PHYSICAL REVIEW VOLUME 166, NUMBER 3 15 FEBRUARY 1968

Infrared Absorption of Aluminum, Copper, Lead, and Nickel at 4.2°K*

MANFRED A. BIONDI AND ABEL I. GUOBADIA†
Physics Department, University of Pittsburgh, Pittsburgh, Pennsylvania

(Received 15 September 1967)

The optical absorptivities of bulk samples of aluminum, copper, lead, and nickel have been determined calorimetrically at 4.2°K over the wavelength range 1–11 μ. At longer wavelengths ($\lambda > 4\,\mu$), Al, Pb, and Cu exhibit absorptivities independent of wavelength and equal to 1.20, 1.16, and 0.41%, respectively. These results are analyzed in terms of photon absorption by conduction electrons which are scattered at the metal surface and in phonon-generating collisions in the skin-depth region. The values for copper and lead are in satisfactory agreement with the predictions of the theories describing these processes; however, the predicted absorptivity value for aluminum is 30% lower than that observed. In ferromagnetic nickel, an attempt was made to study photon absorption resulting from electron scattering at magnon-generating collisions; unfortunately, the measured absorptivity varies with wavelength even at $\lambda = 11\,\mu$, suggesting the persistence of *interband* transitions. The 4.0% absorptivity of nickel at 11 μ is approximately twice the value estimated for *intraband* transitions involving surface, phonon, and magnon scattering of electrons.

I. INTRODUCTION

THE present paper reports an investigation of the processes by which electrons in the conduction bands of metals at low temperatures absorb optical and infrared radiation. To this end we have extended the long-wavelength limit of previous experiments[1,2] from $\lambda \sim 4\,\mu$ to $\sim 11\,\mu$ in an attempt to eliminate absorption resulting from interband transitions. The metals studied are sufficiently pure and the temperature sufficiently low that the electrical-conductivity mean free path l_c is large compared to the skin depth of electromagnetic penetration δ, and hence we are in the "anomalous-skin-effect" region.[3–5]

To the extent that a free-electron model suffices to describe the behavior of the conduction electrons in the metals under study, we can impose the condition that absorption of an optical photon by an electron requires a simultaneous scattering collision with some third agent to permit momentum and energy conservation. If the classical absorption theory[6] applicable at ordinary temperatures, where $l_c \lesssim \delta$, were valid in the present case, we would expect very little absorption by the conduction electrons as a result of the small likelihood of scattering while in the region of penetration of the electromagnetic field. However, it is observed experimentally[1–9] that the low-temperature absorptivity is only slightly smaller than that at room temperature.

The relatively large absorption results from the fact that the electrons in the skin-depth region are scattered much more frequently than one would estimate from a consideration of the ordinary electron mean free path l_c alone. First of all, an electron coming from the interior of the metal into the skin-depth region suffers a scattering collision at the surface. If the collision results in "specular" reflection of the electron, the component of momentum parallel to the surface of the metal is unchanged at the collision and little absorption results. If the collision results in "diffuse" reflection, that is, the parallel-momentum component after the collision is randomly distributed, appreciable photon absorption occurs. The theoretically predicted absorptivity in the optical and infrared regions for an idealized metal (spherical Fermi surface) is given by[4]

$$A_s = p\frac{2\pi ne^2}{m^*\omega^2}\frac{v_0^3}{c^3} + (1-p)\tfrac{3}{4}\frac{v_0}{c}, \tag{1}$$

where p is the fraction of conduction electrons specularly scattered, $(1-p)$ being diffusely scattered by the surface; n, e, m^* are the conduction-electron density, charge, and effective mass, respectively; ω is the radiation's angular frequency, c the velocity of light, and v_0 the Fermi velocity. The subscript s on the absorptivity indicates that the absorption results from surface scattering.

A second source of absorption at low temperatures involves electron-phonon scattering. When considering electrical conductivity one neglects such processes, since the lattice is in zero-point vibration and there are neither phonons present to cause scattering nor does the electron possess sufficient energy to generate a phonon. In the case of absorption of an optical photon, however, the electron clearly possesses sufficient energy (since $h\nu > k\Theta$, where Θ is the Debye temperature) to generate any phonon in the spectrum and hence such scattering processes are important. The theory[10] for

---

* This research has been supported, in part, by the National Science Foundation under Contract No. GP-5242.

† Present address: Physics Department, University of Lagos, Lagos, Nigeria.

[1] M. A. Biondi, Phys. Rev. **102**, 964 (1956).

[2] M. A. Biondi and J. A. Rayne, Phys. Rev. **115**, 1522 (1959).

[3] A. B. Pippard, in *Advances in Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1956), Vol. 6, p. 1ff.

[4] T. Holstein, Phys. Rev. **88**, 1425 (1952).

[5] R. B. Dingle, Physica **19**, 311 (1953).

