

atoms have each a dangling  $p$ -type bond and three trigonal  $sp^2$ -type bonds to the underlying atoms.

(b) The clean (111) and  $(\bar{1}\bar{1}\bar{1})$  surfaces of GaSb have different sticking coefficients for gases, the maximum values being  $10^{-5}$  and  $10^{-4}$  for oxygen on the Sb and Ga faces, respectively, and  $10^{-6}$  and  $10^{-5}$  for  $\text{CO}_2$ , respectively, these values being obtained by the method discussed in reference 2.

(c) Oxygen adsorbs in several layers at room temperature on (111) and  $(\bar{1}\bar{1}\bar{1})$  surfaces of GaSb and on (100) surfaces of InSb.

(d) The above clean surfaces may be regenerated by heat treatment alone after oxygen adsorption. An im-

portant mechanism for oxygen removal during heating to 350–400°C is diffusion into the bulk of the crystal.

#### X. ACKNOWLEDGMENTS

The author has had valuable discussions with Professor H. E. Farnsworth in the course of this work, and is indebted to Dr. P. Handler of University of Illinois for a discussion during which the model for a clean (111) surface was worked out. The single crystals of InSb and GaSb were kindly supplied by Dr. H. C. Gatos of Lincoln Laboratory, Massachusetts. Technical and glassblowing assistance was given by C. Forrest and M. J. Michael.

### Optical Constants of Silver

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The optical constants for electrolytically polished silver samples were determined from normal-incidence reflectance data in the spectral region 2 to 10 ev. The sharp minimum in the curve for  $k$  near 3.8 ev, which is associated with the onset of interband transitions, is deeper than in previous results. A second minimum is observed near 9.2 ev.

#### INTRODUCTION

THE optical properties of metals have been the subject of many studies.<sup>1</sup> In the region of infrared frequencies, where free-electron absorption predominates, these processes may be described by the Drude equations. At higher energy, however, pronounced deviations from the Drude theory are observed in many cases. In the noble metals, this departure takes the form of a sharp minimum in the curve for  $k$ , the extinction coefficient. For silver this structure is particularly pronounced and much attention has been given to reflectance and transmission data in the vicinity of this absorption window.<sup>2</sup> Corresponding theoretical treatment, however, is less complete. There seems little doubt that this anomaly is associated with the onset of interband electronic transitions. The free-electron model, applied to silver with one electron per atom, would predict that the perfectly reflecting region should extend to the plasma frequency at about 9 ev.<sup>3</sup> Thus the free-electron model cannot be applicable to silver.

Recently, Suffczynski<sup>4</sup> has proposed a model which allows the calculation of the contribution of interband transitions to the optical constants of metals. For silver, the results are particularly interesting. The present investigation is a further study of the optical properties of this metal over an extended range of photon energy. The optical constants are determined in the region 2 to 10 ev by applying the Kramers-Kronig relations to normal incidence reflectance data.<sup>5</sup> The results are of especial interest because this range of energy includes the plasma resonance frequency calculated from the free-electron model.<sup>3</sup>

#### EXPERIMENTAL PROCEDURES

The techniques employed in these measurements have been described in a previous paper.<sup>5</sup> Reflectance data at 300°K for electrolytically polished<sup>6</sup> silver samples are shown in Fig. 1.<sup>7</sup> These values were obtained as soon as possible after the etching process and, although subject to conceivable atmospheric contamination, are considered a reasonable approximation to bulk silver reflectance characteristics.

<sup>1</sup> For a review of this subject see M. P. Givens, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 313; L. G. Schulz, *Suppl. Phil. Mag.* **6**, 102 (1957).

<sup>2</sup> For summaries of much of this work see R. S. Minor, *Ann. phys.* **10**, 581 (1903); L. G. Schulz, *J. Opt. Soc. Am.* **44**, 357 (1954); *ibid.*, **44**, 540 (1954); L. G. Schulz and F. R. Tangherlini, *J. Opt. Soc. Am.* **44**, 362 (1954).

<sup>3</sup> D. Pines, *Revs. Modern Phys.* **28**, 184 (1956).

<sup>4</sup> M. Suffczynski, *Phys. Rev.* **117**, 663 (1960).

