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Temperature dependence of the infrared absorptivity of the noble metals*

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The infrared absorptivity of the noble metals from 1.7 to 3.5 μ has been measured in the range of 10 to 310 K. Electropolished bulk specimens of copper, silver, and gold and films evaporated onto polished sapphire have been studied. The results are interpreted in terms of the Holstein theories of phonon-assisted and surface-assisted absorption. These theories are found to provide an accurate description of the absorptivity, when allowance is made for anisotropy of the electron-phonon relaxation time over the Fermi surface. Values of this anisotropy are obtained. The average scattering of electrons at the metal surface is found to be nearly completely diffuse.

I. INTRODUCTION

The Mott-Zener formula[1] for the intraband-transition absorptivity of metals in the near infrared indicates the possibility of determining the electron-phonon relaxation time τ from infrared data. It has been frequently assumed that this infrared τ is identical to the dc-resistivity relaxation time, despite Bethe's early suggestion that a substantial difference would appear at low temperatures. The data of Weiss[3] and Ramanthan[4] on copper have confirmed the existence of such a difference. Roberts[5] established that this difference could not be explained by the theory of the anomalous skin effect.[6]

A quantum theory of τ in the infrared, analogous to the Bloch theory of the dc-resistivity relaxation time, has been derived by Holstein[7] and by Gurzhi.[8] This theory indicates that the absorptivity tends to a nonzero value as the temperature approaches zero, as observed by Ramanathan.[4] Biondi and coworkers[9–11] measured the low-temperature absorptivities of copper and silver and found values in agreement with Holstein's theory, after allowance for the anomalous skin effect. They further confirmed the independence of absorptivity on wavelength for photon energies well below the interband-transition edge.

One of the two principal objectives of the present work is to study the infrared absorptivity over the whole temperature range from $T \ll \Theta$ to $T > \Theta$ (Θ is the Debye characteristic temperature) for comparison with theory. The noble metals are particularly suited for this study since they have well-established electronic structures and are easily electropolished.

Study of the anomalous skin effect[6] led to the discovery of a previously unsuspected mechanism of infrared absorption by conduction electrons, involving the scattering of electrons at the metal surface.[8,12–15] The resulting absorptivity is proportional to $1-p$, where p is the fraction of electrons specularly scattered at the surface. Attempts to evaluate p have given widely differing results. Doremus[16] found $p = 0.5$–0.7, depending on infrared wavelength, while both Lenham and Treherne[17] and Roberts[5] found $p = 0$. Bennett *et al.*[18] found that surfaces of varying roughness gave values from $+1$ through 0 to an apparently unphysical value of -1. The zero-temperature data of Biondi[9–11] indicate $p = 0$, although Doezema and Koch[19] have recently demonstrated rather conclusively that at least partial specularity can be achieved on electropolished copper.

The second principal objective of the present work is to evaluate p for electropolished metals, for comparison with these results. This paper is a continuation and expansion of a preliminary investigation by one of the present authors.[20]

II. THEORY

The absorption of photons by conduction-band electrons requires interaction with the lattice to conserve momentum. Interband transitions are excluded by limiting the photon energy $\hbar\omega$ to well below the absorption edge. Two intrinsic mechanisms of momentum-conserving interactions are known, namely, lattice vibrations and surface collisions. Gurzhi[8] has shown that the two processes can be considered independently and the results simply added.

A. Phonon-assisted absorption

Holstein[7] has derived an expression for the phonon-assisted absorption. His theory is essentially the infrared equivalent of the Bloch theory of dc resistivity, assuming free electrons and a single Debye-model phonon spectrum and excluding umklapp interactions. The resulting expression for the effective relaxation time, as derived in the Appendix, is

$$\frac{1}{\tau} = \frac{1}{\tau_0}\left[\frac{2}{5} + 4\left(\frac{T}{\Theta}\right)^5 \int_0^{\Theta/T} \frac{z^4}{e^z - 1}\,dz\right], \qquad (1)$$

where Θ is the Debye temperature and τ_0 is a con-

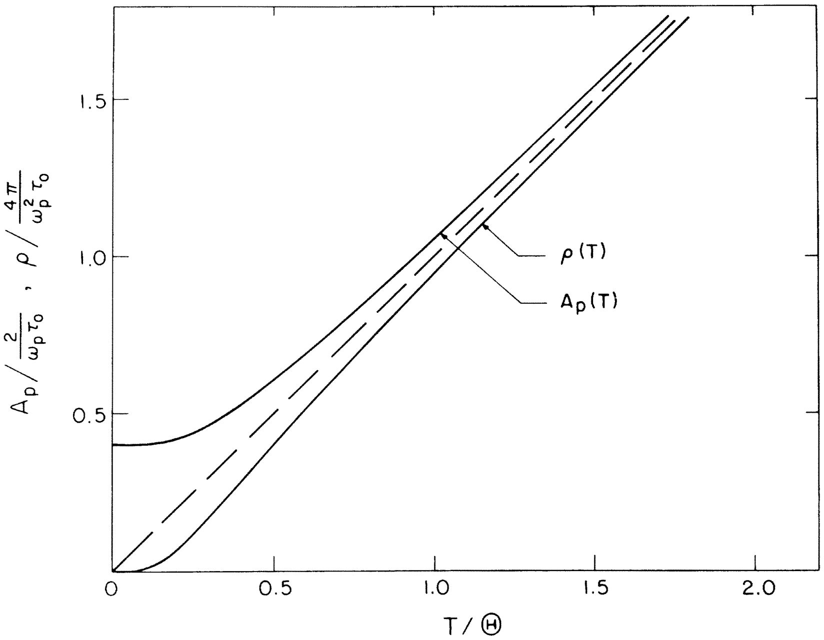

FIG. 1. Theoretical temperature dependence of infrared absorptivity A_p due to phonon-assisted intraband transitions and dc resistivity ρ. Both quantities are expressed as values of τ_0/τ. The broken line is T/Θ, which represents the asymptotic behavior in each case.

stant for each metal. This equation is derived in the limit $E_F \gg \hbar\omega \gg k_BT$ and $k_B\Theta$, $\omega\tau \gg 1$ (E_F is the Fermi energy). The $\frac{2}{5}$ term in (1) is due to spontaneous emission of a phonon by a photon-excited electron, while the temperature-dependent term corresponds to phonon absorption and stimulated-emission processes.

The absorptivity is given by the Mott-Zener formula, $A=2/\omega_p\tau$, where ω_p is the calculated plasma frequency: $\omega_p=(4\pi Ne^2/m)^{1/2}$, N is the electron density, m is the electron effective mass. At low temperatures, the volume absorptivity thus approaches a constant value, corresponding to the spontaneous emission term in Eq. (1). This absorptivity is independent of the bulk resistivity of the metal and is independent of wavelength provided that $\omega\tau \gg 1$ and that the effects of interband transitions are negligible. At high temperatures, the volume absorptivity reduces to the classical result, i.e., it is proportional to the dc resistivity. For the noble metals the condition $\omega\tau \gg 1$ is rather stringent at 300 K and restricts the validity of Eq. (1) to the near infrared. For greater than about 4 μ, the correction term $\omega^2\tau^2/(1+\omega^2\tau^2)$, discussed in the Appendix, leads to a wavelength-dependent absorptivity. Figure 1 shows the temperature dependence of the normalized volume term corresponding to Eq. (1) and the ideal resistivity given by Eq. (2) below.

