	0.29	0.06	
Na	1.13	150	0.02	0.40	~0.05	0.07	0.003
K	1.16	100	0.005	0.31	~0.01	0.10	0.02
Cu	1.43	315	0.06	1.43	0.15	0.04	0.04
Ag	1.06	215	0.05	1.2	−0.07	0.04	0.008
Au	1.11	170	0.08	1.6	0.09	0.05	0.007

TABLE II. Summary of experiments.

	T (K)	τ_0^{-1} (10^{14} sec^{-1})	b (10^{14} sec^{-1}eV^{-2})	Reference
Li	125	0.57	0.34	a
	298	0.97	0.29	a
Na	295	0.40	~0.05	b
K	295	0.31	~0.01	b
Cu	78	0.88	0.24	c
	293	1.43	0.15	c
	423	2.01	0.04	c
Ag	90	0.71	0.04	d
	293	1.2	−0.07	d
	515	1.5	0.04	d
	705	2.2	0.07	d
	795	1.5	0.26	d
Au	90	0.16	0.33	d
	295	1.6	0.09	d
	725	2.1	−0.003	d
	295	0.93	0.08	e

[a] A. G. Mathewson and H. P. Myers, Philos. Mag. 25, 853 (1972).

[b] N. V. Smith, Phys. Rev. 183, 634 (1969).

[c] P. B. Johnson and R. W. Christy, Phys. Rev. B 11, 1315 (1975).

[d] P. Winsemius, thesis, Rijksuniversiteit te Leiden, 1973 (unpublished).

[e] M. -L. Thèye, Phys. Rev. B 2, 3060 (1970).

frequency taken from the experiments listed in Table II. It is obvious that this is a crude estimate, since the plasma frequency is the only property of the individual metals that enters. For the second estimate, we combine Eq. (25) with values of a scattering rate derived from the dc resistivity due to electron-electron scattering,

$$\nu_{ee}(T)=ne^2\rho_{ee}/m \ , \tag{27}$$

as suggested by Hopfield.[4] The results listed for the estimate in Table I use values of ρ_{ee} calculated by Lawrence and Wilkins.[16,17]

It should be noted that ρ_{ee} is proportional to T^2. Thus Eq. (25), combined with the scattering rate of Eq. (26) or of Eq. (27), predicts a temperature-independent b_{ee}.

VI. DISCUSSION

The calculated values of b for the electron-phonon scattering mechanism (Table I) approximate the room-temperature experimental results quite well. The trend for the alkali metals is reproduced, and except for silver, the agreement for the individual metals is probably as good as could be expected for such a simple model (factor of 2). The agreement for silver is poor, but the data for other temperatures (Table II) suggest that the anomaly is in the room-temperature experimental value.

By contrast, the estimates for the electron-electron mechanism do not fit the data well. The first estimate, based on the Gurzhi formula with the free-electron scattering rate, does give reasonable magnitudes for b, especially for the noble metals. However, the trend for Li-Na-K is wrong. The second estimate, based on better calculations of the electron-electron scattering rate, gives considerably poorer agreement with experiment.

We conclude, therefore, that the electron-phonon scattering mechanism probably accounts for the frequency dependence of the optical relaxation time in the alkali and noble metals. Contrary to previous speculations, electron-electron scattering does not appear to play a role in these materials at room temperature or higher. In arriving at this conclusion, we have compared the predictions of the two models with the experimental data for the alkali and noble metals as a group, as the estimates and the data are probably not accurate enough to permit a comparison for the individual metals.

The use of free-electron energy surfaces in the case of the noble metals requires comment, since effects which depend on umklapp scattering can be sensitive to the presence of necks in the Fermi surface. As indicated below, the anisotropy of the surface may indeed have an important effect on the temperature dependence of $b_{e\phi}$. However, the necks themselves probably do not significantly affect the magnitude of our estimate. The important parameters in the calculation of $\tau(\omega)$ are the momentum transfer and the phonon wave vectors involved in a transition. Umklapp transitions are important in the spherical case because the momentum transfers are large while the phonon wave vectors are small. The important neck transitions are of the type indicated in Fig. 1(b). They involve a large momentum transfer and a phonon wave vector equal to the neck diameter. To a first approximation, their contribution to $b_{e\phi}$ should be adequately represented by the free-electron model, since the neck diameter in the noble metals is roughly equal to $G-2k_F$.

