PHYSICAL REVIEW B VOLUME 11, NUMBER 4 15 FEBRUARY 1975

Optical constants of copper and nickel as a function of temperature*

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(Received 12 August 1974)

The optical constants were determined for copper and nickel from reflection and transmission measurements on vacuum-evaporated thin films, in the spectral range 0.5–6.5 eV and at temperatures of 78, 293, and 423 K. The imaginary part of the dielectric constant was nearly independent of temperature for nickel, but for copper it increased with temperature in the intraband region below 2 eV and decreased above 4 eV in the interband region. Interpretation of the increase below 2 eV according to the Drude free-electron expression suggests a temperature and frequency dependence of the relaxation time, which is not completely explained. The thermal behavior in the interband region can be largely understood, however, if the zero-temperature theory of Williams, Janak, and Moruzzi is modified by including a Debye-Waller factor in transitions between nearly-free-electron-like bands.

I. INTRODUCTION

We have previously measured the optical constants of copper[1] and nickel[2] as a function of photon energy (0.5–6.5 eV) at room temperature, and compared the experimental values of ϵ_2, the imaginary part of the dielectric constant, with theoretical values from zero-temperature band-structure calculations.[3] Since the experimental peaks were generally lower and broader than the theoretical ones, it is now important to have values for the dielectric constants of copper and nickel as a function of temperature in order to complete the comparison with these calculations, which neglected atomic vibrations. In addition, accurate values will allow us to discuss the temperature-dependence mechanism; we shall propose that the observed temperature dependence of ϵ_2 in the interband portion of the spectrum is mainly described by the Debye-Waller factor.

Some mechanisms for explaining the temperature dependence of ϵ_2 in metals have been summarized by Rosei and Lynch.[4] Briefly, these mechanisms are volume thermal expansion (and, in thin films, shear strains resulting from different thermal-expansion rates in the substrate and sample), increased phonon population, Fermi-distribution broadening, and shift of Fermi level. These thermal mechanisms cause small energy shifts in the band structure or Fermi level of the metals. These shifts in turn give small shifts in the position of peaks in the ϵ_2–vs–photon-energy curve, which are seen as changes in the magnitude of ϵ_2 at a given energy. In the case of copper, we have measured a relatively large decrease in ϵ_2 with increasing temperature beyond 4 eV, and these mechanisms are inadequate to account fully for the observed changes.

Therefore we consider another mechanism,[5] the Debye-Waller factor, multiplying both the electron excitation energies (to account for energy shifts in ϵ_2) and the transition probabilities (to account for changes in the magnitude of ϵ_2). The Debye-Waller factor is a well-known thermal correction for the potential-energy matrix elements which determine x-ray, neutron, or fast-electron diffraction in a crystal,[6] and more recently for the matrix elements of the pseudopotential used in the calculation of band structures.[7,8] In addition, however, the Debye-Waller factor will also appear as a correction for the momentum matrix elements which describe the probability of electron transitions between free-electron-like bands induced by photon absorption. According to calculations by Williams *et al.*,[3] a contribution to ϵ_2 of copper starting at 4.2 eV is the only one due to transitions between free-electron-like bands in copper or nickel. Therefore we will use the Debye-Waller factor applied to this transition to explain our measured thermal decrease in the magnitude of ϵ_2 in copper, and the absence of a similar effect in nickel. This is, to our knowledge, the first evidence for the appearance of the Debye-Waller factor in the magnitude of ϵ_2 through the momentum matrix elements, although it has previously been recognized as a possible cause of a shift in the peak position through the potential-energy matrix elements and band gaps.[7,8]

Although earlier determinations[9–13] of the dielectric constants as a function of temperature agree as to the general behavior of the values with temperature, they do not agree as to the actual magnitudes of the dielectric constants. These earlier determinations used the ellipsometric method; disagreement in the magnitudes of the dielectric constants may be due to problems of sample preparation, contamination (oxidation of the metal on heating or condensation of water vapor on cooling the samples), or the cryostat windows, since methods which depend on the phase change on reflection are very sensitive to these factors. In addition, all of these investigations were over a more limited spectral range.

We have inverted reflection and transmission measurements made on thin evaporated films in order to determine the optical constants at 78, 293, and 423 K. In the free-electron region of the spectrum, we will use the Drude theory to analyze our measurements on copper films, and discuss the applicability of a frequency-dependent relaxation time. In the interband region we will develop the Debye-Waller factor as an explanation for the observed temperature changes in ϵ_2. Finally, we compare our experimental values with other experiments and state why we believe our measurements to be more accurate.

II. EXPERIMENTAL CONSIDERATIONS

Our preparation of evaporated metal films and the optical instrumentation have been described previously.[1,2] The evaporation was in a vacuum of about 10^{-6} Torr, at a rate of about 100 Å/sec. The transmission and reflection measurements were made with a Unicam SP 700 double-beam spectrophotometer from 0.5 to 6.5 eV. Now we have made measurements on copper and nickel films at 78, 293, and 423 K in a cold-trapped evacuated cryostat.