<sup>5</sup> H. R. Philipp and E. A. Taft, *Phys. Rev.* **113**, 1002 (1959).

<sup>6</sup> L. I. Gilbertson and O. W. Fortner, *Trans. Am. Electrochem. Soc.* **81**, 199 (1942).

<sup>7</sup> The carefully measured reflectance data of Schulz (see work cited in footnote 2) are plotted below 3 ev. The measurements of Fig. 1 are fitted to his value at this point.

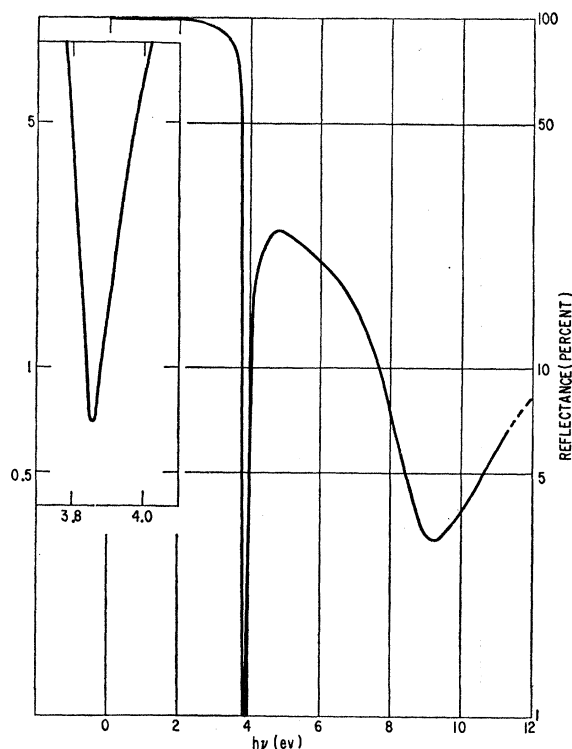


FIG. 1. Spectral dependence of the reflectance of Ag. The data of Schulz are plotted below 3 eV (see work cited in footnote 2).

Curves obtained on mechanically polished and evaporated specimens showed some variations, particularly in the regions of the reflectance minima.<sup>8</sup> Annealing of mechanically polished surfaces was observed at the 3.86-eV minimum, which deepens and narrows after heating to 200°C for several minutes. The reflectance of evaporated layers at this energy was between 2½ and 3%, about the same as for mechanically polished surfaces.

The position of the broader minimum at 9.2 eV is also sensitive to surface treatment. For mechanically polished samples this minimum was shifted to lower energy by as much as 1 eV. Freshly prepared electrolytically polished or evaporated surfaces exhibited the 9.2-eV minimum, the evaporated films giving a less pronounced effect. Aging these samples in air shifted this minimum toward the lower energy.<sup>9</sup>

<sup>8</sup> X-ray diffraction data were obtained on etched, mechanically polished, and evaporated samples. Differences were observed particularly in the relative intensities of the diffraction spectra lines. Although these effects were not studied in any detail, it appears that useful information concerning the nature of these surfaces might be obtained from more comprehensive measurements and analysis of x-ray data. We are indebted to R. F. Reihl for these spectra.

<sup>9</sup> Silver has been observed to "tarnish" when exposed to short wavelength radiation. [See P. R. Gleason, *Proc. Am. Acad. Arts Sci.* **64**, No. 6 (1930)]. This effect is most likely the oxidation of silver by the action of ozone produced by radiation in the oxygen absorption bands above 6.5 eV. In the present work some samples were observed to color (yellow) after long exposure to vacuum monochromator wavelengths under poor vacuum conditions. The yellow film effectively removed the structure at 9.2 eV.