[6] See, for example, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1953).

[7] K. Weiss, Ann. Physik **2**, 1 (1948).

[8] K. Ramanathan, Proc. Phys. Soc. (London) **A65**, 532 (1952).

[9] J. A. Rayne, Phys. Rev. Letters **3**, 512 (1959).

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

this process leads to prediction of an absorptivity

$$A_{\mathrm{ph}}=\tfrac{2}{5}A_{\mathrm{cl}}\Theta/T\,, \tag{2}$$

where $A_{\mathrm{cl}}=(m^*/\pi ne^2)^{1/2}/\tau$ is the classical (high-temperature) absorptivity obtained when $l\ll\delta$, τ being the mean free time between collisions, and T the temperature at which the classical absorptivity is determined.

In the case of ferromagnetic metals, one must also consider an analogous electron-magnon (quantized spin wave) scattering process as a possible absorption mechanism. Again, at low temperatures the magnon spectrum will be unexcited; however, upon absorbing a photon a conduction electron will have sufficient energy to excite any part of the magnon spectrum, inasmuch as $h\nu>kT_c$, where T_c is the Curie temperature. The theory for this effect has not been worked out, but descriptions of scattering processes affecting electrical conductivity in ferromagnets indicate appreciable scattering of electrons by magnons as well as phonons at certain temperatures.[11]

An obstacle to the study of these various mechanisms of optical absorption by conduction electrons is the occurrence of interband transitions in the metal over the wavelength region studied. In addition to the strong absorption resulting from direct interband transitions ($\mathbf{k}_{\mathrm{init.}}=\mathbf{k}_{\mathrm{final}}$), one must consider, in the case of warped energy bands, absorption at longer wavelengths (lower energy) as the result of indirect transitions, $\mathbf{k}_{\mathrm{final}}=\mathbf{k}_{\mathrm{init.}}\pm\mathbf{q}$, where $\mathbf{q}$ is the wave vector of the phonon required to conserve momentum.[1,12] Although the wavelength positions of absorption bands resulting from direct transitions are well known for many metals, the weaker indirect transition contributions are less well known and may contribute to the absorption in the near-infrared region.

The metals studied in the present work, Al, Cu, Pb, and Ni, were chosen for their rather different surface, phonon, and magnon scattering contributions to the optical absorption.

II. METAL SAMPLE PREPARATION

In order to investigate the absorptive properties of bulk metals, solid samples rather than evaporated films were used. To obtain surfaces which represented, as nearly as possible, the undisturbed metal lattice and also exhibited a suitable optical finish, procedures involving cutting, polishing, etching, annealing, chemical brightening, and electropolishing were developed for each metal. The samples, in the shape of disks $\frac{5}{8}$ in. in diameter with a small threaded boss protruding from the back, were machined from high-purity material and then processed as follows:

Aluminum. Samples were machined from 99.999+ % pure material which had been vacuum-melted. Samples were successively mechanically polished, chemically brightened, and electropolished (see Appendix) and then vacuum-annealed at 500–550°C for 6 h. Samples were given a final electropolish and distilled water rinse in a helium-filled dry box, dried in a helium jet, and installed under the helium atmosphere in the apparatus. The samples were checked under intense, grazing incidence light for surface filming or defects. The apparatus was evacuated and cooled to low temperatures as soon afterwards as possible. Installation and examination of the other metal samples also followed this procedure.

Copper. Samples were machined from 99.999+ % pure, vacuum-melted material and were then lightly polished—mechanically, chemically, and at last electrolytically—under a helium atmosphere and installed.

Lead. Samples were machined from 99.999+ % pure material which had been vacuum-melted and then were lightly polished mechanically using 4/0 emery and white oil, then rinsed with ether and alcohol. Following chemical brightening and a rinse in preboiled distilled water, the samples were electropolished under a helium atmosphere and installed.

Nickel. Samples A and B were machined from 99.99% pure material, while sample C was machined from the same material after it had been vacuum-melted. All samples were mechanically polished with diamond dust, electrolytically etched lightly, and rinsed with distilled water. Samples were vacuum-annealed at 750–850°C for 12 h. Samples A and B were chemically brightened and installed in the apparatus. Sample C was electrolytically polished under a helium atmosphere and installed.

III. EXPERIMENTAL APPARATUS

The present apparatus is very similar to the calorimetric optical-absorption apparatus described in detail previously.[1,2] The evacuated envelope housing the samples under study is immersed in the liquid helium (see Fig. 1). The base, in contact with the liquid helium, is electronically temperature-controlled to approximately ±0.0001°K by means of a heater winding (H) and a sensing carbon resistance thermometer (T). The metal sample target is threaded into a copper stage containing a heater and a thermometer and mounted on thin-walled stainless steel tubing connected to the base. A similar stage supports the total absorber, coated with gold black. Fine copper wires from the stages to the base adjust the thermal response time of the stages to energy inputs. The infrared radiation enters the top of the apparatus (not shown) through a Kodak Irtran 2 window (Irtran 2 transmits radiation between ~1 and 13 μ in wavelength), down an electro-

---

[11] For a discussion of scattering mechanisms important in determining the electrical conductivity of nickel, see D. A. Goodings, Phys. Rev. **132**, 542 (1963).