Because of the approximations in the theory, it is not practical to calculate the parameter τ_0, which depends on the phonon-electron coupling C. In the limit $\omega \to 0$, Eq. (A14) shows that the dc relaxation time is given by the Bloch-Grüneisen relation

$$\frac{1}{\tau}=\frac{1}{\tau_0}\left[4\left(\frac{T}{\Theta}\right)^5\int_0^{\Theta/T}\frac{z^5\,dz}{(e^z-1)(1-e^{-z})}\right] , \tag{2}$$

so that τ_0 can be obtained empirically from the dc resistivity $\rho=4\pi/\omega_p^2\tau$. If τ varies with position on the Fermi surface, the value of τ_0 for infrared absorptivity will differ from the value for dc resistivity. It can be shown that[10]

$$\langle\tau\rangle\langle 1/\tau\rangle=\tau_0^{\mathrm{dc}}/\tau_0^{\mathrm{ir}} = \left(\int\frac{v_F}{\tau}\,dS\int v_F\tau\,dS\right)\Big/\left(\int v_F\,dS\right)^2 \geq 1 , \tag{3}$$

where v_F is the position-dependent velocity on the Fermi surface and the equality holds for isotropic scattering.

While $\hbar\omega$ is always well below the absorption edges of the metals in our investigation, the existence of the interband absorption does affect the intraband absorptivity. The absorption edge results in a real term added to the complex dielectric constant, the additional polarizability being nearly constant from well below the absorption edge to $\omega=0$. The effect on the intraband absorptivity can be estimated using the following simple procedure. In terms of the complex index of refraction, $N=n+ik$, the absorptivity in the regime $k \gg n$ is given by $A=4n/k^2$. "Adjusted" values for n and k can be obtained by solving the equations for ϵ_1 and ϵ_2 with $\delta\epsilon_1$ added:

$$\begin{aligned} n'^2-k'^2&=\epsilon_1=n^2-k^2+\delta\epsilon_1 ,\\ 2n'k'&=\epsilon_2=2nk . \end{aligned} \tag{4}$$

With the same approximations used to obtain $A = 4n/k^2$, the result is $A' = A(1 + 3\delta\epsilon_1/2k^2)$ and corresponds to a negligible correction for the present work.

The actual phonon spectra of the noble metals are much more complex than the Debye form used in the derivation of (1) and (2). It is possible to get some idea of the effects of real phonon spectra by examining intermediate equations in the Holstein derivation. With the assumption of an isotropic dispersion relation, but not assuming the Debye form, the infrared absorptivity is proportional to the integral

$$\frac{1}{2}\int_0^{q_0} \frac{q^5}{\epsilon(q)}\left(1 + \frac{2}{e^x - 1}\right) dq \ , \tag{5}$$

where $x = \epsilon(q)/k_B T$, and $\epsilon(q)$ is the phonon dispersion relation. The dc resistivity is proportional to

$$\frac{1}{k_B T}\int_0^{q_0} \frac{q^5\, dq}{(e^x - 1)(1 - e^{-x})} \ . \tag{6}$$

In the high-temperature limit $[\epsilon(q_0) \ll kT]$, the infrared and dc expressions both take the form

$$k_B T \int_0^{q_0} \frac{q^5\, dq}{\epsilon^2(q)} \ , \tag{7}$$

indicating that departures from the Debye dispersion relation will have the same effect on resistivity and absorptivity for $T \gg \Theta$. However, for $T \to 0$ the infrared expression takes the form

$$k_B T \int_0^{q_0} \frac{q^5\, dq}{\epsilon(q)} \ . \tag{8}$$

Hence, the zero-temperature phonon-assisted absorption involves a different weighting of phonon modes from the high-temperature absorption. Since the actual phonon dispersion relations differ substantially from the Debye approximation, the zero-temperature term in (1) may not take the specified value $\frac{2}{5}$ (or, equivalently, a different τ_0 may be required to describe the zero-temperature absorptivity).

B. Surface-assisted absorption

The theoretical magnitude of the surface-collision-assisted absorptivity has been investigated by several workers.[12–14] For a free-electron metal, with specular electron scattering at the surface, the absorptivity is given by the equation

$$A_s = \tfrac{1}{2}(\omega_p/\omega)^2 (v_F/c)^3 \ , \tag{9}$$

where v_F is the electron velocity at the Fermi surface and c is the speed of light. This contribution to the absorptivity is negligible, being about 1×10^{-5} for the noble metals compared to the zero-temperature phonon-assisted absorptivity, which is about 1×10^{-3}.

For diffuse scattering of electrons at the surface, the surface-assisted absorptivity is given by the equation

$$A_d = \tfrac{3}{4} v_F/c \ , \tag{10}$$

which for a typical monovalent metal gives an absorptivity of about 3×10^{-3}. Kaganov and Slezov[21] have extended this formula to the case of a nonspherical Fermi surface with position-dependent velocity. For cubic crystal symmetry, their expression for the effective velocity to be used in (10) is

$$\tilde{v}_F = \frac{8}{3}\left(\oint v_z v_x^2 \frac{dS}{v_F}\right) \Big/ \oint v_x^2 \frac{dS}{v_F} \ , \tag{11}$$

where v_F is the magnitude of the velocity at the Fermi surface, v_z is the component normal to the surface of the metal, and v_x is the component along an x axis, chosen arbitrarily in the plane parallel to the surface. The integrals are over the regions of the Fermi surface with $v_z > 0$.

This integral has been evaluated for the noble metals, using the Halse[22] parameterization of their Fermi surfaces. In contrast to the phonon-assisted absorptivity, the surface absorptivity depends on crystal orientation. Cubic symmetry permits reduction of this calculation to $\frac{1}{48}$th of the sphere representing all crystal orientations. Figures 2–4 show the stereographic projections of this region for copper, silver, and gold, with contours of constant $\tilde{v}_F$. The values of $\tilde{v}_F$ are normalized to the free-electron Fermi-surface velocities; that is, $v_{fe} = (12\pi^2)^{1/3}\hbar/m_0 a$, where a is the lattice spacing and m_0 the free-electron mass.

The question of whether the surface scattering of electrons is specular or diffuse has received a great deal of attention, with conflicting results.[9–11,16–18] Doezema and Koch[19] have shown that specular scattering can be achieved for electrons with trajectories nearly parallel ($\theta < 1°$) to the surface. For infrared absorption the apparent specularity depends on the angular dependence of the probability of specular scattering and the angular dependence of the effectiveness of electrons in photon absorption. The probability of specular scattering of an electron incident on the surface at angle θ (measured from the surface plane) is given by the equation[23]

$$P_s(\theta) = e^{-(4\pi h \sin\theta/\lambda_d)^2} \ , \tag{12}$$

where h is the rms surface roughness and λ_d the de Broglie wavelength of the electron. The effectiveness of an electron is proportional to $\cos^2\theta$, a result that can be obtained from the Holstein treatment[13] and is also apparent in the velocity-averaging integral (11). With a factor $\sin\theta\cos\theta$ for the differential electron current, the net spec-