A. Cryostat

The cryostat consists of an outer brass vacuum can and an inner thin-walled stainless-steel cylinder which serves as a reservoir for either liquid nitrogen or hot oil. A copper bar extending from the brass bottom surface of the reservoir holds the sample. The temperature of the sample was monitored by a thermocouple screwed to the massive copper sample holder about 1 cm away from the sample itself. The spectrophotometer light beam passes through two $\frac{1}{16}$-in.-thick quartz windows and the sample holder. The sample is surrounded by a copper shield which is in good thermal contact with the copper-bar sample holder. There are holes in the shield which allow the light beam to pass through the sample, but the sample is shielded in line of sight from all surfaces except the quartz windows. The vacuum-system pressure with the cryostat at room temperature was 7×10^{-7} Torr. When the sample was cooled to 78 K by pouring liquid nitrogen into the reservoir in the cryostat, the pressure decreased to 4×10^{-7} Torr. To heat the cryostat to 423 K hot oil was poured into the reservoir and maintained at a constant temperature with an immersion heater; the pressure rose to 9×10^{-7} Torr.

The cryostat has two necessary functions beside controlling the sample temperature: At cold temperatures it inhibits water vapor from freezing onto the sample (for which purpose the copper shield is essential), and at hot temperatures it inhibits the sample from oxidizing. Nevertheless, these two effects were still a problem over long time periods. Reflection measurements were found to be much more sensitive to both condensation and oxidation than transmission measurements, which were reproducible over a period of time well within our estimated instrumental accuracy. The reflection measurements were observed to change over long time periods, but from the observed rate of change we concluded that changes due to contamination could be kept within our estimated error,[14] and that the thermal change in the reflectivity could be reliably determined.

The measurements made in the cryostat must be normalized to absolute values of reflectance and transmittance, because the windows of the cryostat introduce multiple reflections and are also slightly absorbing. We have accurately measured the reflectance and transmittance of copper and nickel outside the cryostat at room temperature.[1,2] Since the changes in reflectance and transmittance inside the cryostat between room temperature and the other measured temperatures are small, we can renormalize our measurements in the cryostat according to the ratio of measured room-temperature values outside and inside the cryostat.

B. Evaluation of optical constants

The optical constants n and k of copper and nickel at the different temperatures were obtained by inverting normal-incidence reflection measured from opaque films together with normal-incidence transmission measured from thinner semitransparent films, both in the cryostat but renormalized as explained. The details of inverting reflection and transmission measurements have been described previously.[1,2] In this study we were able to simplify our method of determining the thickness of the semitransparent films. To determine the film thickness, we inverted the normal-incidence room-temperature transmission using our previously determined room-temperature values[1,2] for n and k at each of the 48 measured wavelengths across our entire spectral range. This method gave values for the film thickness at each of the measured wavelengths which agreed to within ± 3 Å. Using the average of these values as the known thickness of the semitransparent film, we were able to invert the normal-incidence reflection and transmission measurements at different temperatures to determine the optical constants. Thermal expansion of the film thickness was negligible.

III. RESULTS AND DISCUSSION

The complex index of refraction $\tilde{n}=n+ik$ of copper at 78, 293, and 423 K is listed in Table I. The

TABLE I. Optical constants for copper at 78, 293, and 423 K.

	78 K		293 K		423 K	
eV	*n*	*k*	*n*	*k*	*n*	*k*
0.64	0.69	13.21	1.09	13.43	1.54	13.85
0.77	0.49	10.99	0.76	11.12	1.04	11.37
0.89	0.41	9.358	0.60	9.439	0.80	9.569
1.02	0.34	8.192	0.48	8.245	0.64	8.379
1.14	0.25	7.184	0.36	7.217	0.47	7.302
1.26	0.23	6.401	0.32	6.421	0.41	6.477
1.39	0.22	5.730	0.30	5.768	0.38	5.928
1.51	0.20	5.156	0.26	5.180	0.32	5.203
1.64	0.19	4.650	0.24	4.665	0.28	4.690
1.76	0.17	4.183	0.21	4.205	0.24	4.208
1.88	0.20	3.728	0.22	3.747	0.25	3.753
2.01	0.29	3.182	0.30	3.205	0.32	3.205
2.13	0.67	2.634	0.70	2.704	0.71	2.767
2.26	1.09	2.500	1.02	2.577	1.02	2.625
2.38	1.22	2.546	1.18	2.608	1.18	2.627
2.50	1.27	2.507	1.22	2.564	1.23	2.582
2.63	1.29	2.427	1.25	2.483	1.24	2.512
2.75	1.28	2.342	1.24	2.397	1.23	2.422
2.87	1.27	2.246	1.25	2.305	1.23	2.332
3.00	1.32	2.144	1.28	2.207	1.27	2.237
3.12	1.35	2.054	1.32	2.116	1.30	2.144
3.25	1.36	1.985	1.33	2.045	1.30	2.075
3.37	1.40	1.916	1.36	1.975	1.33	2.002
3.49	1.41	1.857	1.37	1.916	1.34	1.941
3.62	1.40	1.815	1.36	1.864	1.34	1.883
3.74	1.38	1.776	1.34	1.821	1.32	1.842
3.87	1.41	1.751	1.38	1.783	1.35	1.796
3.99	1.41	1.704	1.38	1.729	1.36	1.740
4.11	1.41	1.650	1.40	1.679	1.38	1.700
4.24	1.45	1.581	1.42	1.663	1.38	1.674
4.36	1.56	1.547	1.45	1.663	1.40	1.676
4.49	1.58	1.560	1.46	1.646	1.41	1.688
4.61	1.56	1.585	1.45	1.668	1.39	1.706
4.73	1.54	1.609	1.41	1.691	1.37	1.730
4.86	1.52	1.664	1.41	1.741	1.34	1.770
4.98	1.50	1.724	1.37	1.783	1.31	1.793
5.11	1.46	1.771	1.34	1.799	1.27	1.805
5.23	1.40	1.789	1.28	1.802	1.22	1.807
5.35	1.35	1.780	1.23	1.792	1.17	1.795
5.48	1.28	1.757	1.18	1.768	1.12	1.774
5.60	1.22	1.728	1.13	1.737	1.07	1.743
5.72	1.16	1.690	1.08	1.699	1.02	1.706
5.85	1.13	1.642	1.04	1.651	0.99	1.661
5.97	1.08	1.598	1.01	1.599	0.94	1.597
6.10	1.07	1.554	0.99	1.550	0.92	1.548
6.22	1.05	1.498	0.98	1.493	0.91	1.485
6.34	1.02	1.446	0.97	1.440	0.90	1.441
6.47	1.01	1.396	0.95	1.388	0.90	1.385
6.59	0.99	1.345	0.94	1.337	0.91	1.336