[12] L. H. Hall, J. Bardeen, and F. J. Blatt, Phys. Rev. **95**, 559 (1954).

polished stainless steel light pipe, and is focused by the Irtran 2 lens onto the target at an angle of incidence of 15°. That part of the radiation not absorbed by the target is reflected into the absorber bucket, where it is essentially totally absorbed. As discussed previously,[1,2] tests are made to eliminate the small effects of stray radiation on the determinations.

In operation, a steady intensity of radiation of the desired wavelength is allowed to fall on the target until the target and absorber stages arrive at stationary temperatures slightly above the base temperature. The resistance values of the thermometers in each stage are then precisely determined. With the radiation turned off, dc power is supplied to the heaters imbedded in the stages to reproduce the target and absorber temperature rises by reproducing the resistance thermometer readings. The required dc powers are then precisely measured and the absorptivity is calculated from the formula $A=P_T/(P_T+P_A)$, where the subscripts T and A refer to the target and absorber stages, respectively.

Radiation at wavelengths $\lambda<3\ \mu$ is obtained from a 120-W tungsten projection lamp dispersed by a Bausch and Lomb high-intensity grating monochromator. Radiation at wavelengths greater than 3 μ is obtained from an open Nichrome wire glower. Two Kodak infrared interference filters have been used to select portions of the spectrum, one having maximum transmission at $\lambda_m=4.55\ \mu$ and a half-intensity width, $\Delta\lambda=0.08\ \mu$, the other $\lambda_m=10.9\ \mu$ and $\Delta\lambda=1.1\ \mu$.

IV. RESULTS AND DISCUSSION

The measured absorptivities (corrected to normal incidence[1,2]) are given as functions of wavelength in Table I for aluminum, copper, lead, and nickel. The values represent averages of several measurements at each wavelength. In the case of nickel, the data given for sample C refer to the electropolished specimen made from vacuum-melted material, which consistently gave values 2–10% lower than for the chemically brightened samples A and B, whose absorptivity values appear in parentheses. A plot of absorptivity versus wavelength for these materials is given in Fig. 2. An estimate of random and systematic errors in the measurements places the errors between 1 and 5%, the larger error being associated with those wavelengths (~2–3 μ) where the available incident radiant energy was small ($<100\ \mu$W) and with the metals having the smallest absorptivities (especially Cu). No estimate of the error due to defective surface preparation is available; we have adopted the procedure of preparing successive samples, until the minimum absorptive values are attained, and give the data for the final sample group.

TABLE I. Measured absorptivities (corrected to normal incidence) as a function of wavelength for metals at 4.2°K.

Wavelength (μ)	Absorptivity (%) Aluminum	Copper	Lead	Nickel C	Nickel A and B
1.0	3.88	···	12.71	21.4	(22.9)
1.1	3.46	···	8.26	20.1	(22.2)
1.3	2.63	0.45	3.42	18.9	(20.7)
1.5	2.38	0.44	1.72	16.8	(17.9)
1.8	2.18	0.41	1.32	14.4	(15.5)
2.0	1.77	0.39	1.25	13.4	(14.6)
2.2	1.74	···	1.24	12.2	(13.8)
2.5	1.66	0.41	1.20	11.2	(12.0)
3.0	1.45	···	1.19	8.6	(10.0)
4.55	1.22	0.41	1.15	5.6	(6.0)
10.9	1.18	0.41	1.16	4.0	(4.1)

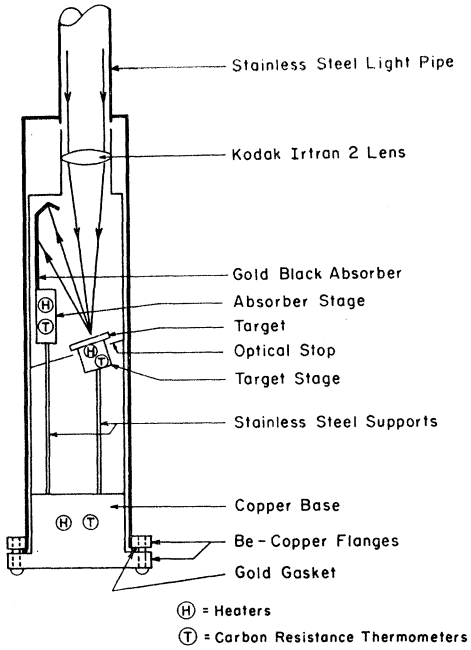

FIG. 1. Schematic diagram showing the evacuated envelope of the optical-absorption apparatus, which is immersed in a liquid-helium bath at 4.2°K.