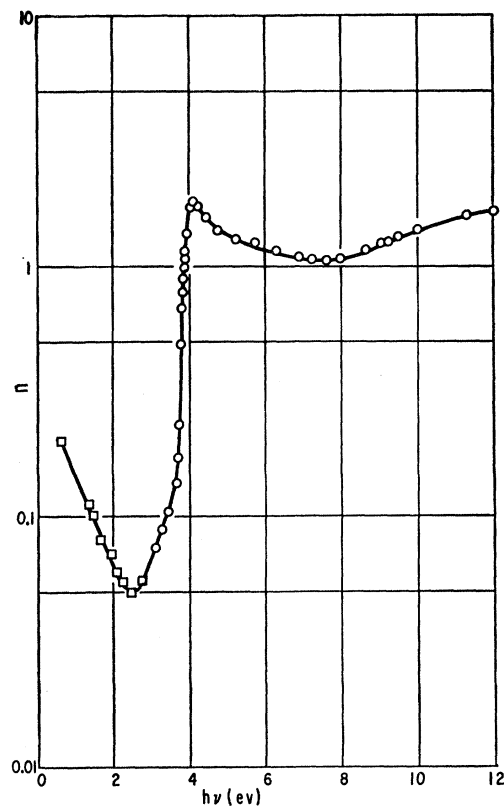


FIG. 2. Spectral dependence of the real part of the index of refraction of Ag. The values of Schulz are plotted below 3 eV (see work cited in footnote 2).

For silver surfaces, measurements of reflectance appearing in the literature have been confined in general to the spectral region below 4 eV.<sup>2</sup> The values of Fig. 1 are in accord with these data although there are differences in some details. The minimum near 3.8 eV is deeper than in previous studies. At higher energy the present results are at variance with published data.<sup>10</sup> The minimum near 9.2 eV has not been previously reported.

Reflectance data were obtained, for a range of sample temperatures, in the region of pronounced structure near 3.8 eV. As the temperature is decreased from 350° to 250°K, the minimum deepens and sharpens, and shifts by an amount  $4 \times 10^{-4}$  eV/°K toward higher energy. In the range 250° to 80°K, little dependence on temperature was found.

## RESULTS AND DISCUSSION

Values for  $n$  and  $k$  derived from the reflectance data of Fig. 1 are shown in Figs. 2 and 3.<sup>11</sup> Values of absorp-

<sup>10</sup> W. C. Walker, O. P. Rustgi, and G. L. Weissler, *J. Opt. Soc. Am.* **49**, 471 (1959); G. B. Sabine, *Phys. Rev.* **55**, 1064 (1939).

<sup>11</sup> Details relating to this calculation are given in the work cited in footnote 5. Following the results of the work cited in footnote 10, the curve of Fig. 1 is assumed to rise to 9% reflectance at 13 eV and remain constant at this value to 25 eV. Above this energy, the curve is linearly extrapolated in a plot of  $\ln R^{\frac{1}{2}}$  vs  $\ln h\nu$  to 0.026% at 1000 eV.

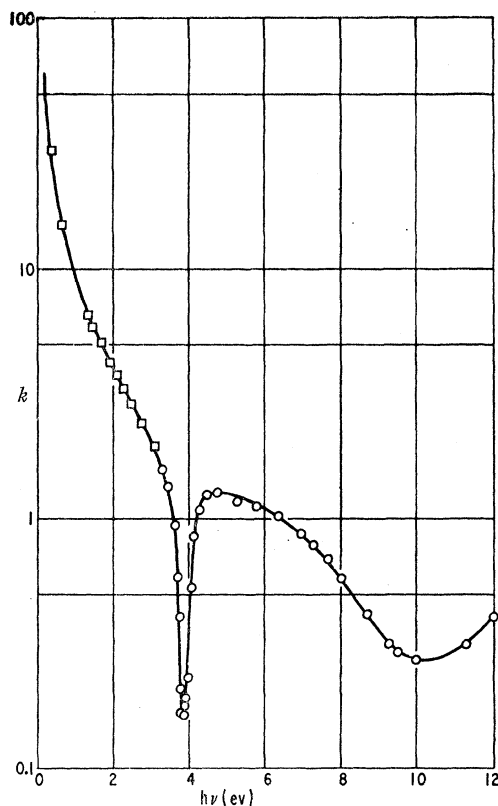


FIG. 3. Spectral dependence of the extinction coefficient (the imaginary part of the index of refraction) of Ag. The values of Schulz are plotted below 3 ev (see work cited in footnote 2).