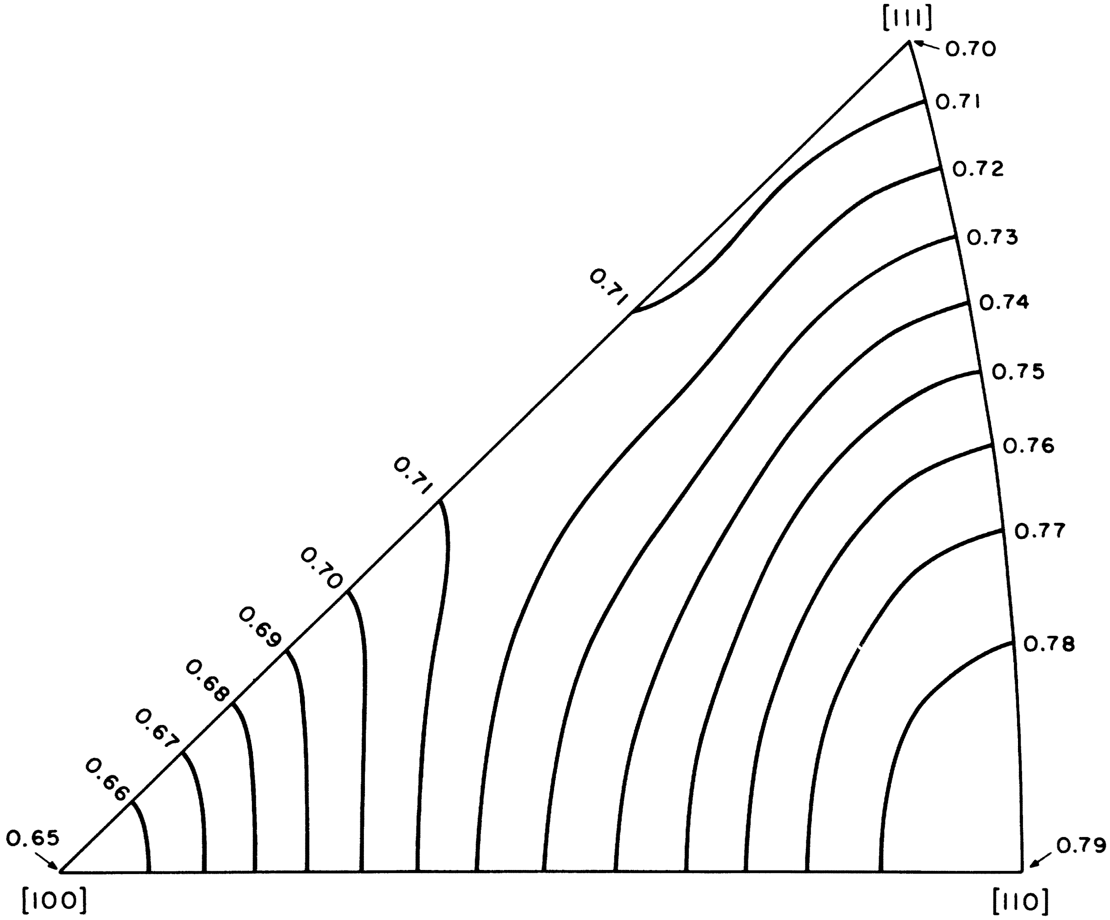

FIG. 2. Calculated orientation dependence of v_F [Eq. (11)] for copper. The values are normalized to the free-electron value $(12\pi^2)^{1/3}\hbar/m_0 a$.

ularity for a free-electron distribution is given by the equation

$$p=\left(\int_0^{\pi/2} e^{-(4\pi h\sin\theta/\lambda_d)^2}\cos^3\theta\,\sin\theta\,d\theta\right)\Big/\int_0^{\pi/2}\cos^3\theta\,\sin\theta\,d\theta\quad . \qquad (13)$$

This function is shown in Fig. 5. Since λ_d is 3 Å for copper and 5 Å for silver and gold, it is clear that the surface must be virtually perfect before even partially specular electron scattering, as measured by infrared absorption, can be achieved.

III. EXPERIMENT

A. Apparatus

The calorimetric technique is best suited for measuring the small absorptivity of the noble metals in the infrared.[9–11,20] Reflectivity measurements require two orders of magnitude greater precision for a given accuracy in the absorptivity and require optical finishes better than those produced by electropolishing. Ellipsometry is highly sensitive to surface contamination and oxidation, and again requires good optical finishes. The nearly unavoidable 20-Å oxide film of copper[24] affects ellipsometric measurements seriously. A calculation of the effect of this oxide on a typical ellipsometric measurement of n and k indicates that the value of k obtained would be in error by 8%, and the value of absorptivity calculated from n and k would be 15% low. This oxide film reduces the absorptivity as measured by normal-incidence calorimetry by only 0.5%.

The very low sensitivity of the calorimetric method at high temperatures necessitates an infrared source of substantial power. In the presence of a suitable laser, a broad-spectrum source was used, taking advantage of the wavelength independence of the absorptivity at low temperatures.[9] At room temperature the measured absorptances for copper and silver have a slight wavelength dependence, and gold is more strongly wavelength dependent in the region where theory predicts a constant value $(2-^{r}$

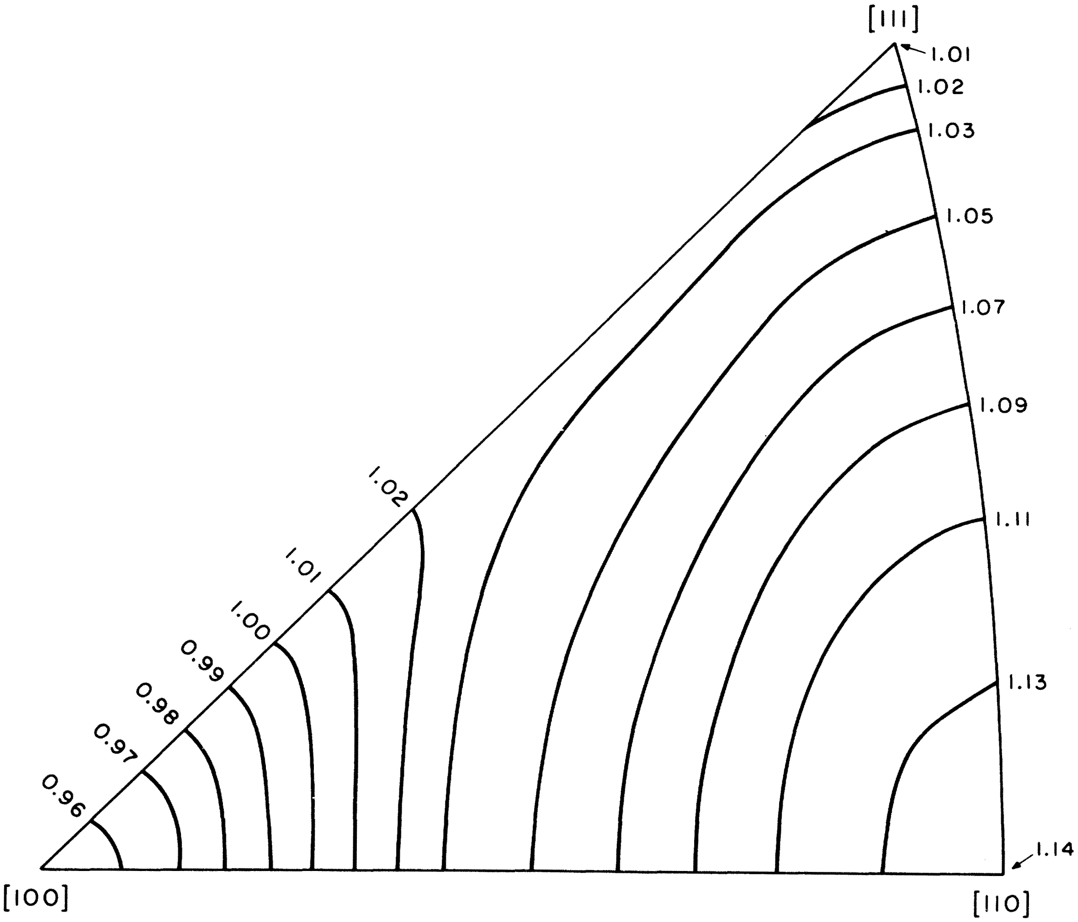

FIG. 3. Calculated orientation dependence of $\tilde{v}_F$ for silver.