corresponding values of $\epsilon_2 \equiv 2nk$ are plotted in Fig. 1. Figure 2 shows the results in differential form:

$$\frac{\Delta\epsilon_2}{\Delta T} = \frac{\epsilon_2(423) - \epsilon_2(78)}{423 - 78} \; K^{-1} .$$

The results were obtained by inverting reflection measurements from opaque films together with transmission measurements on a 347-Å semitransparent film. Reflection measurements on two separate sets of opaque films and transmission measurements on two different simultaneously evaporated 347-Å films both agreed well.

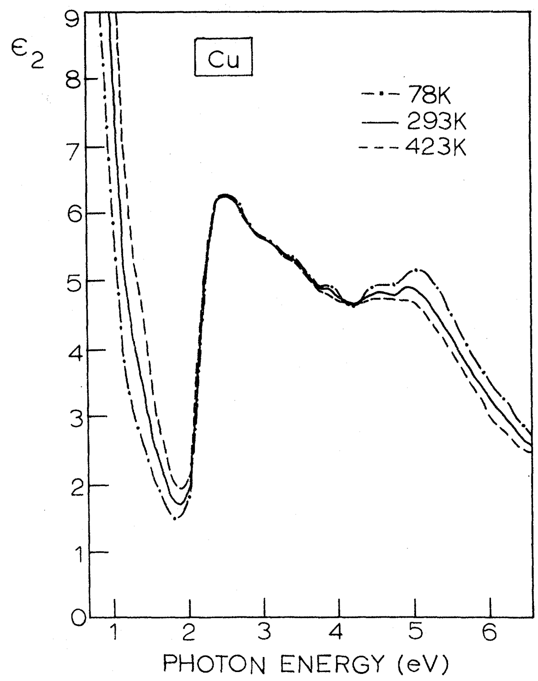

FIG. 1. Imaginary part of the dielectric constant for copper at 78, 293, and 423 K vs the photon energy.

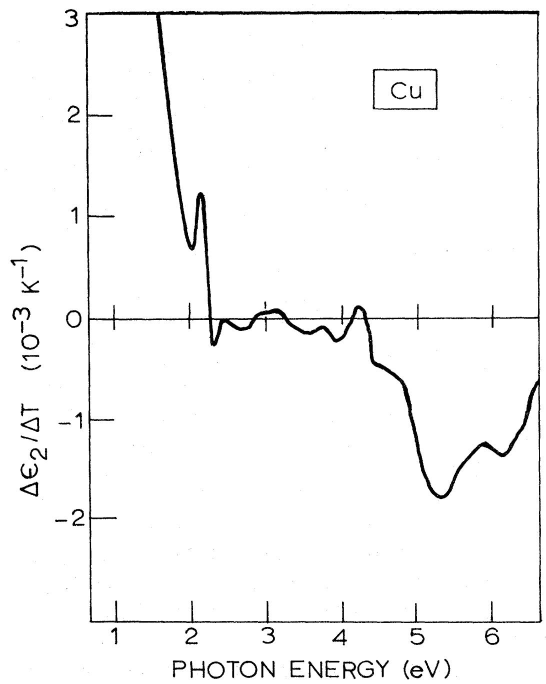

FIG. 2. Difference between ϵ_2 at 423 and 78 K, divided by the temperature difference, from Fig. 1.

