Values of the Optical Constants for Beryllium, Magnesium, and Zinc

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Reflectivities of evaporated metal films have been observed under varying conditions, allowing the computation of conductivities and dielectric constants by a previously described method. A reflectometer employing both a photo-cell and a thermopile permitted measurements in the visible and near infra-red regions. Curves are included showing the values of the constants for beryllium, magnesium, zinc, and copper. Comparisons are made with other published results.

PREVIOUS investigations of the optical constants of metals have for the most part been limited in frequency range by the nature of the methods of measurement. A second common drawback has been the questionable nature of the metallic surfaces employed, since mechanically polished bulk metals or very thin films (the properties of which are not truly characteristic of bulk material) have generally been used. The present investigation has sought to avoid these difficulties. The method of measurement employed has been described in detail elsewhere.[1]

Though the actual optical quantities determined are usually the index of refraction n and the extinction coefficient k (both as functions of frequency), the modern theory of solids interprets more directly the conductivity for frequency $\nu(=\sigma_\nu=nk)$ and the dielectric constant for frequency $\nu(=\epsilon_\nu=n^2-k^2)$. These significant quantities are found directly in the method employed and, plotted as functions of frequency, give information concerning the nature of the electronic energy bands in the solid state.[2]

The measurement of reflectivities, which is the basis of the method employed here, is effected as readily in the infra-red region of the spectrum as in the visible and ultraviolet regions. For this reason the spectral range chosen was that extending from $\lambda=4800A$ to $\lambda=24,000A$; this allows observations in a new range of frequencies as well as comparison with results obtained by other methods in the visible region. The arrangement of apparatus used is shown in Fig. 1. The

image of an incandescent light source is thrown upon the entrance slit (S_1) of a monochromator; the collimating mirror M_1 is an off-axis parabola which reflects light in a homogeneous beam to the constant deviation prism P, from which light proceeds to M_2 (a duplicate of M_1) to be refocused in a slit image at S_2, the exit slit of the monochromator. The radiation is recollimated (L_1) in the reflectometer, polarized by the Nicol prism N, and reflected by the metallic mirror on which measurements are being made (MM); the reflected intensity is observed by the photo-cell or thermopile (T). The apparatus may be set to measure the intensity of the incident radiation, or that for radiation reflected at angles of incidence of 80°, 70°, 60°, or 50°.

Some guidance in the choice of metals for measurements was furnished by the theorists' picture of the solid state, which portrays energy bands for divalent metals as overlapping one another more than for monovalent or trivalent materials. This results in smaller energy differences for the transitions which may be observed; the first anomalous absorption peak for monovalent materials is usually in the ultraviolet
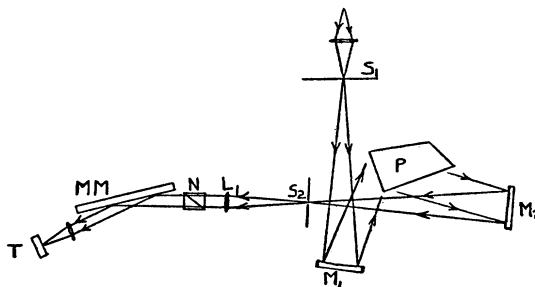

FIG. 1. Optical system employed for reflectivity measurements.

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[1] J. R. Collins and R. O. Bock, Rev. Sci. Inst. 14, 135 (1943).
[2] See, for example, F. Seitz, *Modern Theory of Solids*.

region, whereas this occurs in the near infra-red for most divalent metals. Measurements were made on magnesium, beryllium, zinc and, in testing apparatus, copper.

Evaporation technique was employed in the preparation of the metallic surfaces. Accepted methods were used, the metal sources being heated in vacuum by electric currents in tungsten coils or troughs. The $1\frac{1}{2}''\times6''$ plate glass blanks upon which the films were deposited were tested for flatness, cleaned thoroughly, and mounted at a distance of 10 to 15 cm from the source of evaporated metal. A vacuum of about 10^{-6} millimeter of mercury was maintained. Evaporation was carried on until the mirrors appeared "opaque" to a bright incandescent light.

The accuracy and reliability of results depend upon the nature of the material deposited as regards oxidation and ease of deposition (repeatability) of the films. A second and perhaps more important factor is the nature of the graphical intersections obtained in the method of reducing the data.[1]

RESULTS

Beryllium (Fig. 2)

The samples of beryllium used were 99.9 percent pure and formed durable, easily duplicated films at an evaporating temperature of about 1400°C. Figures for the estimated probable errors in σ and ϵ (Table I) are arrived at as
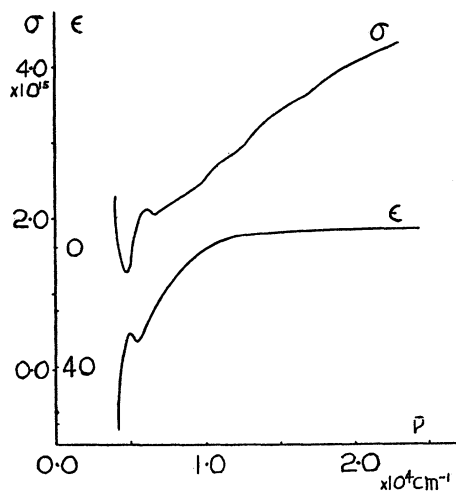
TABLE I. Errors in constants for beryllium.