μ). Hence measurements made at an average wavelength of 2.6 μ may differ from those made at a longer wavelength. A sketch of the apparatus is shown in Fig. 6. One major modification of previously described calorimetric methods has been made. Rather than tilting the sample and collecting the reflected beam, the sample is mounted close (6 mm) to the light-pipe aperture at true normal incidence. Incident-beam power is measured sequentially by rotating a copper plate coated with a heavy layer of gold black into the beam. This arrangement avoids the difficulties of (a) small amounts of scattered light reaching the sample mount and contributing spurious heating, (b) collecting all the reflected infrared, noting again that the electropolished silver and gold are optically rough, and (c) adjusting the results to compensate for oblique incidence,

The infrared source must be very stable to provide useful results with this sequential procedure. The lamp used in these measurements is a 1000-W tungsten-halogen photographic lamp, type DXW. Tests showed no detectable variation in infrared power from this source over the lengths of time required to make the absorptivity measurements. Incident-power data from run to run were generally consistent to within the accuracy of measurement, which is about ± 1.5%. Data over many runs showed variations with lamp aging, but these variations were very slow and did not affect the absorptivity measurements. Wavelengths shorter than 1.7 μ are removed by a thick (1.6-mm) germanium filter. The long-wavelength limit is about 3.5 μ, determined by the tailing of the radiation function and the transmission of a Pyrex vacuum-seal window. The calculated spectrum is fairly sharply peaked at 2.0 μ, the total infrared power incident on the sample being about 3×10^{-3} W. It is clear that the resulting absorptivity should conform to the equations developed in Sec. II.

The sample is thermally nearly isolated, with a thermal relaxation time relative to the temperature-controlled base of about 60 min at 100 K. Hence, the temperature rise under excitation is practically linear for the periods of 2–6 min used in the measurements. The rate of temperature rise is on the

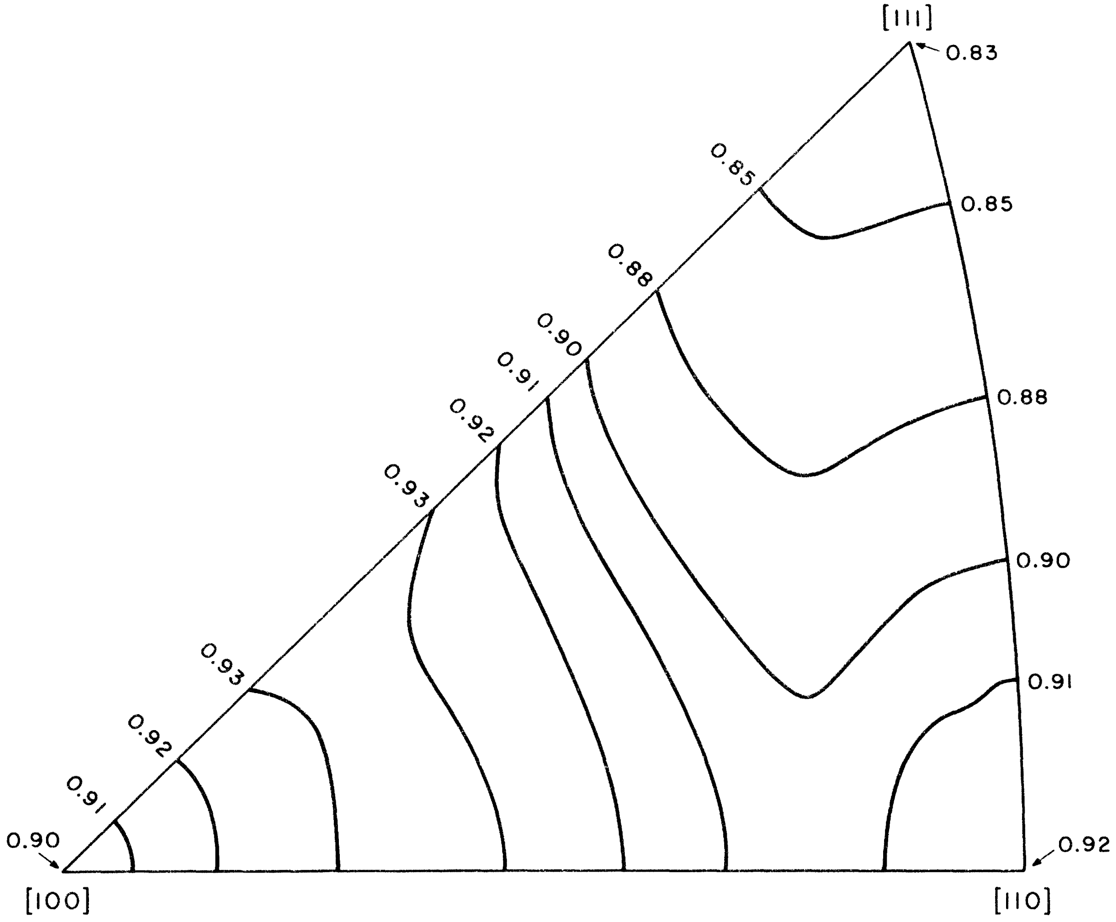

FIG. 4. Calculated orientation dependence of v_F for gold.

order of 5×10^{-4} K/min above 100 K. This temperature change is detected with thermistors: an Artronix model TH-1 for the temperature range 10–125 K, a Veco model 05A2 for 125–250 K, and a Veco model 21A2 for 180–310 K. Accurate measurement of this temperature rise requires high background-temperature stability. Temperature variations due to thermal radiation from the vacuum container are eliminated by immersing the container in liquid nitrogen or helium. Electrical leads to the sample are thermally grounded to a massive base controlled by a Cryogenic Research TC-103 temperature controller, modified for improved performance.

Because the thermal link from sample to base is weak, high-temperature operation requires setting the base temperature significantly above sample temperature to compensate for thermal radiation from the sample mount. It is necessary to depend on the thermistors for absolute temperature measurement as well as for temperature-change detection. With a good thermal link attached from sample mount to base, the thermistors were calibrated against the platinum resistance thermometer used for temperature control of the base. Since the temperature-precision requirements of this experiment are relatively low, this procedure was quite adequate.

B. Sample preparation

The bulk samples were prepared from single-crystal or polycrystalline boules with resistivity ratios in excess of 500 to 1. They were machined in the form of disks 2.5 mm thick and 1.29 cm diam with a threaded stud for screwing the sample into the mount. These disks were then abrasion polished by hand to moderate optical finishes, ending with 1 μ alumina. The silver and gold specimens were etched in hot acid until all traces of machining damage were removed. Because copper can be electropolished to great depths, only a light clean-up etch was used for this metal. The samples were annealed in vacuum (10^{-6} Torr) and allowed to cool by radiation. After electropolishing, they were quickly rinsed, dried, and placed in the apparatus for immediate evacuation. Subsequent

Laue x-ray photographs showed that the copper and gold samples were strain-free single crystals with normals along the [211] and [100] directions, respectively. The silver sample was polycrystalline with grain size less than 10 μ.

Film specimens were prepared by Hoffman of Westinghouse Research Laboratories. The films were rapidly evaporated onto thin, polished sapphire wafers soldered to copper bases. The substrate temperature during the depositions was 65–85 °C; the thickness of the films was 2000–3000 Å. A measure of the roughness of these films was obtained by Choyke of Westinghouse Research Laboratories through measurement of the amplitude of the surface-plasmon absorption of a silver film.[25] This indicated an rms surface roughness on the order of 16 Å. A dc-resistivity measurement at room temperature was made on the evaporated gold, using a strip on a glass slide placed next to the absorptivity sample during evaporation. The result was identical to the handbook value for bulk gold to within 10%. No residual resistivity data were obtained for the films.

IV. RESULTS AND DISCUSSION

Figures 7–9 show the data obtained for the three metals. The single-crystal data for copper are a composite of measurements on four samples: (▵) annealed 60 min at 475 °C, 12 μ removed in electropolishing; (▿) the same specimen after removal of an additional 17 μ by electropolishing; (○) annealed 820 °C, 60 min, 48 μ removed in electropolishing; (□) the same specimen after removal of an additional 11 μ by electropolishing. The close agreement among these four sets of data is evidence that lattice distortion produced by the mechanical polishing has probably been eliminated. However, there is still the possibility of absorbed oxygen being present on all copper samples since the annealing was not done in ultrahigh vacuum, and copper is known to be an excellent getter for oxygen. The samples were prepared in essentially the same way as those described by Koch in his magnetic surface-state experiments and by Biondi and Rayne[9] in their original low-temperature absorptivity measurements. Thus the present results should be comparable to these earlier ones. In every case the absorptivity of the film is higher than the absorptivity of the electropolished bulk metal. In the case of silver the difference is small, so the film data have been shifted up in Fig. 8 by 0.0010 to avoid confusion with the bulk-silver data.