As mentioned in the Introduction, data on the temperature variation of b are available only for the noble metals. In silver, b shows an uneven increase with T, while in copper and gold it decreases. This behavior is of course incompatible with the prediction for the electron-electron scattering mechanism that b_{ee} is independent of temperature. The decrease of b with T in copper and gold also disagrees with the prediction of our model for the electron-phonon scattering mechanism that $b_{e\phi}$ increases with temperature from a constant value of $T=0$. However, a decrease of b with T is not incompatible with the electron-phonon scattering mechanism *per se*. The reason for this is subtle. Note that according to Eqs. (8a) and (20), the electron-phonon $\tau^{-1}(\omega)$ at fixed ω must increase with T. This property of $\tau^{-1}(\omega)$ $=\tau_0^{-1}+b(\hbar\omega)^2$ is indeed satisfied by the experimental data for all the noble metals. In the frequency range to which the data apply (up to 1 or 2 eV), the decrease in b is easily outweighed by the increase in τ_0^{-1} with T. Thus the derivative $[\partial\tau^{-1}(\omega)/\partial T]_\omega$ is positive at all relevant frequencies. The decrease of b means that the magnitude of this derivative decreases with increasing frequency. That our model predicts b as well as $\tau^{-1}(\omega)$ to increase with T appears to depend on the assumption of isotropy for the electron energy and the phonon spectrum. With anisotropy, transitions at different frequencies could primarily sample different phonon populations, and so could respond at different rates to a change in temperature.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation through Grant No. NSF-DMR-77-2010. One of us (J. B. S.) thanks the NSF for financial support. We are grateful to L. Huisman for a preliminary survey of the literature.

---

[*] Present address: Harvard Medical School, Boston, Massachusetts 02115.

[1] H. Ehrenreich and B. O. Seraphin, Report on NSF Symposium, 1975 (unpublished).

[2] M.-L. Thèye, Phys. Rev. B 2, 3060 (1970).

[3] P. O. Nillson, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1974) Vol. 29 p. 139.

[4] J. J. Hopfield, in A. I. P. Conf. Proc. 4, 358 (1972).

[5] S. R. Nagel and S. E. Schnatterly, Phys. Rev. B 9, 1299 (1974).

[6] T. Holstein, Phys. Rev. 96, 535 (1954).

[7] R. N. Gurzhi, Zh. Eksp.Teor. Fiz. 35, 965 (1958) [Sov. Phys.—JETP 8, 673 (1959)].

[8] W. Götze and P. Wölfle, Phys. Rev. B 6, 1226 (1972).

[9] A. Lonke and A. Ron, in *Optical Properties and Electronic Structure of Metals and Alloys,* edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 613.

[10] P. B. Allen, Phys. Rev. B 3, 305 (1971).

[11] A partial discussion along these lines was given by D. J. Stevenson, Phys. Rev. B 7, 2348 (1973).

[12] B. Velický and K. Levin, Phys. Rev. B 2, 938 (1970).

[13] J. M. Ziman, Proc. R. Soc. London Ser. A 226, 436 (1954); *Electrons and Phonons* (Oxford University Press, Oxford, 1960), p. 363.

[14] A. O. E. Animalu and V. Heine, Philos. Mag. 12, 1249 (1965); W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[15] M. L. Cohen and V. Heine, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 38.

[16] W. E. Lawrence and J. W. Wilkins, Phys. Rev. B 6, 2317 (1973).

[17] W. E. Lawrence, Phys. Rev. B 13, 5316 (1976).