The index of refraction of nickel at room temperature is listed in Ref. 2. Reflection and transmission measurements made on nickel films were independent of temperature (within the accuracy of our spectrophotometer) over the temperature range 78–423 K. Our dielectric constants for nickel are

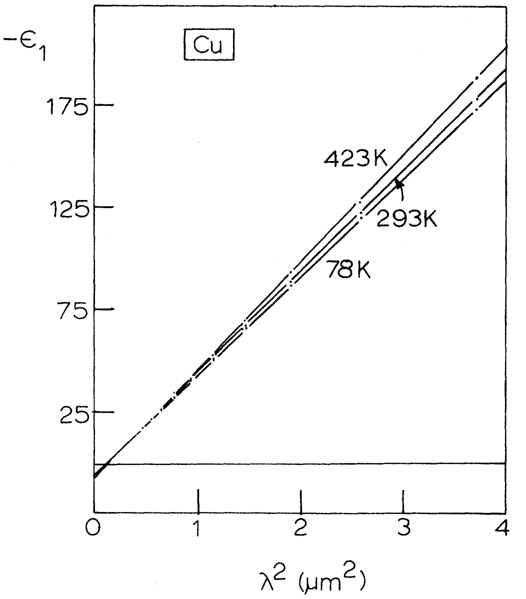

FIG. 3. Negative of the real part of the dielectric constant for copper at 78, 293, and 423 K vs the square of the wavelength.

therefore identical to the previously measured room-temperature values.[2]

A. Comparison with theory

The complex dielectric constant and the complex index of refraction are related as follows: $\tilde{n}^2=\tilde{\epsilon}=\epsilon_1+i\epsilon_2$, so that $\epsilon_1=n^2-k^2$ and $\epsilon_2=2nk$. The Drude free-electron theory predicts values for the dielectric constants of metals for photon energies below the onset of interband transitions. In copper[1] this occurs near 2 eV; however, in nickel interband transitions are dominant throughout our entire measured range and the free-electron effects are negligible.[2] We have therefore observed the temperature dependence of the optical constants in the free-electron range only for copper, but for both copper and nickel in the interband region.

1. Free-electron region

According to Drude's free-electron theory

$$\tilde{\epsilon}^f(\omega)=1-\frac{\omega_p^2}{\omega(\omega+i/\tau)},$$

where $\omega_p^2=4\pi Ne^2/m_0$. If $\omega\tau\gg 1$ then values for the optical mass m_0 could be determined from the slope of a plot, over the free-electron range, of $-\epsilon_1$ versus λ^2 (Fig. 3); and then values for the relaxation time τ from the slope of a plot of ϵ_2/λ versus λ^2 (Fig. 4). In the latter plot, although the points actually lie reasonably close to straight lines, the best lines do not pass through the origin, as predicted by the Drude theory with a constant relaxation time. As a result the relaxation time might be taken to be frequency dependent.[15] Accordingly, we have determined different values for τ at each of the measured frequencies in the free-electron range, from the slopes of straight lines drawn from the or-

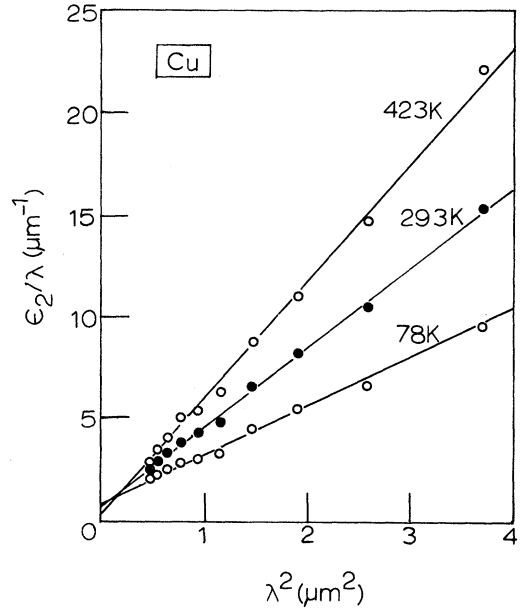

FIG. 4. Imaginary part of the dielectric constant for copper at 78, 293, and 423 K divided by the wavelength, vs the wavelength squared.

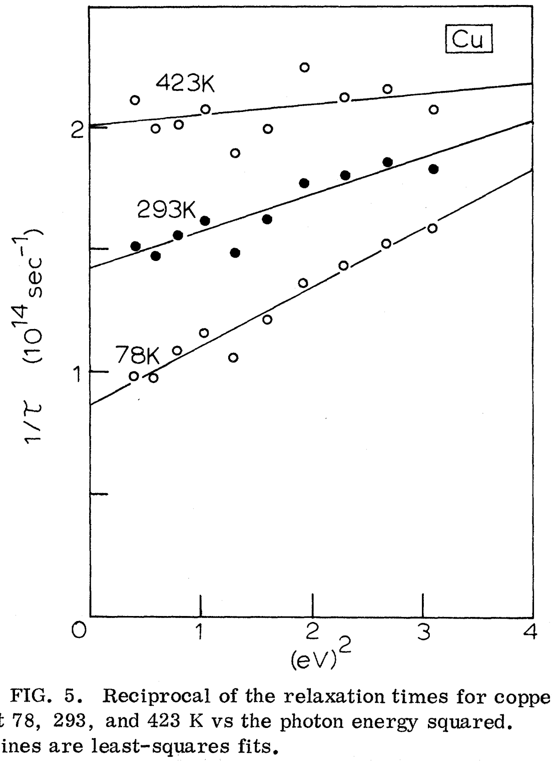

FIG. 5. Reciprocal of the relaxation times for copper at 78, 293, and 423 K vs the photon energy squared. Lines are least-squares fits.

igin through each of the points shown in Fig. 4. If we plot these values as $1/\tau$ versus photon energy squared (Fig. 5), we get acceptable straight lines at each temperature of measurement. [Plots of $1/\tau$ versus eV and τ versus eV also give equally straight lines; however, $1/\tau$ versus $(\mathrm{eV})^2$ is related to theory, as discussed below.] The resulting values of τ for different temperatures are nearly identical above 2 eV, the upper end of the free-electron range. The intercepts at zero frequency correspond to dc values for τ. The results for the optical masses and dc relaxation times at 78, 293, and 423 K are shown in Table II.