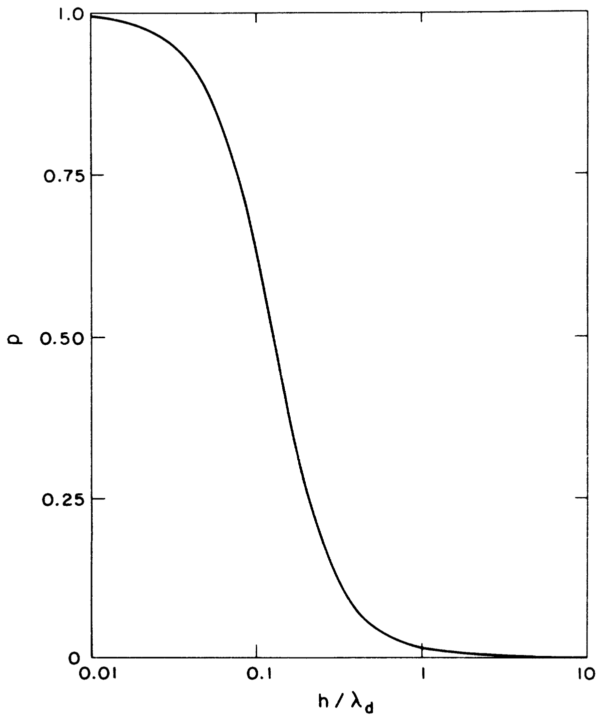

FIG. 5. Apparent infrared specularity p as a function of h/λ_d, where h is rms surface roughness and λ_d is the electron de Broglie wavelength.

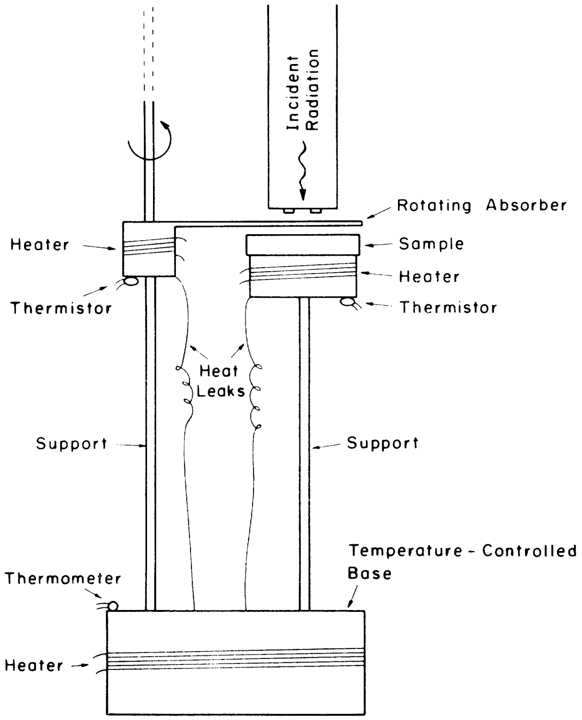

FIG. 6. Schematic view of absorption apparatus.

It is extremely difficult to obtain any unambiguous information about the absorption mechanisms from room temperature data alone. Therefore, a detailed comparison of the present results with previous measurements at or near 300 K will not be

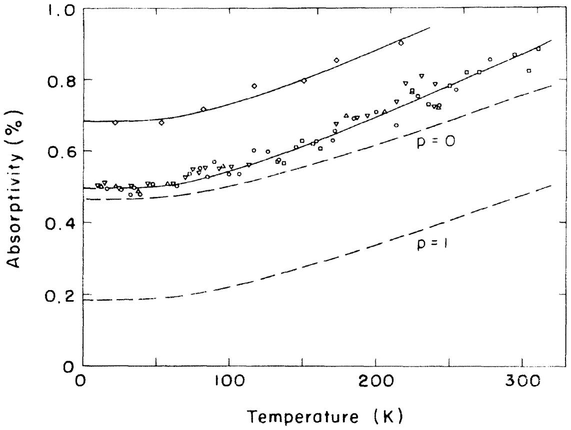

FIG. 7. Temperature dependence of the absorptivity for copper. The broken lines are calculated curves assuming isotropic τ and the solid lines are fitted curves. Data for films indicated by (◇).

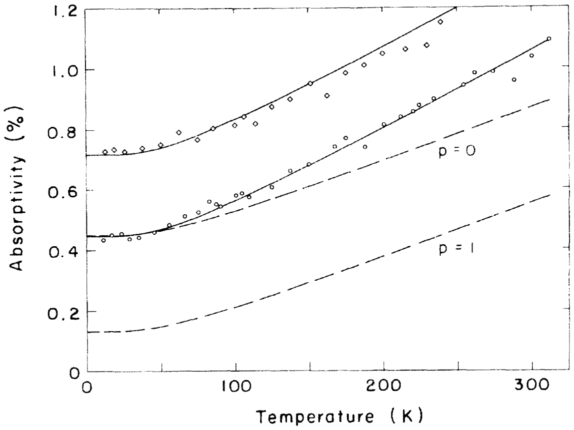

FIG. 9. Temperature dependence of the absorptivity for gold. Data for films indicated by (◇).

attempted. The theoretical background presented previously shows that the temperature dependence of the absorptivity allows a more definitive analysis. Accordingly we focus attention on the curves in Figs. 7–9, which are calculated from the equations given in Sec. II. The lower theoretical curve corresponds to completely specular electron scattering at the surface ($p=1$), the upper to completely diffuse scattering ($p=0$) assuming isotropic τ. The data do not agree precisely with either calculated curve. While disagreement with the $p=0$ curve at zero temperature is small for copper and practically zero for silver and gold, there is in each case a divergence with increasing temperature.

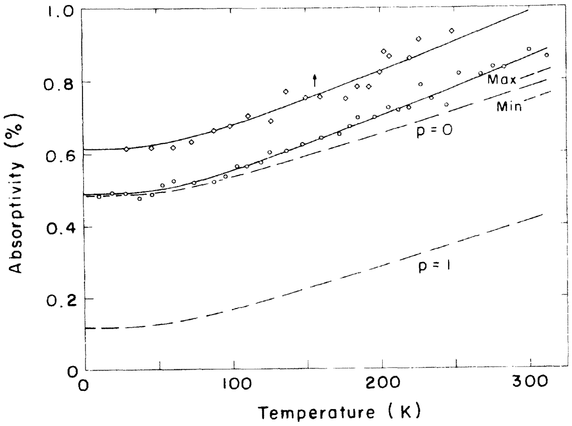

FIG. 8. Temperature dependence of the absorptivity for silver. The broken lines "Max" and "Min" refer to the range of surface absorptivity as a function of crystal orientation. The calculated curve for $p=0$ is for an average over-all crystal orientation. For clarity the film data have been displaced upward by 0.1% in absolute absorptivity. Data for films indicated by (◇).

