

tron diffraction patterns obtained at high temperatures from Cu_3Au and from CuAu is remarkable, and deserves emphasis and attention. Both are patterns of face-centered cubic structures; but, whereas the pattern from Cu_3Au exhibits a diffuse inner ring or rings due to

vestigial order, there is no discernible trace whatever of such indication of order on patterns from CuAu films above 400°C . We believe that the difference may be fundamentally important, and certainly should be taken into account in any theory of the ordering process.

MAY 1 AND 15, 1942

PHYSICAL REVIEW

VOLUME 61

The Optical Dispersion of Copper and Beryllium

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(Received February 17, 1942)

The optical constants of copper and beryllium have been measured over a wave-length range from 2200Å to 9800Å. The observations were made by examining the state of polarization of light after reflection from a plane surface of the metal, the incident light having been linearly polarized. The surfaces were formed on a glass backing by evaporation. The absorption band of copper usually found in the neighborhood of 5000Å was not found; copper oxide is believed to have been the source of that band. Positive values of the dielectric constant were also found. In the beryllium spectrum a strong absorption band was found near 3000Å.

THE quantum mechanical development of a theory of solids has produced a new interest in the optical properties of metals, since a study of these properties provides some experimental evidence of the width of the conduction band and the position, widths, and density of states for the unoccupied bands immediately above the conduction band. This is one of the comparatively few direct checks on the theory of solids.

According to the theoretical picture,¹ the energy levels of the atom spread into bands when the atoms are brought together to form a solid. The low energy or "inner" levels are relatively unaffected, remaining quite narrow and not appreciably changed in position. For the levels containing the valence electrons and for the unoccupied levels of higher energy the situation is quite different. The level will, in the solid, become a band of levels, usually a few volts in width and containing as many "levels" as there are atoms in the solid. The bands may remain separate and distinct or may spread out to such an extent as to overlap.

¹For a general discussion of the theory see N. Sommerfeld and H. A. Bethe, *Handbuch der Physik* (1933), volume 24, part 2 or F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940).

If the electrons in the solid completely fill the valence band, and if the next band of higher energy is well separated from the valence band, then the solid is an insulator. When the valence band is only partly filled or overlaps an empty band, then the solid is a conductor allowing a net transfer of charge by some of the electrons moving from their equilibrium states into states of slightly higher energy. Under the influence of an alternating electric field, such as a light beam of low frequency, energy may be absorbed from the beam by raising the electron into a higher energy level in its own band. Such a process would give rise to an absorption rate which changes regularly with increasing frequency until the frequency is reached at which the electron is raised to the top of the conduction band. If the next band is well separated from the first, there will then be a portion of the spectrum for which the solid does not absorb energy. For incident light of frequency ν sufficiently great for a quantum $h\nu$ to move an electron from the valence band into the band above, there will exist the so-called anomalous absorption. Overlapping of the energy bands removes the transparent region of the spectrum and the regular and anomalous absorptions also

overlap. For still higher frequencies electrons may be raised from the inner or "x-ray" levels to unoccupied portions of the valence band or to higher bands; such frequencies are beyond the range of this work. Selection rules also influence the absorption.

Classical electrodynamics may be employed as a tool to evaluate, in terms of measurable quantities, the constants which a quantitative study of the theory would predict. The quantities are the conductivity σ and the dielectric constant ϵ . The quantities are related to the measurable optical constants n_0 and k_0 by means of the equations

$$\begin{aligned}\sigma &= n_0 k_0 \nu, \\ \epsilon &= n_0^2 - k_0^2,\end{aligned}$$

where ν is the frequency.

There are two essentially different methods of measuring the optical properties of metals with reflected light. The first of these two methods requires the measurements of the relative phase shift Δ between the components of the light for which the electric vector is parallel to and perpendicular to the plane of incidence, and also the ratio of the reflectivities of these two components at some known angle of incidence ϕ . The ratio of the reflectivities is usually denoted as $\tan \psi \equiv R_p/R_n$, where R_p is the reflectivity for the component having its electric vector parallel to the plane of incidence, and R_n is for the perpendicular component. If the incident light is linearly polarized at azimuth 45° , then ψ represents the azimuth of the reflected light after the phase shift Δ has been compensated by a Babinet compensator or its equivalent. From the quantities Δ , ψ , and ϕ , the optical constants may be computed by simple equations.

The other method consists in finding R_p and R_n independently of each other at known angles of incidence. The relative phase shift is not necessary, but the difficulties of measuring absolute reflectivity compensate for this. An additional disadvantage of this method is the fact that there is no convenient calculating formula giving the optical constants as functions of the measured quantities, but the constants are contained implicitly in expressions giving the measured quantities. Also this method is more affected

than the other by the surface condition of the metal.