There are two features apparent from these curves; with the exception of Ni, as we go further into the infrared the absorptivity values appear to become independent of wavelength, as expected for the conduction-electron absorption processes discussed in the Introduction. The second feature is the sharp rise in absorption at shorter wavelengths noted for all four metals (earlier work on Cu[1,2] showed this sharp rise at $\lambda\sim0.6\ \mu$, beyond the range of the infrared optical elements used in the present experiment). The sharp rise to large absorptivity values is taken as an indication of the onset of direct, interband transitions. That portion of the spectrum in which a rather gradual rise in absorptivity is noted for all four metals is discussed later. Inasmuch as the physical quantities necessary for calculations of the absorptivities (e.g., the conduction-electron density) are not equally well

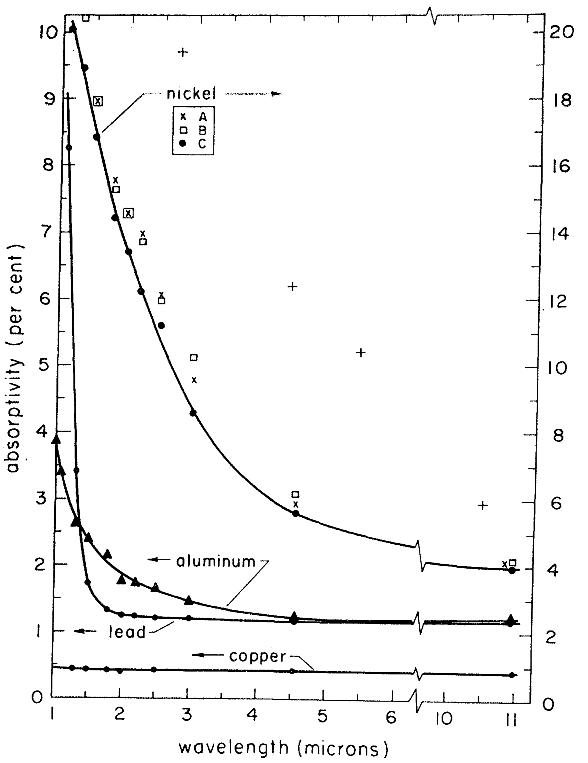

FIG. 2. Measured optical absorptivities versus wavelength at 4.2°K of nickel, aluminum, lead, and copper. The + symbols refer to values deduced from room-temperature determinations of the complex index of refraction of nickel by I. N. Shkharevskii and V. G. Padalka, Opt. Spectry. 6, 45,505 (1959).

known for the four metals, we discuss them in the order of decreasing available information.

Copper. The finding of an absorptivity independent of wavelength for $\lambda > 1.8\ \mu$ (see Table I and Fig. 2) is in agreement with the results of earlier studies[1,2,9]; however, the value $A = (0.41 \pm 0.02)\%$ is somewhat smaller (10–20%) than the previous values, perhaps owing to a somewhat better surface finish by use of both chemical polishing and electropolishing. We may compare the observed value with the predictions of theory by the use of Eqs. (1) and (2). For copper we take an effective mass $m^* = 1.38m$ and a Debye temperature $\Theta = 344°\mathrm{K}$ from specific-heat data.[13] The conduction-electron density n is $8.5 \times 10^{22}\ \mathrm{cm}^{-3}$ and the dc conductivity at $T = 300°\mathrm{K}$ is $\sigma_0 = 5.33 \times 10^{17}$ esu.[14] These parameters may be used to evaluate the absorptivity through Eqs. (1) and (2) by noting that the one-electron model[15] gives

$$v_0 = (h/m^*)(3n/8\pi)^{1/3}, \tag{3}$$

where h is Planck's constant, and

$$1/\tau = ne^2/m^*\sigma_0. \tag{4}$$

Using these values in Eqs. (1) and (2), we obtain, on the assumption of completely diffuse surface scattering ($p = 0$),

$$A = A_s + A_{\mathrm{ph}} = 0.28 + 0.17 = 0.45\%,$$

in good agreement with the measured value, considering both the experimental and theoretical uncertainties.