There is some uncertainty in the determination of the parameters used in obtaining the calculated absorptivity curves. Four parameters are involved in calculating the phonon-assisted absorptivity: the electron density N, the electron effective mass m, the Debye characteristic temperature Θ, and the inverse relaxation time coefficient $1/\tau_0$. The electron density is taken to be 1 electron per atom, so that $N=4/a^3$, where a is the cubic lattice spacing. Following White and Woods[26] Θ is taken to be the high-temperature limit of the specific-heat value. Their values of resistivity at $T=\Theta$ are used to obtain $1/\tau_0$ from Eq. (2) and the relation $\rho=4\pi/\omega_p^2\tau$, ω_p being calculated from N and m. The latter can be computed from the Halse parameterization of the Fermi surfaces, using the formula[27]

$$\frac{1}{m}=\frac{1}{12\pi^3 N\hbar}\int v_F\,dS\,, \tag{14}$$

where the integral is over the entire Fermi surface. Values obtained in this manner are listed in Table I, which also gives empirical effective masses obtained by several workers from optical data.[28–30] The calculated values, based on cyclotron resonance data, should be higher than the optical values by the factor $(1+\lambda)$, where λ is the electron-phonon mass enhancement. Although the mass enhancement is supposed to be about 0.10,[31] no consistent difference is apparent. Therefore, we have chosen to use the optical values of Ehrenreich *et al.*[29] in both Eqs. (1) and (2), disregarding the question of mass enhancement.

Calculation of the surface-assisted absorptivity for $p=0$ is straightforward, using results obtained from Eq. (11). The appropriate values of $\tilde{v}_F$ for copper and gold are taken from Figs. 2 and 4, respectively, given the crystal orientations from x-ray analysis. For the polycrystalline silver an

TABLE I. Electron effective masses for the noble metals, as ratios to the free-electron mass. The values in column 1 are calculated from Eq. (14) and the values in columns 2–4 are calculated from optical data.

	Effective mass			
Metal	Theory	Experiment		
Copper	1.43	1.45[a]	1.42[b]	1.49[c]
Silver	0.98	0.97[a]	1.03[b]	0.99[c]
Gold	1.08	0.98[a]	1.04[b]	0.99[c]

[a] Reference 28.

[b] Reference 29.

[c] Reference 30.

average over-all orientation is used, the segments labeled "Max" and "Min" in Fig. 8 indicating the range of displacement of the $p = 0$ curve for extremal values of $\bar{v}_F$. Table II lists the values of the parameters used in the calculations of the absorptivity.

Taking N and m as fixed, three parameters describe the infrared absorptivity: Θ, τ_0, and p. Ideally, all three could be obtained by fitting curves to the data, but the lack of structure in the absorptivity and the limited accuracy of the data prevent reasonable determination of all three. It is possible, for example, to set $p = 1$ and fit the copper data acceptably by adjusting Θ and τ_0. However, the results are difficult to accept, since the resulting anisotropy factor $(\tau_0^{\text{dc}}/\tau_0^{\text{ir}})$ is 2.7 and the Debye temperature is 470 K. The number of curve-fitting parameters must therefore be reduced. It is most reasonable to fix Θ, taking the high-temperature specific-heat value as before. Curve fitting then proceeds by subtracting the measured zero-temperature absorptivity from all the data and fitting the remainder to the temperature-dependent term of Eq. (1), thus giving the value of τ_0^{ir}. Disregarding the possible effects of non-Debye dispersion relations discussed in Sec. II, the term $0.8/\omega_p\tau_0^{\text{ir}}$ is subtracted from the zero-temperature absorptivity and the remainder attributed to surface-assisted absorption. Comparison with the calculated value for $p = 0$ yields the value of p shown in Table III.

TABLE II. Parameters used to calculate τ_0^{dc} and the free-electron Fermi-surface velocity v_{fe}.

	Copper	Silver	Gold
a	3.608	4.0776	4.0702 Å
m	1.42	1.03	1.04 m_0
$\rho(T=\Theta)$[a]	1.80	1.16	1.32×10^{-6} Ω cm
Θ[a]	310	220	185 K
τ_0^{dc}	3.111	5.054	4.460×10^{-14} sec
v_{fe}	1.58	1.39	1.40×10^6 m/sec

[a] Reference 26.

TABLE III. Values of anisotropy factor τ_0^{ir} and specularity p from infrared-absorptivity data.

Metal	τ_0^{ir} (10^{-14} sec)	Anisotropy $\langle\tau\rangle\langle 1/\tau\rangle$	p
Copper	2.39 ± 0.19	1.30 ± 0.10	0.10 ± 0.10
Silver	4.00 ± 0.20	1.26 ± 0.10	0.07 ± 0.10
Gold	3.05 ± 0.20	1.46 ± 0.10	0.21 ± 0.10

The uncertainty limits listed in Table III are determined by the range of values that permit reasonable fit to the data. No allowance is made for uncertainty in the input parameters Θ and m, nor is allowance made for possible refinements of the theory. One possible refinement is correction of the approximations that lead to the expression $A = 2/\omega_p\tau$. Because the theory leading to Eq. (1) was developed specifically for this expression, it is not certain how such corrections should be made; the simplest assumption is that τ as given by Eq. (1) can be used in the complete Drude formulation. The effects of the approximation $1 + \omega^2\tau^2 \simeq \omega^2\tau^2$ are on the order of 1×10^{-4} and can be neglected. A more serious approximation is

$$A = 4n/[(n+1)^2 + k^2] \simeq 4n/k^2 \ .$$

Taking $k = \omega_p/\omega$ and evaluating n from the measured absorptivity with the exact expression, it is found that the exact and approximate expressions differ by about 1%. Adjustment for this approximation increases the anisotropy factor of Table III by 1% and increases the quantity $1 - p$ by 1%.

Another possible refinement is allowance for the interband transitions, using the method described in Sec. II. For the interband contribution to ϵ_1, Ehrenreich and Philipp[29] found $\delta\epsilon_1(\omega = 0)$ to be 4.7 for copper and 2.3 for silver. The effects of including this refinement are to change the anisotropy factor and p for copper to 1.26 and 0.13, respectively, while for silver the corresponding values are 1.24 and 0.08. These adjustments are smaller than the experimental uncertainties. More important is the uncertainty in the value of Θ, since one might choose to use Θ_R, the resistivity Debye temperature, instead of the specific-heat value. Small changes in Θ will change τ_0^{ir} approximately in inverse proportion, maintaining the product $\Theta\tau_0^{\text{ir}}$ constant. Since τ_0^{dc} will be changed in the same manner, there is no change in the anisotropy factor although the specularity p will be altered. With $\Theta = 335$ K instead of 310 K for copper, for example, p increases from 0.10 to 0.17.

Kelly[32] has studied the temperature dependence of Θ_R, considering both the range of Debye temperatures to be expected and the general validity of the theoretical model. Over the appropriate temperature range 100–300 K, Θ_R for copper varies from 320 to 340 K while Θ_R for silver is less constant, varying from 210 to 260 K. For gold Θ_R varies from 180 to 330 K, indicating a basic failure of the theoretical model. This observation renders our values of anisotropy and specularity for gold of somewhat uncertain significance. There is also the possibility that Θ is different in the infrared case from both the dc-resistivity and specific-heat situations. The photon energy is on the order of one-tenth the Fermi-surface energy and this may affect the mix of umklapp transitions, changing the averaging over the different phonon modes and directions. Only a detailed computation with realistic phonon descriptions and Fermi-surface geometry can predict the changes in Θ and τ_0^{ir} due to this complication.

The values of the anisotropy factor listed in Table III are distinctly different from unity. Few other quantitative estimates of this anisotropy factor are available for comparison. Ziman[33] has observed that the Hall effect in the noble metals implies anisotropic τ, although Dugdale and Firth,[34] also using Hall-effect data, come to the opposite conclusion. Springford[35] concludes that τ is isotropic except at very low temperatures. Nowak[36] has calculated τ for copper in the small-angle scattering limit; a crude evaluation of the integrals of Eq. (3) with his results yields an anisotropy factor of just 1.02. The calculations of Taylor[37] indicate that τ is isotropic for $T > \frac{1}{5}\Theta$. However, Fletcher *et al.*[38] conclude from Righi-Leduc data that τ is significantly anisotropic. Our results indicate substantial anisotropy, but must be considered conditional in the absence of the computations that would resolve the effects of high photon energy and non-Debye dispersion relations.