Using our extrapolated dc values for τ one can calculate values for the optical dc conductivity of copper, $\sigma = Ne^2\tau/m_0$. These values along with measured electrical dc values[16] are also listed in Table II. Our extrapolated values at 293 and 423 K are both about five times smaller than the corresponding measured dc values. At 78 K, however, our extrapolated value is about 30 times smaller than the measured value. The larger discrepancy at 78 K may be due to the limitation imposed on the mean free path of the electrons by the thickness or grain size of our metal films. The mean free path is equal to the product of the Fermi velocity and the relaxation time, $l = v_F\tau$. The resulting values for l are presented in Table II. At 78 K the mean free path is comparable to the sample thickness (possibly equal to the grain size in the film). The resulting limitation would cause a decreased relaxation time in comparison to the phonon-scattering limitation in bulk specimens.

We have shown that, if we use the Drude free-electron theory with a single relaxation time,[10] then we must assume that the relaxation time is frequency dependent in order to account for the positive intercept in the plot of ϵ_2/λ versus λ^2. The contributions to the relaxation times due to phonons[17] and static impurities[18] are not expected to be frequency dependent over our measured frequency and temperature range.[15] A functional form for a frequency-dependent relaxation time has been calculated by Gurzhi,[19] however, on the basis of the electron-electron interaction. Although his expression fairly accurately describes the frequency dependence of our room-temperature relaxation time, it does not predict the correct temperature dependence: Gurzhi's formula predicts that the rate of change of $1/\tau$ with ω^2 is independent of temperature; however, the plot of our data (Fig. 5) clearly suggests that the rate of change is temperature dependent. More recently, Schnatterly and Nagel[20] have calculated a functional form for a frequency-dependent relaxation time based on scattering in crystallites and grain boundaries in the sample. Their theory also predicts a linear rate of change of $1/\tau$ with ω^2 which is independent of temperature.

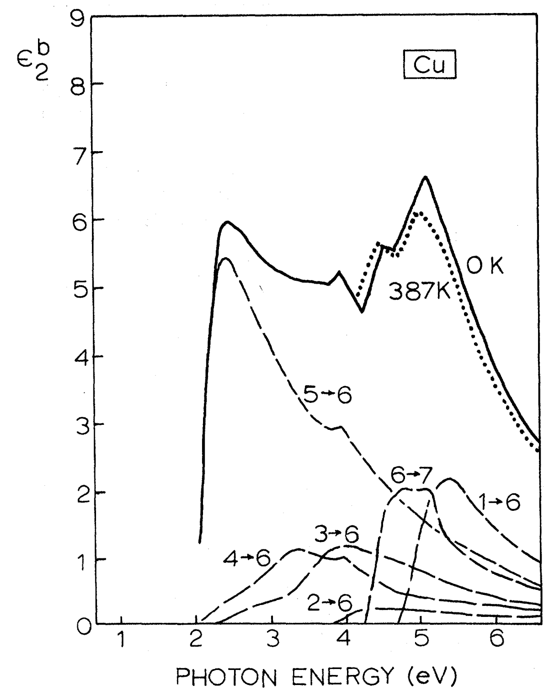

FIG. 6. Band-by-band decomposition (dashed lines) of the imaginary part of the dielectric constant for copper (full line) as calculated by Williams *et al.* (Ref. 3). The dotted curve represents an 8% decrease in magnitude and a 4% shift (2% near 4 eV) in energy of the 6 → 7 transition, to simulate the change in the Debye-Waller factor between 0 and 387 K (or between 78 and 423 K).

TABLE II. Free-electron parameters for copper calculated from data of Table I using the Drude theory, compared with handbook values of electrical conductivity.

	78 K	293 K	423 K
Extrapolated dc relaxation time (sec)	11.4×10^{-15}	6.99×10^{-15}	4.97×10^{-15}
Optical mass (electron mass)	1.56	1.49	1.43
Optical dc conductivity (sec^{-1})	1.56×10^{17}	1.00×10^{17}	0.739×10^{17}
Electrical dc conductivity (sec^{-1})	45.0×10^{17}	5.32×10^{17}	3.46×10^{17}
Mean free path (Å)	200	125	90

Alternatively, the failure of the lines in Fig. 4 to pass through the origin could be ascribed to an excess contribution to ϵ_2 from interband effects (possibly indirect transitions, for example) below the sharp absorption edge at 2 eV.

2. *Interband region*

Williams, Janak, and Moruzzi[3] have made self-consistent band-structure calculations for copper and nickel, neglecting atomic vibrations. In addition, they calculated the transition-matrix elements at each of 240 k points in $\frac{1}{48}$ of the Brillouin zone and, using them, evaluated the interband contributions to the imaginary part of the dielectric constant at $T=0$. Their theoretical values for copper are shown in Fig. 6, together with their resolved contributions from transitions between different bands (numbered in order of increasing energy). We will discuss our results for copper and nickel in terms of these calculations, introducing into their calculation for copper modifications to take into account the temperature dependence of the Debye-Waller factor for transitions between the free-electron-like bands ($6\rightarrow 7$).