Rayne[9] obtained a value of $A_{\mathrm{ph}} = 0.38\%$ in his analysis by using a Debye temperature $\Theta_L = 1.5\Theta$ appropriate for the longitudinal-phonon spectrum in the volume-scattering formula, inasmuch as Holstein's formulation[10] discusses a particular photon–electron–phonon coupling interaction which involves only the longitudinal phonons. Rayne was led to this analysis by his absorption measurements at higher temperatures, which seemed to require substantial specular surface scattering ($p > 0$), leading to a smaller surface contribution and hence the need for a larger volume contribution to bring theory into agreement with experimental results.[9] We do not agree with this analysis because, as Holstein points out,[16] measurements of the temperature dependence of electrical resistivity agree with the predictions of a theory employing the ordinary Debye Θ, indicating that transverse as well as longitudinal phonons contribute significantly to the scattering. Thus, in the volume-optical-absorption theory one should expect coupling mechanisms in addition to the one Holstein considered explicitly, which should then bring both transverse and longitudinal phonons into play. Further, microwave absorption studies of copper,[17] where the skin depth is only an order of magnitude larger than in the optical case (~200 Å), indicate best agreement with theoretical predictions for completely diffuse ($p = 0$) scattering.

It therefore appears that photon absorption by the conduction electrons during diffuse surface scattering and phonon-generating volume collisions explains the observed optical absorptivity of copper rather well, for the wavelength region $1.8\ \mu < \lambda < 11\ \mu$. The gradual increase in absorptivity with decreasing wavelengths below $\lambda = 1.8\ \mu$ and before the main absorption edge at $\lambda = 0.6\ \mu$ has been attributed to indirect (phonon-generating) interband transitions,[1] as discussed in the Introduction. As we shall see in the discussion of lead, it is possible that, instead, the effect results from conduction-electron (intraband) absorption and a change of the electromagnetic penetration depth on approaching a strong absorption edge.

Lead. In order to provide a better test of the theory describing the volume absorptivity arising from phonon generation, we chose the metal lead, with the expectation that the volume-scattering term would substantially outweigh the surface-scattering term. Unfortunately, the quantities needed in the theoretical evaluation are less well known; we have taken $m^* = m$,

---

[13] W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, Phys. Rev. 98, 1699 (1955).

[14] R. B. Dingle, Physica 19, 348 (1953).

[15] See, for example, Frederick Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Co., Inc., New York, 1940), Chap. IV.

[16] T. D. Holstein (private communication).

[17] R. G. Chambers, Proc. Roy. Soc. (London) A215, 481 (1952).

$n=1.32\times10^{23}$ cm^{-3} (four conduction electrons/atom), $\Theta=110$°K [18,19] and $\sigma_0=4.6\times10^{16}$ esu at 293°K.[18] The Fermi velocity in the second zone of lead has been determined[20] as 8.4×10^7 cm/sec.[21] For these values, we find from Eqs. (1)-(4),

$$A=A_s+A_v=0.21+1.18=1.39\%.$$

This value is in fair agreement with the long-wavelength experimental value $A=(1.16\pm0.02)\%$, in view of the uncertainties in the quantities used in the evaluation of the theoretical formulas. Until better values of such quantities as m^* are available, we can only note that, in a metal where the decreased conductivity suggests stronger electron-phonon scattering, the contribution to the absorptivity of the phonon-generating process seems to account for most of the observed value.

In preliminary studies of lead[22] we sought to explain the gradual increase in absorptivity with decreasing wavelength below $\lambda\sim2\,\mu$, but before the main absorption edge at $\lambda\sim1\,\mu$ (see Fig. 2). We considered the effect on the electromagnetic penetration depth of the existence of a strong interband absorption at $\lambda\sim1\,\mu$ and the attendant effect on the conduction electrons' absorption in the infrared. Using the observed absorption versus frequency curve, extended in physically reasonable fashion to zero and to high frequencies, Bieringer[22] made a rough numerical integration of the Kronig-Kramer relationship and found a small ($\lesssim10\%$ at $1.4\,\mu$) progressive increase in the penetration depth δ at frequencies approaching, but less than, the threshold for interband absorption. (In the anomalous skin-effect theory, δ is considered to be independent of wavelength.) Thus, it appears that the gradual increase in A with decreasing wavelength noted for a number of metals, e.g., Pb, Cu, Ag, Al, may result in part from increased penetration of the radiation as one approaches a strong absorption edge. This explanation of the increasing absorption is physically more satisfying than that based entirely on indirect interband transitions. Such transitions require warped energy bands (so that the minimum energy gap does not correspond to a "vertical," $\mathbf{k}_i=\mathbf{k}_f$, transition), and it does not seem reasonable to expect all metals to exhibit the appropriate warped band structure.

Aluminum. The shape of the absorptivity versus wavelength curve for aluminum suggests that for $\lambda>4.5\,\mu$ the absorptivity approaches the constant value, $A=(1.20\pm0.03)\%$. This value is in reasonable agreement with Ramanathan's value,[8] $A=1.11\%$, obtained with room-temperature blackbody radiation ($\lambda_{\max}\sim14\,\mu$) incident on his sample. In order to compare our value with theoretical predictions, we have used the values $n=1.8\times10^{23}$ cm^{-3},[23] $m^*=1.5m$,[24] and $v_0=1.34\times10^8$ cm/sec,[25] together with $\sigma_0=3.5\times10^{17}$ esu at $T=293$°K and $\Theta=428$°K.[18,24,26] The resultant value of absorptivity, assuming diffuse-surface scattering, is

$$A=A_s+A_v=0.34+0.50=0.84\%.$$

This value is 25–30% less than Ramanathan's or our value.