As anticipated by the calculation of Sec. II, electron scattering at the surface is essentially diffuse. This is not in disagreement with the observation of magnetic surface-state resonances in electropolished copper by Doezema and Koch.[19] Their experiment involves only glancing-incidence electrons, for which the probability of specular scattering may be quite high. If h/λ_d is such that $P_s(\theta = 1^\circ)$ is equal to 0.98, the infrared specularity p is still just 0.007. Considering the difficulty experienced by Doezema and Koch in producing copper surfaces with adequate specularity for their experiment, the $p \simeq 0$ result of the infrared measurement must be considered in good agreement with their observations.

The investigation of evaporated films of the present work was quite cursory, intended only to be a rough check of the possibility that p might be increased on smooth films. Bennett *et al.*[18] have found a transition from a physically anomalous $p = -1$ to full specularity, $p = +1$, around an rms roughness of 60 Å, far above the transition roughness predicted by the theory. A proper investigation of films is a formidable task, requiring metallurgical and galvanomagnetic studies of film structure and theoretical work relating this structure to the optical properties. Aggregation phenomena[39] and the possibility of a wavelength-dependent relaxation time[40,41] must be considered. Our investigation was limited to measuring the absorptivity to see if a well-prepared film on smooth sapphire might have lower absorptivity than the bulk metal. Such a result would be evidence that increased specularity had been achieved. Our results are negative, in that the films invariably showed higher absorptivity. This result does not necessarily refute the claim of increased specularity, because it is possible that absorption related to lattice defects is dominating in a reduction in surface-assisted absorption. For copper and silver, the film absorptivities are related to the bulk absorptivities by a simple vertical translation of the fitted curve, indicating a temperature-dependent extrinsic absorption, as is expected for absorption due to lattice defects. For copper, the difference in absorptivity is 0.0019 and for silver the difference is 0.0002. It is to be noted that the film data for silver have been shifted upward by 0.001 in Fig. 8 to prevent confusion. In the case of the gold film, the fit achieved by an upward translation is not very good, there being a systematic divergence between the displaced curve and the data. The fit is nonetheless within the error limits for most points.

In this paper it has been assumed that the measured absorptance is independent of wavelength when $\omega\tau \gg 1$ and the effect of interband transitions is negligible. While this assumption has been shown to be valid at low temperatures,[9] it is less true at room temperature, and particularly for gold some measurements of the absorptance show a large percentage change in the 2–5-μ wavelength region.[42] Thus if the temperature-dependent absorption measurements were made at a longer wavelength where the theoretical assumptions were still valid, the shape of the measured curves might be in closer agreement with the shape of the calculated curves.

V. CONCLUSIONS

The expression derived by Holstein and Gurzhi for the temperature dependence of the conduction-electron intraband-transition infrared absorptivity of metals does provide an accurate description for copper, silver, and gold, with the parameter τ_0 differing from its value for dc resistivity. From the adjusted τ_0 are obtained estimates of the anisotropy of τ over the Fermi surface. The infrared-average scattering of electrons at the metal surface is nearly completely diffuse, as anticipated by a simple theoretical calculation. Smooth films show higher absorptivities than bulk samples, failing to show positive indication of increased specularity of electron scattering.

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APPENDIX

The transport properties of an electron-phonon gas have been treated in detail by Gurzhi[8] and Holstein.[7,43] In this Appendix we present a brief derivation of Eq. (1) based on these references. The electrons are assumed to have an effective mass m different from the free-electron mass m_0, while the phonons are described by a simple Debye model.

From Eq. (5.33) of Ref. 3 or from standard second-order perturbation theory, the probability per unit time for an electron to make a transition between states $\vec{k}$ and $\vec{k}'$, with simultaneous photon and phonon emission or absorption, is given by

$$P^{(\pm)}_{(\pm)}(\vec{k}\rightarrow\vec{k}')=[e^2(\vec{E}\cdot\vec{q})^2/4Vm^2\omega^4]A^{(\pm)}(\vec{q})$$
$$\times[1-f(E_{\vec{k}'})]\delta(E_{\vec{k}}-E_{\vec{k}'}\pm\hbar\omega_{\vec{q}}\pm\hbar\omega)\ . \quad \text{(A1)}$$

In this expression the superscript (±) refers to phonon emission and absorption, respectively, while the subscript refers to the corresponding photon processes. The electric field amplitude is $\vec{E}$, V is the sample volume, $\omega_{\vec{q}}$, ω are the phonon and photon frequencies, respectively, while $f(E_{\vec{k}})$ is the usual Fermi distribution function. Momentum conservation gives the condition

$$\vec{q}=\pm(\vec{k}-\vec{k}')\ . \quad \text{(A2)}$$

The quantities $A^{(\pm)}(\vec{q})$ can be written in the form

$$A^{(\pm)}(\vec{q})=\frac{Dq^2}{\omega_{\vec{q}}}\begin{pmatrix} n_{\vec{q}}+1 \\ n_{\vec{q}} \end{pmatrix}\ , \quad \text{(A3)}$$

where the bracketed terms refer to phonon absorption and emission, respectively, where $n_{\vec{q}}$ is the original phonon occupation number and D is a constant. In terms of the usual coupling constant C,[44] the latter is given by

$$D=\pi C^2/NM\ , \quad \text{(A4)}$$

where N is the atomic density and M is the ion mass.

Averaging Eq. (A1) over all states $\vec{k}'$ and over all field directions with respect to $\vec{k}$ (or equivalently with respect to $\vec{q}$), we obtain

$$P^{(\pm)}_{(\pm)}(\vec{k})=\frac{e^2E^2}{48\pi^2m^2\omega^4}\int_0^{q_0}\int_0^{\pi}q^2A^{(\pm)}(q)\delta\Big(\frac{\hbar^2q^2}{2m}+\frac{\hbar^2}{m}$$
$$\times kq\cos\theta\pm\hbar\omega_{\vec{q}}\pm\hbar\omega\Big)[1-f(E_{\vec{k}+\vec{q}})]q^2dq\,d\theta\ . \quad \text{(A5)}$$

Here $q_0=(6\pi^2N)^{1/3}$, and it is assumed that $n_{\vec{q}}$, $\omega_{\vec{q}}$, and hence $A^{(\pm)}(\vec{q})$ depend only on q the magnitude of $\vec{q}$. Further integration over θ gives

$$P^{(\pm)}_{(\pm)}(\vec{k})=\frac{e^2E^2}{48\pi^2m\omega^4\hbar^2k}\int_0^{q_0}q^3A^{\pm}(q)$$
$$\times[1-f(E_{\vec{k}}\mp\hbar\omega_q\mp\hbar\omega)]\,dq\ . \quad \text{(A6)}$$

We now average over all occupied states to obtain expressions for the corresponding relaxation rates, namely

$$\frac{1}{\tau^{(\pm)}_{(\pm)}}=\Big(\sum_{\vec{k}}P^{(\pm)}_{(\pm)}(\vec{k})f(E_{\vec{k}})\Big)\Big/\sum f(E_{\vec{k}})$$
$$\cong\frac{3}{2\zeta}\int P^{(\pm)}_{(\pm)}(\vec{k})f(E_{\vec{k}})\,dE_{\vec{k}}\ , \quad \text{(A7)}$$

where ζ is the Fermi energy. Substituting Eq. (A6) into this result gives

$$\frac{1}{\tau^{(\pm)}_{(\pm)}}=\frac{e^2E^2}{48\pi^2m\omega^4\hbar k_0}\int_0^{q_0}q^3A^{(\pm)}(q)G^{(\pm)}_{\pm}(q)\,dq\ , \quad \text{(A8)}$$

where k_0 is the Fermi wave number. The quantity $G^{(\pm)}_{(\pm)}(q)$ is an integral

$$G^{(\pm)}_{(\pm)}(q)=\frac{3}{2\zeta}\int_0^{\infty}\frac{1}{1+e^{(E-\zeta)/k_BT}}\,\frac{e^{(E-\zeta\mp\hbar\omega_q\mp\hbar\omega)/k_BT}}{1+e^{(E-\zeta\mp\hbar\omega_q\mp\hbar\omega)/k_BT}}dE\ , \quad \text{(A9)}$$

which can be readily evaluated, namely

$$G^{(\pm)}_{(\pm)}(q)=\frac{3}{2\zeta}\,\frac{\pm\hbar\omega_q\pm\hbar\omega}{e^{(\pm\hbar\omega_q\pm\hbar\omega)/k_BT}-1}\ . \quad \text{(A10)}$$