The first method was used for this work and except for a few changes the apparatus is that designed by Voigt² and used by Minor³ and others to study the optical properties of metals. The apparatus (Fig. 1) will be described briefly and the changes from Minor's apparatus will be pointed out. By means of a quartz lens L_1 an image of the source 0 was formed on the entrance slit of the monochromator. The exit slit of the monochromator was removed and this instrument so placed that the image formed at the customary position of the exit slit was formed on S , the entrance slit of the main polarograph. After passing the slit S the light was formed into a parallel beam by the quartz lens L and is linearly polarized by means of N_1 , an air-spaced polarizing prism having its faces normal to the path of the light; this prism was mounted so that its azimuth could be determined by a vernier with a least count of 0.1° . The light is then reflected by the metal surface xx_1 (which is so

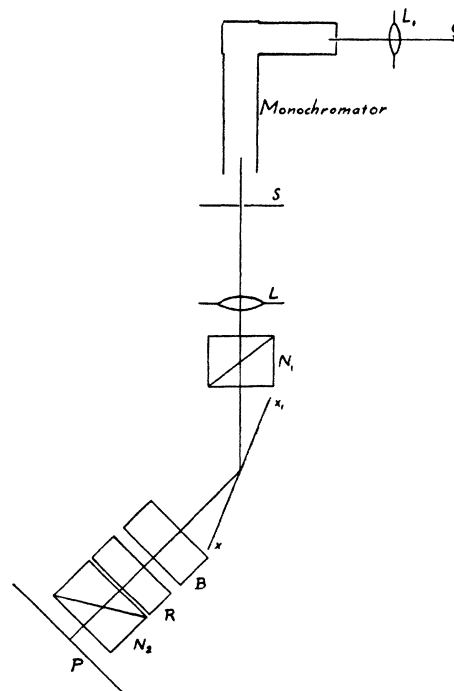


FIG. 1. Diagram of apparatus.

² W. Voigt, *Phys. Zeits.* **2**, 303 (1901).

³ R. S. Minor, *Ann. d. Physik* **10**, 581 (1903).

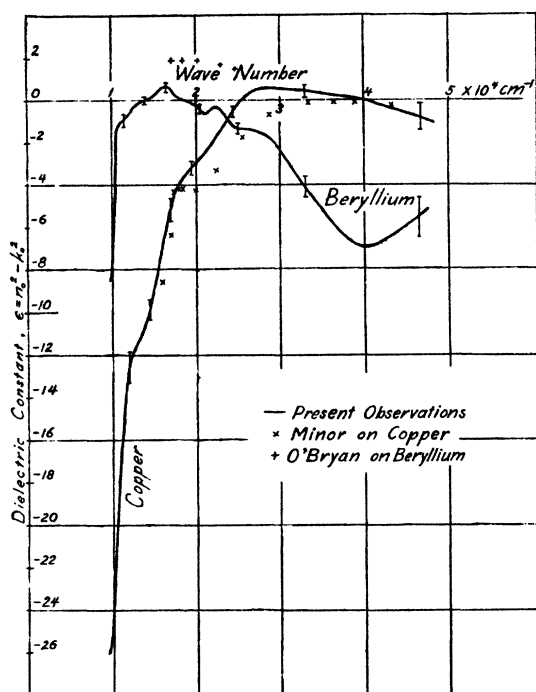


FIG. 2. Dielectric constant of copper and beryllium.

placed as to contain the axis of the polarograph) and enters the analyzing system. The analyzing system is similar to that designed by Voigt, the light first passes through a Babinet compensator (B) with its wedge edges horizontal. Next it passes through a pair of rotary wedges (R) having their wedge edges vertical; this pair of wedges is cut so that the path of the light is along the optic axis of the quartz, one of the pair being of right-handed quartz and the other of left-handed quartz. The two wedges are put together to form a parallel plate which rotates the plane of polarization by an amount which is a linear function of the distance across the plate. After passing the rotary wedges the light passed through an analyzing prism (N_2) similar in its construction to the polarizer N_1 except that the least count of the vernier for N_2 was $1'$. The light then falls on a photographic plate P or a ground glass viewing screen to form a pattern of dark spots on a light background. The positions of the spots provide the necessary information about the relative phase and azimuth of the reflected light. The positions of the spots along a horizontal direction is a linear function of the restored azimuth of the polarized light, there being one spot every 180° .