The lack of agreement may indicate the deficiencies of attempting to apply the theory, based on spherical Fermi surfaces, to actual metals having more complicated Fermi surfaces. However, aluminum has probably the least-distorted Fermi surface of the metals studied, and therefore we should have expected greater success with the free-electron model in this case. It should be noted that the assumption of less than total diffuse scattering (i.e., $p>0$) makes for even poorer agreement between experiment and theory. Finally, the gradual increase in absorptivity going toward shorter wavelengths may result from indirect interband transitions or a changing penetration depth, as discussed for the cases of copper and lead.

Nickel. In earlier, unpublished studies of nickel over the wavelength range $0.4-3.3\,\mu$ we observed strong absorption ($\gtrsim10\%$), indicating the persistence of interband transitions even at $\lambda=3\,\mu$. The present study was therefore undertaken to obtain data at longer wavelengths, $\lambda=11\,\mu$, where interband transitions hopefully would not longer occur. Nickel, like lead, exhibits the reduced dc electrical conductivity, which suggests strong volume-electron scattering and therefore should exhibit an optical absorption resulting from volume-electron scattering which strongly outweighs the surface-scattering contribution. A complication, not appreciated at the outset, is that the volume-electron scattering can result not only from phonon-generating collisions, as in lead, but also from magnon-generating collisions, owing to the ferromagnetic properties of nickel.

From Table I and Fig. 2 it will be seen that nickel, unlike the other metals studied, apparently has *not* reached a constant absorptivity value, even at $\lambda=11\,\mu$. Also, the smallest value found, $A=4.0\%$, is much too large to be accounted for by the surface and volume scattering of electrons, as can be seen from the following

---

[18] *American Institute of Physics Handbook* (McGraw-Hill Book Co., Inc., New York, 1963), 2nd ed.

[19] R. L. Dolecek, Bull. Inst. Intern. Froid, Annexe 3, 300 (1955).

[20] A. V. Gold, Phil. Trans. Roy. Soc. London **A251**, 85 (1958).

[21] The first zone of lead is filled; the third and fourth zones represent smaller sections of the Fermi surface; therefore we have used the second-zone Fermi velocity as most representative of the absorbing electrons in lead.

[22] R. Bieringer, M.S. Thesis, University of Pittsburgh, 1962 (unpublished).

[23] T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 38 (1955).

[24] N. Phillips, Phys. Rev. **114**, 676 (1959).

[25] E. Fawcett in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 197.

[26] N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **34**, 1116 (1958) [English transl.: Soviet Phys.—JETP **7**, 773 (1958)].

estimate. The available data on the relevant properties of nickel are meager; we use the magnetic moment value of 0.6 conduction electrons/atom[27] to estimate that $n=5.5\times10^{22}$ cm^{-3} (copper has $n=8.5\times10^{22}$ cm^{-3}). If we assume $m^*=m$, then $A_s=0.34\%$.

From the analysis of Beattie and Conn[28] of the optical constants of nickel, we obtain $\sigma_0=1.15\times10^{17}$ esu and $\tau=8.4\times10^{-15}$ sec at 270°K, which values are consistent with those given by Mott and Jones,[27] $\sigma_0=1.36\times10^{17}$ esu and $\tau=9.76\times10^{-15}$ sec at 273°K. The Debye temperature of nickel is taken as 450°K.[18,29,30] If we neglect for the moment the magnon contribution to scattering in determining σ_0 and the volume absorptivity, we obtain an estimate of the absorptivity, $A_{\text{ph}}=1.9\%$. Thus the total absorptivity is estimated to be of the order of $A=A_s+A_{\text{ph}}=2.2\%$, or approximately half the value observed at $\lambda=11\,\mu$. No reasonable adjustment of such quantities as m^* seems likely to provide significantly better agreement with the observed value.

It does not seem probable that the dc conductivity at high temperatures and the optical absorption at low temperatures are affected differently enough by the magnon and the phonon scattering of electrons to account for the factor-of-two discrepancy between the theoretical and experimental values of the absorptivity. This statement is based on the fact that the Debye and Curie temperatures ($T_c=631$°K) of nickel, the phonon and magnon spectrums, and the electron-scattering powers of magnons and phonons do not appear to differ sufficiently to account for the effect. However, the present theory of volume optical absorptivity[10] restricts itself to consideration of *intraband* transitions of the conduction electrons.