Case I ($\hbar\omega\ll k_B\Theta, k_BT$). These conditions conform to the classical case. Here the power expended by the electromagnetic field is

$$W=\sum_{(\pm)}\operatorname*{Lim}_{\hbar\omega\rightarrow0}\Big(\frac{1}{\tau^{(\pm)}_{(-)}}-\frac{1}{\tau^{(\pm)}_{(+)}}\Big)\hbar\omega$$
$$=\sum_{(\pm)}\frac{e^2E^2}{24\pi^2m\omega^2k_0}\int_0^{q_0}q^3A^{(\pm)}(q)\,\frac{\partial G^{(\pm)}_{(-)}}{\partial(\hbar\omega)}dq\ , \quad \text{(A11)}$$

where the summation includes both phonon emission and absorption. From Eqs. (A3) and (A10), and the relation $\omega_q=c_lq$, where c_l is the (isotropic) longitudinal sound velocity, it is easy to show that this relation can be written

$$W=\frac{e^2E^2}{16\pi^2m\omega^2k_0}\int_0^{q_0}\frac{\hbar q^5D}{k_BT}\,\frac{e^{\hbar c_lq/k_BT}}{(e^{\hbar c_lq/k_BT}-1)^2}dq. \quad \text{(A12)}$$

Introducing the Debye temperature Θ we then have

$$W=\frac{e^2E^2(k_BT)^5D}{16\pi^2m\omega^2k_0\zeta\hbar^5c_l^6}\,\mathcal{J}_5(\Theta/T)$$

where $\mathcal{J}_5(x)$ is the usual transport integral, i.e.,

$$\mathcal{J}_5(x)=\int_0^{x}\frac{z^5\,dz}{(e^z-1)(1-e^{-z})}\ .$$

Finally,

$$W=\frac{9\pi^3e^2E^2\hbar^2NC^2}{4m\omega^2(2m)^{1/2}k_B\Theta M}\left(\frac{T}{\Theta}\right)^5\mathcal{J}_5(\Theta/T)\ , \tag{A13}$$

using Eq. (A4).

At high temperatures the corresponding dc relaxation time τ_{dc} is[44]

$$\frac{1}{\tau_{\text{dc}}}=\frac{9\pi^3}{2}\,\frac{\hbar^2C^2N}{(2m)^{1/2}\zeta^{3/2}Mk_B\Theta}\left(\frac{T}{\Theta}\right)^5\mathcal{J}_5(\Theta/T)\ , \tag{A14}$$

which when inserted into (A13) yields

$$W=\frac{e^2E^2}{2m\omega^2}\,\frac{1}{\tau_{\text{dc}}}\ . \tag{A15}$$

This corresponds to the usual formula for the high-frequency conductivity ($\omega\tau\gg1$), namely,

$$\sigma_{\text{HF}}=\frac{ne^2}{m\omega^2}\,\frac{1}{\tau_{\text{dc}}}\ . \tag{A16}$$

Case II ($\hbar\omega\gg k_B\Theta, k_BT$). These conditions conform to the case of interest in the present experiments. Here we have

$$\begin{aligned} &G^{(\pm)}_{(-)}(q)\cong3\hbar\omega/2\zeta\ ,\\ &G^{(\pm)}_{(+)}(q)\cong(3\hbar\omega/2\zeta)e^{-\hbar\omega/k_BT}\ll G^{(\pm)}_{(-)}(q)\ , \end{aligned} \tag{A17}$$

which gives the result

$$1/\tau_-^{(\pm)}\ll1/\tau_+^{(\pm)}\ . \tag{A18}$$

The power expended by the field is now given by

$$W=\hbar\omega\sum_{(\pm)}\frac{1}{\tau^{(\pm)}_{(-)}}\,\frac{e^2E^2}{32\pi^2m\omega^2\zeta k_0}\sum_{(\pm)}\int_0^{q_0}q^3A^{\pm}(q)\,dq\ , \tag{A19}$$

which can be written

$$\begin{aligned} W&=\frac{e^2E^2\pi C^2}{32\pi^2m\omega^2\zeta k_0NMc_l}\left(\frac{q_0^5}{5}+\int_0^{q_0}\frac{2q^4\,dq}{e^{\hbar c_lq/k_BT}-1}\right)\\ &=\frac{e^2E^2}{m\omega^2}\,\frac{9\pi^3\hbar NC^2}{8\zeta k_0M}\left(\frac{1}{5}+\int_0\frac{2x^4\,dx}{e^{x\Theta/T}-1}\right)\ . \end{aligned} \tag{A20}$$

It is convenient to introduce a relaxation time τ_0 such that

$$\frac{1}{\tau_0}=\frac{9\pi^3}{8}\,\frac{\hbar^2C^2N}{(2m)^{1/2}\zeta^{3/2}Mk_0\Theta}\ , \tag{A21}$$

so that

$$\frac{1}{\tau_{\text{dc}}}=\frac{T}{\Theta}\,\frac{1}{\tau_0}\ . \tag{A22}$$

Defining $z=x\Theta/T$, Eq. (A20) then becomes

$$W=\frac{e^2E^2}{2m\omega^2}\,\frac{1}{\tau_0}\left[\frac{2}{5}+4\left(\frac{T}{\Theta}\right)^5\int_0^{\Theta/T}\frac{z^4\,dz}{e^z-1}\right]\ , \tag{A23}$$

which corresponds to an effective relaxation time given by Eq. (1) of the main text, viz.,

$$\frac{1}{\tau}=\frac{1}{\tau_0}\left[\frac{2}{5}+4\left(\frac{T}{\Theta}\right)^5\int_0^{\Theta/T}\frac{z^4\,dz}{e^z-1}\right]\ . \tag{A24}$$

At high temperatures ($\Theta/T\ll1$) this equation reduces to

$$W=\frac{e^2E^2}{2m\omega^2}\,\frac{1}{\tau_0}\,\frac{\Theta}{T}=\frac{e^2E^2}{2m\omega^2}\,\frac{1}{\tau_{\text{dc}}}\ , \tag{A25}$$

which is the classical result. For low temperatures ($\Theta/T\gg1$), (A24) reduces to

$$W=\frac{e^2E^2}{2m\omega^2}\,\frac{2}{5}\,\frac{1}{\tau_0}\ , \tag{A26}$$

which is a constant *independent* of the dc resistivity. The detailed variation of the absorptivity with temperature is shown in Fig. 1.

The above equations are only applicable in the absence of interband transitions and for $\omega\tau_{\text{dc}}\gg1$. If the latter condition is not satisfied, then the absorptivity involves an additional factor $\omega^2\tau^2/(1+\omega^2\tau^2)$. This factor leads to the usual Drude formula for the absorptivity in the classical limit. It is responsible for the observed wavelength dependence of the infrared absorptivity of the noble metals at room temperature. However, in the present experiments the range of wavelengths present in the incident radiation satisfy the conditions for the applicability of (A24) at *all* temperatures. For example, in copper at 273 K taking $\tau=2.7\times10^{-14}$ sec, we obtain $\omega\tau\simeq15$ and $\lambda=3.5\ \mu$. The resulting correction to Eq. (A24) is thus negligible even in this worst case.

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