$\bar{\nu}$ (cm^{-1})	Error in ϵ	Error in σ
2.22×10^4	0.14	0.13×10^{15}
0.833	0.32	0.12
0.526	2.1	0.12
0.476	6.4	0.27

follows: determine a probable error in measurement of reflectivity (0.8 percent was the figure used here), apply this difference arbitrarily to some value obtained for reflectivity and observe the change introduced in the values of σ and ϵ in reducing the data. (Note that this does not take into account possible systematic errors in the nature of the films used.)

The results, shown in Fig. 2, agree very well with those obtained by Givens[3] in the frequency range covered by both observers. Differences in the conductivity are of the order of a few percent, but are somewhat larger for the dielectric constant.

Magnesium (Fig. 3)

Impurities in the magnesium used totaled about 0.07 percent. The material was readily evaporated, but duplication of the films was not easy since oxidation begins at once upon exposure to air. This fact throws a little uncertainty on the results in addition to the errors shown (Table II).
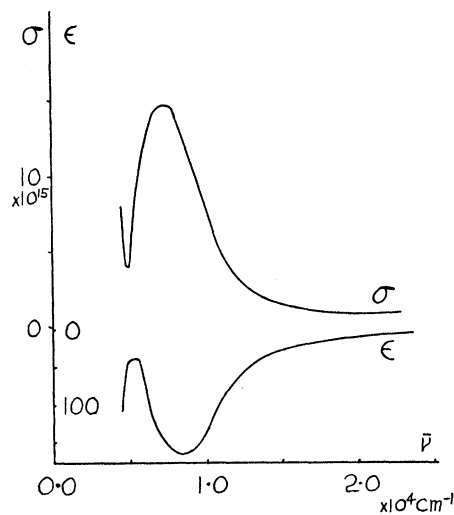

FIG. 2. Conductivity and dielectric constant vs. wave number for beryllium.

FIG. 3. Conductivity and dielectric constant vs. wave number for magnesium.

[3] M. P. Givens, Phys. Rev. 61, 626 (1942).

Table II. Errors in constants for magnesium.

$\bar{\nu}$ (cm⁻¹)	Error in ϵ	Error in σ
2.22×10^4	1.8	0.11×10^{15}
1.67	1.4	0.12
1.33	2.0	0.18
1.11	38.0	1.9
0.667	27.0	5.6
0.625	11.0	3.2
0.571	2.4	2.1
0.500	1.6	0.45
0.465	11.0	0.96

No previous results are available for comparison. It is thought that the large peak in conductivity at $\bar{\nu}=0.7\times10^4$ cm⁻¹ represents the first anomalous absorption.

Zinc (Fig. 4)

Zinc of Kahlbaum purity was evaporated readily upon a thin layer of chromium, since this technique diminishes the haziness which tends to characterize the zinc surface.[4] Deterioration is slow, and repeated attempts on new films showed practically identical results (Table III).

The flattening of the curve for the dielectric constant at the low frequency limit of the work makes another absorption peak appear likely in the infra-red. It should be born in mind, however, that this occurs in a part of the spectrum where the accuracy of the work is not great.

An interesting comparison exists between these results and those of Bor, Hobson, and Wood,[5] who used polished bulk zinc. Their conductivity curve resembles this one in shape, the principle peaks being about 0.07×10^4 cm⁻¹ apart for both observers. The absolute value of the conductivity reported here (in the region of the peak) is only about half that found by Bor, Hobson, and Wood, but it is worth noting that lower values of conductivity generally result when amorphous surface layers on a metal have been reduced.[6]

The separation of the p and s bands in a metal tends to increase with atomic number. The first anomalous absorption peak generally represents a transition between these bands, hence the peak should shift toward the ultra-violet as the atomic number increases. This

[4] G. B. Sabine, Phys. Rev. 55, 1064 (1939).
[5] J. Bor, A. Hobson, and C. Wood, Proc. Phys. Soc. 51, 932 (1939).
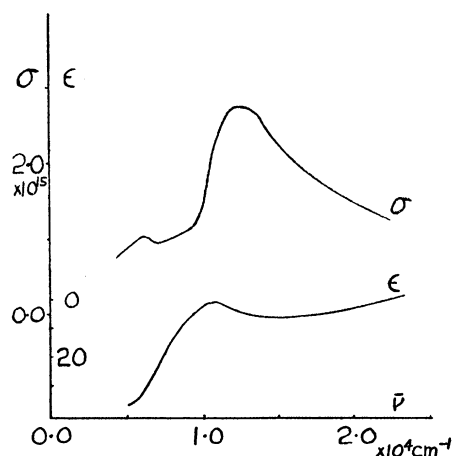[6] Mott and Jones, Properties of Metals and Alloys, p. 118.