In nickel, if one considers *interband* scattering between the overlapping s and d bands, the relative contribution of magnon (and phonon) scattering to high temperature dc conductivity and to low-temperature optical absorption may be quite different. In low-temperature optical absorption, the electron can reach final energy states $\epsilon_f\simeq\epsilon_i+h\nu$, and final wave-vector states $\mathbf{k}_f=\mathbf{k}_i+\mathbf{q}$ [where $\mathbf{q}$ indicates the wave vector of the generated magnon (or phonon)]. Since $h\nu$ is not negligible ($\gtrsim0.1$ eV), a different part of the neighboring band is accessible to the scattered electron in this case than in that of the high-temperature electrical conductivity, where $\epsilon_f\simeq\epsilon_i$ and $\mathbf{k}_f=\mathbf{k}_i\pm\mathbf{q}$ (the $\pm$sign indicating either generation or absorption of a magnon or phonon).[31] Thus, *interband* transitions between the unfilled $3d$ and $4s$ bands of nickel may account for the added absorption.

The observed decrease in absorption with increasing wavelength also is consistent with an indirect, *interband* transition effect. Theoretical calculations[32] suggest that interband transitions below 0.2 eV energy are possible. These s-d interband transitions evidently lead to an internal photoelectric absorption band, weakly peaking at $\lambda\sim1.0\,\mu$.[33] Very recent studies of direct, interband optical-absorption transitions in nickel films have been carried out by Hanus *et al.*,[34] using a thermally modulated reflectivity technique. These studies indicate additional structure at $\lambda\simeq3\,\mu$ ($h\nu=0.4$ eV) and at $\lambda\simeq5\,\mu$ (0.25 eV). The band-structure models suggested by them[34] to explain various data on nickel (optical reflectivity, ferromagnetic Kerr effect, magnetoresistance, and de Haas–van Alphen effect) admit the possibility of the longer-wavelength indirect interband transitions apparently required by our results.

Thus, it appears that in nickel we have not been able to carry out measurements at sufficiently long wavelengths to avoid *interband* transitions. One can not proceed to much longer wavelengths to test the *intraband* volume absorption theory, inasmuch as the present theory[10] is based on the assumption that $h\nu>k\Theta$, which places a long-wavelength limit at about $20\,\mu$ for complete excitation of the phonon spectrum. (For excitation of the magnon spectrum, the related condition $h\nu>kT_c$ would limit measurements to wavelengths shorter than $\sim15\,\mu$.)

V. CONCLUSIONS

Our attempts to study low-temperature optical absorption resulting from phonon-generating, electron-scattering collisions in the skin-depth region have been successful only in lead, where the surface scattering contribution to the optical absorption is rather small ($<20\%$) and the effect of interband transitions at long wavelengths seems to be absent. We have been able to verify, within experimental error, the earlier results obtained for copper.[1,2,9] Our attempts to study the long-wavelength absorption in nickel resulting from *intraband* electron transitions involving phonon- and magnon-generating collisions appear to be frustrated by continuing *interband s-d* scattering even at $\lambda=11\,\mu$ ($h\nu\sim0.1$eV). Studies at longer wavelengths ($\lambda\gtrsim20\,\mu$) may avoid interband effects; however they will require a modification of the available theory[10] to take into account the inability of the electron, having absorbed the photon, to excite the full phonon or magnon spectrum.

ACKNOWLEDGMENTS

The authors wish to thank their colleagues, especially M. P. Garfunkel and J. A. Rayne, for helpful dis-

---

[27] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications Inc., New York, 1958).

[28] J. R. Beattie and A. K. T. Conn, Phil. Mag. **46**, 989 (1955).

[29] W. K. Keesom and C. W. Clark, Physica **6**, 513 (1939).

[30] J. A. Rayne and W. R. G. Kemp, Phil. Mag. **1**, (8) 918 (1956).

[31] At high temperatures, thermal excitation of the magnons and phonons makes them available for absorption at a collision with an electron.

[32] S. Wakoh, Technical Report of the Institute of Solid State Physics, Ser. A, No. 168, University of Tokyo, 1965 (unpublished).

[33] H. Ehrenrich, H. R. Philip, D. J. Olechna, Phys. Rev. **131**, 2469 (1963).

[34] J. Hanus, J. Feinleib, and W. J. Scouler, Phys. Rev. Letters **19**, 16 (1967).

cussions of this work. They are grateful to R. Bieringer for permission to quote unpublished results of his research.

APPENDIX: CHEMICAL BRIGHTENING AND ELECTROPOLISHING SOLUTIONS

The following solutions and procedures were used in the preparation of the various target samples:

Aluminum. Electropolishing: Al cathode. Electrolyte; 200:112:100 solution of orthophosphoric acid, sulfuric acid, and distilled water at 94°C. Current density, 0.8 A/cm^2. Polishing time 3–5 min.

Copper. Chemical brightening: 4:11:5 solution of nitric acid, orthophosphoric acid, and glacial acetic acid at 60–70°C. Polishing time 30–60 sec.