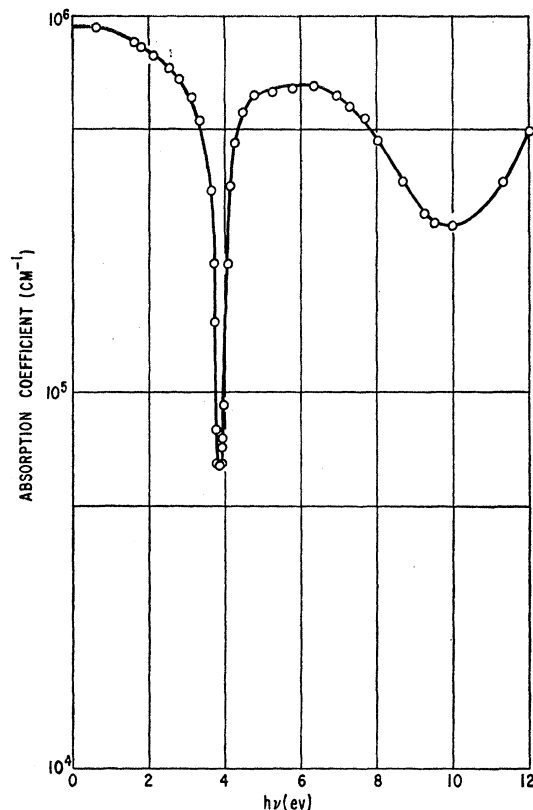


FIG. 4. Spectral dependence of the absorption coefficient ( $\alpha = 4\pi k\lambda$ ) of Ag.

tion constant  $\alpha = 4\pi k/\lambda$  are shown in Fig. 4. There are two salient features in these curves. First, the absorption exhibits a sharp minimum near 3.8 eV and second, there is a much broader minimum in the vicinity of 10 eV. The real part of the dielectric constant,  $\epsilon_1 = n^2 - k^2$ , is found to be zero at 3.75 eV and remain positive for higher energy as far as the measurements were carried.

The structure in the curve for  $k$  near 3.8 eV has been associated with the onset of interband electronic transitions. Suffczynski<sup>4</sup> has recently calculated the contribution of interband transitions to the optical constants of metals. In his model for silver, excitations from the occupied (conduction) band to the next higher empty band are considered.<sup>12</sup> By choosing the energy gap and parameters which describe the bending of the energy bands and the manner in which the Fermi surface approaches the Brillouin zone boundary, a curve consistent with experiment may be obtained. The sharp minimum in  $k$  in the theoretical curve results from the particular way in which the dielectric constant associated with interband transitions adds to

the dielectric constant from conduction electrons (Drude theory) in the vicinity of the band separation, 3.8 eV.

The reflectance data for silver exhibit a second minimum near 9.2 eV which has not been previously observed. This structure occurs near the energy of plasma oscillations calculated from the free-electron model but in fact can have nothing to do with a collective oscillation since the real part of the dielectric constant  $\epsilon_1$  is positive throughout this region.<sup>13</sup> The necessary condition for a collective oscillation is that  $\epsilon_1$  be zero and that the imaginary part of the dielectric constant,  $\epsilon_2 = 2nk$ , be small and roughly constant.<sup>14</sup> This condition is satisfied in silver at 3.75 eV. Thus a collective oscillation evidently occurs in silver at this latter energy which is much below the prediction of the free-electron model because of the influence of the interband transitions.

<sup>12</sup> See N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936). Optical transitions from the filled  $3d$  band are essentially neglected in this treatment. This may not be a realistic assumption. See J. Friedel, *Proc. Phys. Soc. (London)* **B65**, 769 (1952).

<sup>13</sup> The computed values of  $n$  and  $k$  above about 8 eV depend quite strongly on the way the reflectance curve is extended beyond 11.3 eV (see work cited in footnote 11). The data of the work cited in footnote 10 are consistent with one another and indicate that the reflectance is indeed constant in the energy range 13 to 25 eV.

<sup>14</sup> P. Nozières and D. Pines, *Phys. Rev.* **113**, 1254 (1959).