Fig. 4. Conductivity and dielectric constant vs. wave number for zinc.

Table III. Errors in constants for zinc.

$\bar{\nu}$ (cm⁻¹)	Error in ϵ	Error in σ
2.08×10^4	0.093	0.029×10^{15}
1.56	0.21	0.089
1.11	0.20	0.070
0.910	0.24	0.054
0.625	3.7	0.12

behavior is roughly indicated by the magnesium and zinc curves, where the peaks appear at $\bar{\nu}=0.75\times10^4$ cm⁻¹ and at $\bar{\nu}=1.27\times10^4$ cm⁻¹, respectively. The accompanying data for beryllium do not verify this shift. A further measurement was sought for cadmium, but the experimental difficulties encountered in the preparation of the film have postponed the work. A preliminary rough observation by Collins has indicated a peak somewhere in the vicinity of that found for zinc.

Copper (Fig. 5)

A high grade of copper was used, the total of impurities being about 0.01 percent. Though evaporation proceeds readily enough, the resulting films are extremely sensitive in their characteristics to the pressure maintained in the chamber, the cleanliness of the glass blank and apparently to a few other unknown conditions. Deterioration of the resulting film is very rapid, and much care must be exercised in obtaining readings. In most of the spectral range covered here, the experimental errors are very large (Table IV).
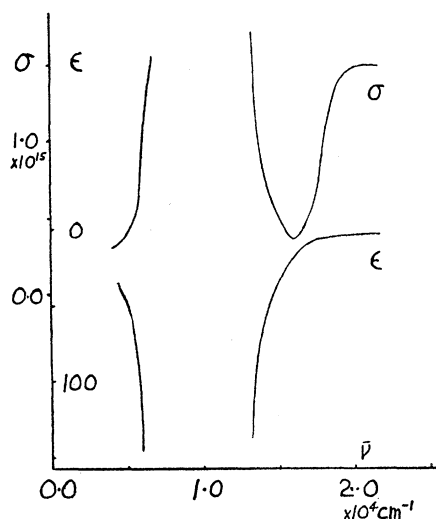
FIG. 5. Conductivity and dielectric constant
vs. wave number for copper.

Many sets of values have been published for copper. Among the more recent are those of Lowery, Bor, and Wilkinson,[7] who used lightly polished surfaces in order to minimize the formation of small crystals and amorphous layers. They obtained conductivities in the frequency

[7] Lowery, Bor, and Wilkinson, Phil. Mag. 20, 390 (1939).

TABLE IV. Errors in constants for copper.

$\bar{\nu}$ (cm^{-1})	Errors in ϵ	Errors in σ
2.08×10^4	0.14	0.060×10^{15}
1.85	0.16	0.035
1.60	5.2	0.10
1.43	23.0	0.32
0.476	12.0	0.12

range $\bar{\nu} = 2.08 \times 10^4$ cm^{-1} to $\bar{\nu} = 1.67 \times 10^4$ cm^{-1} which agree almost identically with the values obtained here. Numerous other workers have reported similar shapes to the curves though the quantitative agreement is not so striking. Givens[3] does not observe this absorption, believing the peak usually reported to be due to copper oxide. While the data here are not on the same films used by Givens, extreme caution was exercised to duplicate as nearly as possible the films employed in his measurements. The discrepancy is unexplained.

In conclusion, the author wishes to express his gratitude to Professor J. R. Collins for his suggestion of the problem and his constant help and encouragement throughout the work; and to Professor D. H. Tomboulian for his aid and advice in the preparation of the evaporated metal films.

Erratum: A Generalization of the Dielectric Ellipsoid Problem

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[Phys. Rev. 68, 93 (1945)]

THE symbols used in the article are somewhat confusing, inasmuch as there is only a slight correlation between the font of the symbol and the type of physical quantity which it represents. The symbols **E**, **P**, **r**, and **i** represent vectors, and the symbols **ε**, ε, **σ**, **α**, *A*, *B*, and *T* represent tensors.

Equations (13) and (16) should be printed as follows:

$$\mathbf{P}_\epsilon = \frac{\varepsilon_1 - 1}{4\pi} \mathbf{E}_1, \tag{13}$$

$$\mathbf{P} = \mathbf{P}_\epsilon + \mathbf{P}_\sigma = \frac{\varepsilon_1 - 1}{4\pi} \mathbf{E}_1. \tag{16}$$

Editor's Note.—Difficulties in obtaining distinctive type and errors made in the editorial offices account for the confusing notations and typographical errors in the original article. For these the author is not responsible.