Electropolishing: Cu cathode. Electrolyte, 2:1 solution of orthophosphoric acid and distilled water at 20–25°C. Voltage drop across cell 1.5–2.0 V. Polishing time ~5 min.

Lead. Chemical brightening: 7:3 solution of acetic acid and hydrogen peroxide at 25°C.

Electropolishing: Stainless steel cathode. Electrolyte, 7:3 solution of acetic acid and perchloric acid at 20–30°C. Voltage drop across cell 10 V. Polishing time 1–2 min.

Nickel. Chemical brightening: 5:3:1:1 solution of glacial acetic, nitric, sulfuric, and orthophosphoric acids at 90°C. Polishing time 10–15 sec.

Electropolishing: Ni cathode. Electrolyte, 39:29 solution of sulfuric acid and distilled water at 30°C. Current density 0.5 A/cm^2. Polishing time ~30 sec.

PHYSICAL REVIEW VOLUME 166, NUMBER 3 15 FEBRUARY 1968

Optical Phonons in BeO Crystals*

EUGENE LOH
Physical Sciences Department, Douglas Aircraft Company Santa Monica, California

(Received 5 October 1967)

The optical phonons of BeO crystals have been studied by measurements of polarized infrared reflection spectra in the range 400–4000 cm^{-1}. Raman spectra for shifts in the range 100–1500 cm^{-1} at room temperature were analyzed. Oscillator fits to the reflectivity spectra lead to values for the frequency, linewidth, and strength of the A_1 and E_1 vibrations. The infrared data are confirmed by the Raman measurements, which also give the Raman-active-only E_2 vibrations. Within experimental error, the high-frequency E_2 mode at 684 cm^{-1} coincides with the A_1 transverse mode and is at about twice the frequency of the low-frequency E_2 mode. The multiple-phonon absorptions at zone boundaries have also been measured at room temperature on the high-energy side of the reststrahlen band up to 4000 cm^{-1}.

I. INTRODUCTION

THE metal oxide of smallest cation radius 0.34 Å is beryllium oxide. It therefore has many unique properties. These are, for example, high heat conductivity[1] due to large Debye temperature, high electrical resistivity due to high-energy gap,[2] and simple crystal structure (wurtzite).[3,4] BeO is also one of the principal reactor-moderating materials.[5] The dielectric and lattice properties of BeO single crystals have been studied by several authors. Austerman *et al.*[6] and Smith *et al.*[4] have studied its polar properties by measuring piezoelectric, dielectric, and pyroelectric constants. Brugger *et al.*[7] have measured some parts of the dispersion relations of BeO by inelastic neutron scattering. Morrow[8] and others[6,9] have measured the infrared transmission of thin BeO single crystals. Recently, Cline *et al.* have determined the volume compressibility[10] on polycrystalline BeO and elastic constants[11] by measuring ultrasonic velocities in BeO single crystals.

Lattice vibrations of BeO were studied by measurement of the polarized spectra of both infrared reflectance and Raman scattering on single crystals at room temperature. The spectra are simple, yet they clearly show the effect of the anisotropy of the wurtzite

---

* This work was partially supported by the Douglas Independent Research and Development (IRAD) Program.

[1] E. Ryshkewitch, Intern. Sci. Technol. **1962**, 54 (1962).

[2] E. Loh, Solid State Commun. **2**, 269 (1964); F. Wooten and G. A. Condas, in H. W. Newkirk and D. K. Smith, University of California Radiation Laboratory Report No. UCRL 7466, 1963 (unpublished).

[3] W. L. Bragg, Phil. Mag. **34**, 647 (1920).

[4] D. K. Smith, H. W. Newkirk, and J. S. Kahn, J. Electrochem. Soc. **111**, 78 (1964).

[5] *Proceedings of The First International Conference on Beryllium Oxide, Sydney Australia, 1963*, edited by R. Smith and J. P. Howe (North-Holland Publishing Co., Amsterdam, 1965).

[6] S. B. Austerman, D. A. Berlincourt, and H. H. A. Krueger, J. Appl. Phys. **34**, 339 (1963); S. B. Austerman (private communication).

[7] R. M. Brugger, K. A. Strong, and J. M. Carpenter, J. Phys. Chem. Solids **28**, 249 (1967).

[8] R. Morrow, in H. W. Newkirk and D. K. Smith, University of California Radiation Laboratory Report No. UCRL 7466, 1963 (unpublished); R. Morrow (private communication).

[9] J. R. Durig, R. C. Lord, W. J. Gardner, and L. H. Johnston, J. Opt. Soc. Am. **52**, 1078 (1962).

[10] C. F. Cline and D. R. Stephens, J. Appl. Phys. **36**, 2869 (1965).

[11] C. F. Cline, H. L. Dunegan, and G. W. Henderson, J. Appl. Phys. **38**, 1944 (1967).