The Fourier components V_G of the electron pseudopotential should be multiplied by the temperature-dependent factor e^{-W}, where $W=wF(T/\Theta)$ in the Debye approximation to the phonon spectrum. The constant w and the function $F(T/\Theta)$ are defined as follows[6]:

$$F(T/\Theta)\equiv(T/\Theta)^2\int_0^{\Theta/T}dz\,z/(e^z-1)+\tfrac{1}{4}$$

and

$$w\equiv 3\hbar^2G^2/2Mk\Theta,$$

where $2\pi\hbar$ is Planck's constant, G is a reciprocal-lattice vector, k is Boltzmann's constant, Θ is the Debye temperature, and M is the mass of an atom. The above integral is approximately

$$\begin{aligned}F(T/\Theta)&\simeq\tfrac{1}{6}\pi^2(T/\Theta)^2+\tfrac{1}{4},\quad T\ll\Theta\\&\simeq(T/\Theta)+\tfrac{1}{4},\quad T\gg\Theta.\end{aligned}$$

The temperature-dependent potential V_Ge^{-W} has two effects for free-electron-like bands. First, at the zone boundary G the band gap[21] is $2V_Ge^{-W}$, and so the transitions near this boundary will shift in energy as a function of temperature. Secondly, the same factor enters into the transition probability between the bands, i.e., into the momentum matrix elements: The probability of finding an electron, initially in a state ψ_i, in a higher energy state ψ_f, due to the absorption of a photon, is[22] approximately proportional to $|\langle\psi_f|\nabla|\psi_i\rangle|^2$, where ∇ is the gradient operator. The wave functions ψ_i and ψ_f for electrons in free-electron-like states separated by an energy $2\Delta E$ near a zone boundary are linear combinations of two plane waves[21] such that[14]

$$|\langle\psi_f|\nabla|\psi_i\rangle|^2\cong G^2|V_G/\Delta E|^2,$$

which is the result given by Harrison.[23] (Just on the boundary $\Delta E=V_G$, but away from the boundary ΔE is approximately independent of V_G.) Now when V_G is multiplied by e^{-W}, the probability of electron transitions is proportional to the Debye-Waller factor e^{-2W}, and therefore so is the contribution to ϵ_2, which is due to transitions between the free-electron-like bands. The wave functions for electrons in localized states, on the other hand, are given in the tight-binding approximation as Bloch functions[6] with atomic orbitals for a free atom. Since the atomic functions do not overlap significantly, the evaluation of $\langle\psi_f|\nabla|\psi_i\rangle$ removes[14] the plane-wave functions, leaving only the atomic functions which are not affected by the Debye-Waller factor. As a result, we would roughly approximate the theoretical values of ϵ_2 at temperature T as follows: For the contributions from the free-electron-like bands ($6\rightarrow 7$) we modify the static-ion calculation,[3] decreasing the band gap by e^{-W} and decreasing the transition probability by e^{-2W}, but for the other contributions (involving d-band states) we make no change. (Strictly speaking, the first effect occurs only not too far from the zone boundary and the second only not too near.)

In the case of nickel, over our measured spectral range no transitions between free-electon-like bands are calculated.[3] If the Debye-Waller factor is assumed to account for the main temperature dependence of ϵ_2, one would expect no appreciable change in the dielectric constants with temperature. This prediction is in agreement with our experiments on nickel films. On the other hand, in the case of copper there is an energy range from 4.2 eV up, where transitions are calculated (Fig. 6) between two free-electron-like bands ($6\rightarrow 7$). These occur mainly in a volume of k space near the L point. Over this same spectral range our measured values of ϵ_2 show a relatively large temperature dependence (Figs. 1 and 2) which can be qualitatively explained by our use of the Debye-Waller factor.

The temperature dependence of the experimental curve of ϵ_2 for copper above 4.2 eV is seen primarily as a progressive decrease in the magnitude of the 5-eV peak with increasing temperature, by about 10%. Using as values for copper $\Theta=315$ K, $G=2\pi\sqrt{3}/a$ in the [111] direction, $a=3.608$ Å, and $M=1.063\times10^{-22}$ g, our Debye-Waller factor e^{-2W} predicts that there should be an 8% decrease in the contribution to ϵ_2 from the $6\rightarrow 7$ transition with an increase in temperature from 78 to 423 K. (In the case of x-ray diffraction data on copper, this Debye-Waller factor exactly describes the measured change in the intensity.[24]) The $6\rightarrow 7$ transition accounts for about 30% of the calculated total ϵ_2 value from 4.2 to 6.6 eV (Fig. 6) and so this effect would be seen as a 3% decrease in the theoretical value of ϵ_2. (The other transitions are not between free-electron-like bands. In addition, in the case of nickel where the $1\rightarrow 6$ transition accounts for the entire high-energy peak, there is no appreciable temperature dependence experimentally.) Besides decreasing the magnitude of the contribution to ϵ_2 due to transitions between free-electron-like bands, the Debye-Waller factor also causes these transitions to shift in energy.