The positions of spots in alternate rows correspond to complementary angles so that the zero position and thus the azimuth of the light may be determined without the use of any reference plate. The positions of the spots along a vertical direction is a linear function of the phase difference, there being one spot every 360° . In this case a reference plate must be used. Immediately in front of the plate is a set of cross wires which cast shadows on the photographic plate, the shadows serving as reference lines when the plates are measured. The system employed a beam 2 cm in diameter. A telescope containing a Gauss eyepiece was mounted behind the photographic plate and by removing the plate holder this telescope could be used to line up the apparatus, or determine the angle of reflection. The whole analyzing system was mounted on one arm of the polarograph so that its position could be determined to $20''$.

In Minor's apparatus a camera was used to photograph the pattern of spots. The camera, containing a pair of simple quartz lenses, was focused on the cross wires which in his work were placed between the B and R wedge systems. According to Minor,⁴ the camera, when used at unit magnification, produced only negligible distortions. The distortions produced by a similar arrangement in this apparatus were not considered negligible and the camera was discarded in favor of this simpler arrangement which records a "shadow picture" of the wedge system. The cross wires were then moved back to be as close as possible to the photographic plate so they would cast a more distinct shadow. Although this method removes the distortions in the camera, it requires parallel light from a very small source and not the so-called parallel light which emerges from a collimator with a slit source. A pin hole was, therefore, indicated and some loss in intensity results. A good pattern could be obtained with a pin hole as large as 2 mm in diameter, but such an opening admitted too large a spectral range. In the final arrangement a slit 2 mm long and of adjustable width was used.

The apparatus was put into adjustment according to the same method described by Minor,⁵ except that the zero position of the analyzing

⁴ R. S. Minor, Diss. Gottingen (1902).

⁵ R. S. Minor, Diss. Gottingen (1902).

prism was determined by the method due to Collins.⁶ Several of the other adjustments depend upon this one.

The calculating equations for this procedure are

$$n_0 k_0 = \frac{\sin 2\psi \cos 2\psi \sin \Delta}{(1 - \cos \Delta \sin 2\psi)^2} \sin^2 \phi \tan^2 \phi,$$

$$n_0^2 - k_0^2 = \sin^2 \phi \tan^2 \phi \frac{\cos^2 2\psi - \sin^2 2\psi \sin^2 \Delta}{(1 - \cos \Delta \sin 2\psi)^2} + \sin^2 \phi.$$

These equations may be obtained by the application of electromagnetic theory.

Copper and beryllium were selected because theoretical calculations⁷ have already been started for these metals. Copper had been examined before, but since that time the technique of evaporation in a vacuum has been developed, providing surfaces unaffected by mechanical or chemical polishing. Metallic films evaporated on glass were used. These films were of sufficient thickness so that the reflection phenomena were independent of the thickness.

COPPER

The copper used was obtained from the Bureau of Standards and contained 0.002 percent iron; 0.010 percent tin; no antimony; and no lead as impurities. Data were taken every 200Å from 2200Å to 9800Å, and in some cases data were again taken after the film had aged in air. The data, obtained from photographs, consisted of the phase change Δ and the azimuth ψ of the reflected beam when linearly polarized light of 45° azimuth was reflected from the metal surface at an angle of incidence ϕ . The data so obtained were plotted on a graph and smooth curves drawn through the points (Figs. 2 and 3). From these curves information was taken allowing the calculation of the optical constants as a function of wave-length or frequency. The vertical lines about the curves indicate the probable error in the various regions of the spectrum.

These curves differ from the previous data in two important ways. First, the dielectric constant is positive near $\bar{\nu} = 3 \times 10^4 \text{ cm}^{-1}$. Second, previous

data show a strong absorption band (increase in conductivity) near $\bar{\nu} = 2 \times 10^4 \text{ cm}^{-1}$. These differences probably result because the surface is free from copper oxide. One consequence of these differences is the color of the copper mirror, the fresh copper surface does not have the red copper oxide color usually associated with copper surfaces. The slight suggestion of a band obtained there may be due to traces of the oxide. A good vacuum during the evaporation is necessary if this copper oxide band is to be avoided.

Rudberg,⁸ had previously suggested that this band might be due to copper oxide. He did not find the corresponding band in his experimental studies of the energy lost by electrons when scattered from copper.