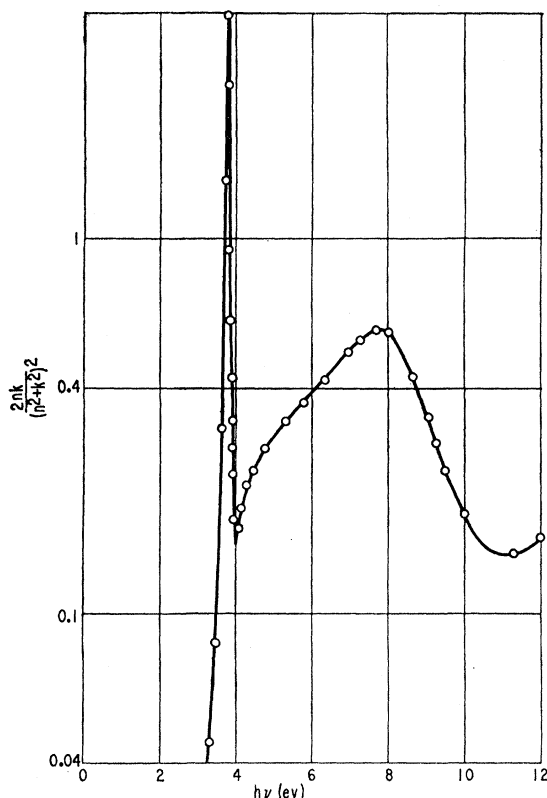


FIG. 5.  $\text{Im}[1/\epsilon]$  as a function of  $h\nu$  for Ag.

Information pertinent to experiments on characteristic energy losses of electrons in silver<sup>15,16</sup> may be obtained from the present data. In the dielectric formulation of the characteristic energy loss problem, the rate of energy transfer from the incident charged particle to the solid is contained in the imaginary part of  $1/\epsilon(\omega)$ .<sup>14</sup> This quantity is readily evaluated from

<sup>15</sup> D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 432.

<sup>16</sup> P. A. Wolff, *Phys. Rev.* **92**, 18 (1953), suggests that in metals with occupied  $d$  bands, such as silver, there is a strong coupling between the plasma wave and the  $d$  electrons which gives rise to frequency broadening. Energy widths should be of order  $\omega_p nk$ . The plasma frequency may also be shifted in energy by a considerable amount.

a knowledge of the optical constants as follows<sup>17</sup>:

$$\text{Im}[1/\epsilon(\omega)] = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} = \frac{2nk}{[n^2 + k^2]^2},$$

and is plotted in Fig. 5 as a function of  $h\nu$ . A sharp peak is observed at the energy of the collective oscillation, 3.75 eV, where  $\epsilon_1$  is zero. A second broad peak occurs near 8 eV but this is not related to a collective oscillation since  $\epsilon_1$  is positive in this region. Both peaks should show up in the characteristic energy loss spectrum.

#### ACKNOWLEDGMENTS

We are indebted to T. Timusk, now at Cornell University, for his assistance during the summer of 1959 in placing our vacuum monochromator into operation and for obtaining corroborating evidence for structures in the reflectance spectrum of silver. We are particularly grateful to H. Ehrenreich and F. Ham for many stimulating conversations concerning the interpretation of these data.

*Note added in proof.* Recently W. Steinmann [*Phys. Rev. Letters* **5**, 470 (1960)] and R. W. Brown, P. Wessel, and E. P. Trownson [*Phys. Rev. Letters* **5**, 472 (1960)] have observed radiation at 3300 Å from thin silver films bombarded with high-energy electrons. This radiation conforms with predictions by R. A. Ferrell [*Phys. Rev.* **111**, 1214 (1958)] on the possibility of observing radiation due to collective oscillations in thin metal films. Thus these experiments appear to provide an independent way of showing that a characteristic frequency for collective oscillations occurs in silver at  $3.75 \pm 0.1$  eV, in agreement with the value obtained in the present paper by finding from the optical constants the energy at which the real part of the dielectric constant is zero.

Steinmann also gives a characteristic energy loss spectrum for silver which shows a broad peak at 7.4 eV in addition to a sharp peak near the energy of the collective oscillation. These peaks are thus in general agreement with those calculated from the optical constants in Fig. 5.

<sup>17</sup> H. Fröhlich and H. Pelzer, *Proc. Phys. Soc. (London)* **A68**, 525 (1955).