At the L point the free-electron-like bands are bands 6 and 7, separated by $2V_G$. Here the factor e^{-W} will cause a decrease in the energy of band 7 and an increase in the energy of band 6 so that the gap decreases by about 4% with a change in temperature from 78 to 423 K. As a result, the contribution to ϵ_2 from $6 \rightarrow 7$ must be shifted down in energy by 4%. But since the Fermi level remains unchanged, the low-energy edge of the $6 \rightarrow 7$ contribution, which starts with transitions at the Fermi level, is shifted down in energy by only about 2%. A plot of the theoretical ϵ_2 with an 8% decrease in magnitude and a 4% shift in energy (2% on the low-energy side) of the $6 \rightarrow 7$ transition is included in Fig. 6, showing reasonable agreement with the experimental behavior in Fig. 1. (The 0-K theoretical curve itself was not modified for the 0-K Debye-Waller factor; inclusion of this modification would further improve the absolute agreement of the theoretical and experimental curves.) From 4.2 to 4.5 eV the theoretical temperature dependence due to the shift of band 7 is incorrect. This effect may be cancelled because by raising band 6 in energy we actually decrease the number of electron states just below the Fermi level, further reducing the contribution of the $6 \rightarrow 7$ transition below 4.5 eV.[25]

B. Comparison with other experiments

Early studies of the temperature dependence in nickel and copper were made by Roberts,[9,10] who measured the optical properties at 90, 300, and 500 K from 0.5 to 3 eV. The behavior of his values of ϵ_2 for copper as a function of temperature is qualitatively similar to ours. Above 2 eV there is no temperature dependence up to 3 eV, and below 2 eV the values of ϵ_2 increase significantly with increasing temperature. In his experiments on nickel Roberts, like us, determined that the optical constants were independent of temperature. More recent measurements were made by Pells and Shiga,[11,12] who used mechanically polished samples in ultrahigh vacuum. They made measurements on copper from 1.7 to 5.9 eV and over the temperature range 77–920 K. Their values qualitatively agree with ours in that ϵ_2 increases with temperature below 2 eV, does not change much with temperature from 2 to 4.2 eV, and decreases with temperature above 4.2 eV. Nevertheless, their values for ϵ_2 are as much as 50% larger than ours at some photon energies. They also made measurements on nickel samples from 0.5 to 5.9 eV. With a temperature change from 295 to 470 K they observed only a very small change in ϵ_2; in this case their values were as much as 20% larger than ours. Finally, Stoll[13] determined the optical constants of copper from 0.5 to 3.3 eV over the temperature range 77–600 K. Stoll's values for ϵ_2 are in close agreement with ours and a similar temperature dependence is observed in his more limited energy range.

The general behavior of the dielectric constants for copper and nickel as a function of temperature is consistent in all of these ellipsometric studies, but the magnitudes differ. These differences may be due to the surface condition of the samples, which depends on preparation techniques as well as any oxidation or condensation which may occur. In addition, distortions may result from the windows of the cryostat. Since our measurements are normalized to our room-temperature measurements made outside the cryostat, we believe that our values are the most accurate in magnitude. Only our measurements covered the whole spectral range, including both the infrared and ultraviolet regions. Knowledge of $\tilde{\epsilon}$ over this wider range is essential to tie together the behavior in the free-electron region and the interband region.

Comparison can also be made with thermomodulation experiments[4] on copper. In the thermomodulation technique, the temperature of the sample is modulated with about 10-K modulation amplitude. The resulting ac component in the reflectance, ΔR, and transmittance, ΔT, is measured. Values for $\Delta\epsilon_1$ and $\Delta\epsilon_2$ can be calculated from ΔR and ΔT, provided that values for ϵ_1 and ϵ_2 at the average temperature of the sample are known. This technique is a useful tool for precisely locating structure in the interband absorption of solids, although its absolute accuracy is limited by knowledge of the thermomodulation amplitude and by the choice of known values for ϵ_1 and ϵ_2. Rosei and Lynch[4] used their measurements of ΔR and ΔT in conjunction with the ϵ_1 and ϵ_2 values of Pells and Shiga[11] to determine values for $\Delta\epsilon_2$ from 1 to 5 eV. The structure in our $\Delta\epsilon_2/\Delta T$ curve (Fig. 2) agrees well with that of Rosei and Lynch, considering that from 2 to 4 eV our $\Delta\epsilon_2$ is smaller than our estimated absolute error. The differences in magnitude are not surprising, since Pells and Shiga's values for ϵ_2 which they used are as much as 50% larger than ours. Furthermore, their $\Delta\epsilon_2$ values were obtained as differences of two large quantities.

Thermomodulation measurements of ΔR have also been made on nickel.[26] The magnitude of the structure in these ΔR measurements is much smaller than our estimated error, thereby confirming that any change in the dielectric constants with temperature would be very small in nickel. Thus our absolute measurements of ϵ_2 as a function of temperature for both nickel and copper are in satisfactory agreement with the thermomodulation experiments, which provide a sensitive test for fine structure in ϵ_2.