If the anomalous band is assumed to be linear at its low frequency side it would begin at about 2.5 electron volts, and the conduction band, which is the remainder, is estimated to end at about 4.0 electron volts. These results are in qualitative agreement with the calculations by Rudberg and Slater⁹ which indicate the conduction band should end about 4.0 electron volts and that the first anomalous band should begin about 2.9 electron volts. Slater¹⁰ does not consider the

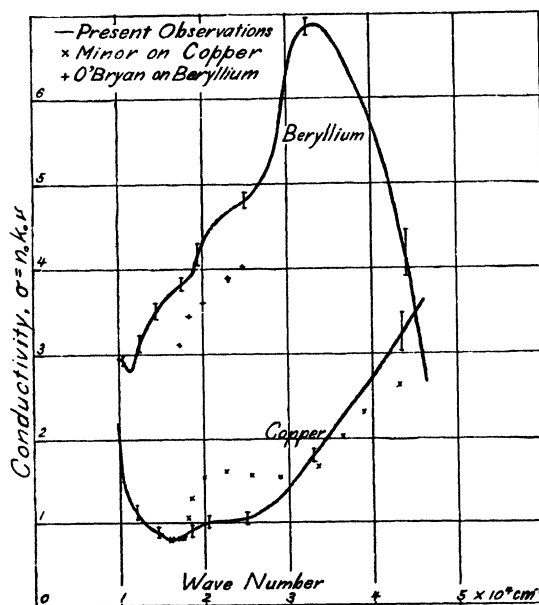


FIG. 3. Conductivity of copper and beryllium.

⁶ J. R. Collins, *Rev. Sci. Inst.* **9**, 81 (1938).

⁷ E. Rudberg and J. C. Slater, *Phys. Rev.* **50**, 150 (1936); C. Herring and A. G. Hill, *Phys. Rev.* **58**, 132 (1940).

⁸ E. Rudberg, *Phys. Rev.* **50**, 144 (1936).

⁹ E. Rudberg and J. C. Slater *Phys. Rev.* **50**, 155 (1936).

¹⁰ J. C. Slater, personal letter.

results of the calculations to be more than qualitative, so that it is probably coincidence that the experiment and the theory agree as well as they do. From the theory¹¹ the quantity

$$f = \frac{4m}{n_0 e^2} \int \sigma d\nu$$

represents the average number of electrons per atom contributing to the absorption in the frequency range over which the integration is carried out. m and e are the electronic mass and charge, respectively, and n_0 represents the number of atoms per unit volume. The integral is the area under the conductivity curve; for copper this was measured from the minimum ($\bar{\nu} = 1.5 \times 10^4 \text{ cm}^{-1}$) to the high frequency end of the experimental range ($\bar{\nu} = 4.5 \times 10^4 \text{ cm}^{-1}$). In that region the contribution to f was found to be 0.29. From the curve it would seem that this represents only a small portion of the band, since the conductivity is still increasing sharply at the end of the experimental range. For the whole band the f number is probably more than one (1). This band then probably does not arise by transitions from the 4s band to the 4p band because there is only one 4s electron per atom, and it already has an f number for the conduction band¹² of $f_0 = 0.37$. Therefore the band in the near ultraviolet may be due to transitions from the 3d band to the empty portion of the 4s band. There are ten 3d electrons per atom.

BERYLLIUM

The beryllium used was obtained from the Brush Beryllium Company. Two samples were used, one was "better than 99 percent pure," and

¹¹ F. Seitz, *Modern Theory of Solids*, (McGraw-Hill, 1940), p. 646.

¹² N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford, 1936), p. 121.

the other was "99.9 percent pure" with impurities of iron, magnesium, and silicon. The data were worked up in the same manner as for copper and are presented in the figures.

The conductivity has a maximum near $\bar{\nu} = 3.3 \times 10^4 \text{ cm}^{-1}$ or $\lambda = 3000 \text{ \AA}$ and the dielectric constant has a minimum near $\bar{\nu} = 4.4 \times 10^4 \text{ cm}^{-1}$ or $\lambda = 2500 \text{ \AA}$. The fact that the minimum of the dielectric constant is at a higher frequency than the conductivity peak indicates that there is no other absorption band near the high frequency side of the one at 3000 Å. The sharp decrease in conductivity near the end of the experimental range also agrees with this. The band is unusually narrow.

The irregularities in the curves for beryllium may not be real. However, judging from the probable errors as calculated from the experimental data, and also from the smoothness of the copper curves, one would conclude that the variations are probably real.

Theoretical calculations¹³ which have been undertaken for beryllium are not yet sufficiently advanced that they may be checked by experiment.

In the range $\bar{\nu} = 1.1 \times 10^4 \text{ cm}^{-1}$ to $\bar{\nu} = 4.5 \times 10^4 \text{ cm}^{-1}$ the contribution to f is 0.63, which indicates that this is a fairly strong band of the beryllium spectrum.

In conclusion the author wishes to express his indebtedness to Professor J. R. Collins for his constant help and thoughtful criticism, to Professor D. H. Tomboulian for his advice and help during the preparation of the mirrors, to Professor H. A. Bethe for his assistance in interpreting the results, and to the Brush Beryllium Company for the donation of the necessary amount of beryllium.

¹³ C. Herring and A. G. Hill, *Phys. Rev.* **58**, 132 (1940).