IV. SUMMARY AND CONCLUSIONS

We have made reflection and transmission measurements on evaporated copper and nickel films at 78, 293, and 423 K from 0.5 to 6.5 eV and inverted these measurements in order to determine values for the optical constants. The reflection measurements were made on opaque films and the transmission measurements on semitransparent films (~350 Å). Since all of the measurements were made in a cryostat where the windows may introduce distortions, we normalized our measurements to room-temperature measurements made outside the cryostat. In addition, we observed the rates for condensation of water vapor on our samples at 78 K and oxidation of the samples at 423 K, and determined that these effects were within the estimated error of our optical measurements.

We detected some interesting changes in the dielectric constants for copper as a function of temperature, and found that by contrast they are absent in nickel. In copper below 2 eV, where intraband free-electron effects are thought to be dominant, we fit our results to Drude theory. Values for the optical mass, which are determined by ϵ_1, decreased very slightly with temperature, an effect which we believe to be real. The relaxation time, which is determined from the values of the optical mass and ϵ_2, was found to be frequency and temperature dependent. Using the observed frequency dependence we extrapolated to the zero-frequency values for optical dc relaxation time, to compare with the measured electrical dc conductivity for copper. Our extrapolated values for the optical dc conductivity were about five times smaller than measured electrical values, except at 78 K, where a greater discrepancy can be explained by the mean-free-path limitation due to our sample thickness and grain size. At room temperature the high-frequency dependence of the relaxation time predicted from electron-electron or boundary-region scattering gives reasonable agreement with our experiments, but our indicated change in the frequency dependence with temperature is not predicted. Possibly the grain boundary mechanism dominates at 78 K and the electron-electron scattering at higher temperatures. A contribution to the frequency dependence calculated from electron-phonon scattering theory[27] seems to be much too small.[28] Previous optical measurements on noble metals in the near infrared have likewise exposed difficulties of interpretation in terms of free-electron theory; these were summarized recently by Winsemius.[29] Precision reflectance measurements on gold[30] show a deviation above 0.4 eV, which might also be expected in copper. Similar effects are found in alkali metals[31] as well. Perhaps it is not surprising that the assumption of a parabolic band fails to account for intraband transitions at energies as large as 2 eV. (Another approach is to consider the discrepancies as a low-energy tail of interband processes.) No intraband effects were expected or observed in nickel.

Above 2 eV interband processes are dominant in copper as well as nickel. We observed only very small thermal changes in ϵ_2 from 2.2 to 4.2 eV, and the observed change above 5.2 eV in copper can be reasonably well described by a Debye-Waller factor in the matrix elements for transitions between free-electron-like bands and for the electron excitation energy. We modified the zero-temperature theoretical calculation of Williams *et al.* by incorporating (rather crudely) the Debye-Waller factor in order to explain this thermal change in ϵ_2 of copper. The energies at which experimental and theoretical changes occur agree excellently, and the magnitudes of the changes agree reasonably well. This mechanism predicts no thermal change in nickel. Thus we conclude that the large negative values of $\Delta\epsilon_2/\Delta T$ in copper around 5.2 eV are due mainly to the Debye-Waller factor, rather than to volume thermal expansion or changes in the Fermi distribution. The experimental effect of volume expansion can be estimated from Gerhardt's volume-strain modulation results[32] if they are multiplied by the thermal-expansion coefficient of copper. The result agrees well with our positive peak at 2.1 eV but is only one-fifth of our negative peak at 5.2 eV. The theoretical volume effect which we expect on the basis of energy-band calculations[33] is a downward shift of less than 0.1 eV (~1.5%) for the $6\to7$ and $1\to6$ peaks around 5 eV. The predicted shifts of the $5\to6$ peak at 2.1 eV and the $4,5\to6$ ($X_5\to X_{4'}$) peak at 4.0 eV are much smaller yet, as is the effect of thermal changes in the Fermi distribution. The Debye-Waller mechanism therefore seems to account for the largest thermal interband changes. The Debye-Waller factor might also cause a temperature change in alkali metals,[34] but this has not been verified to our knowledge.

Our conclusion that the interband contribution is nearly independent of temperature from 2 to 4 eV in copper, as expected from the Debye-Waller mechanism, actually depends on the crossing of the intraband curves (Fig. 4) at 2 eV. If one simply used the temperature-dependent (but frequency-independent) values of τ calculated from the slopes to extrapolate the free-electron expression into the interband region above 2 eV, a compensating temperature dependence would thereby be introduced into the interband contribution to ϵ_2 as well (because experimentally the sum is almost independent of temperature). Since almost no temperature dependence is observed in the experimental ϵ_2 from 2 to 4 eV, we assume that the intraband contribution remains independent of temperature in the interband portion of the spectrum, or else that it decreases more rapidly with frequency at all temperatures than is described by our Drude expression.

Finally, we have compared our values for the dielectric constants with other experiments and found qualitative agreement as to the thermal behavior. The differences in the magnitudes of the dielectric constants we attribute to the sensitivity of the previous ellipsometric measurements to the condition of the sample surface and to the windows of the cryostat. We find fairly good agreement between our thermal changes and the structure observed by the thermomodulation technique in copper.

ACKNOWLEDGMENTS

The Debye-Waller factor as an explanation of the interband temperature dependence was suggested to us by Dr. A. R. Williams. We are also grateful to him and V. L. Moruzzi for sending us unpublished results and permitting us to use them here. We thank Professor W. E. Lawrence for many very helpful discussions.

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*Partially supported by the NSF.

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