DETERMINATION OF THE MICROSCOPIC CHARACTERISTICS OF INDIUM FROM ITS INFRARED OPTICAL CONSTANTS AND ELECTRICAL CONDUCTIVITY

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Submitted to JETP editor July 7, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) 44, 48-52 (January, 1963)

The optical constants in the $0.7-10 \mu$ range, static conductivity, and density of evaporated indium mirror coatings were measured at room temperature. The normal character of the skin effect for indium in this range was taken into account in treating the data. An additional correction was introduced for the surface loss incurred in diffuse reflection of electrons from the metal surface. The concentration of conduction electrons, electron velocity on the Fermi surface, electron-phonon collision frequency, electron-electron collision frequency, and frequency of collisions between electrons and impurities were determined.

INDIUM, an element of the third group, occupies an intermediate position between metals and semiconductors. Measurements of the real and imaginary parts of the complex refractive index $\sqrt{\epsilon'}$ = $n - i\kappa$ for the interval 0.7-10 μ at room temperature have shown that indium resembles metals with regard to its optical properties. The constants n and κ were measured by a polarization technique involving quadruple reflection from the investigated mirrors; a detailed description of the apparatus is given in ^[1]. For each wavelength λ the incident angle, the phase shift between the reflected p and s components, and the azimuth were measured. Measurements for different incident angles, while yielding different values for the phase shift and azimuth, gave identical values for n and κ ; this served as a check of correct mirror adjustment. Light from a dc source was monochromatized by a prism spectrograph having a sodium chloride prism. A stack of selenium films served as a polarizer. We prepared a germanium bolometer as the light receiver.

The indium mirrors were prepared by vacuum evaporation of the metal followed by condensation on polished glass plates at a pressure $\sim 4 \times 10^{-6}$ mm Hg. In the course of the work it was found that in order to obtain good mirror coatings it is very essential to have an intermediate coating of some metal between the glass and the indium coating. Lead was found to provide the best intermediate coating among several tested metals. It was also found that a very thin lead coating (less than 0.03μ) is sufficient for the production of good indium mirrors. Lead and indium were deposited successively from two different evaporators; the vacuum apparatus was not filled with air between the two operations. The indium coatings, which were slightly bluish, were 0.6μ thick.

The optical constants were measured both immediately after deposition of the coatings and following a day of exposure to air; no appreciable difference was observed between the two sets of measurements of n and κ . The results are listed in the accompanying table.

Optical	constants	of	indium
in th	e infrared	re	gion

λ	n	×	λ	n	×
$0.71 \\ 1.05 \\ 1.56 \\ 2.22 \\ 2.68$	$1.38 \\ 1.83 \\ 2.31 \\ 3.53 \\ 4.43$	6.24 7.94 11.3 15.8 18.2	3,14 4.00 5.95 8.0 10,0	5.50 7.60 13.4 19.2 23.8	21,2 26,1 35,6 42,2 51,7

In order to determine the microscopic characteristics of indium the optical constants and static conductivity had to be measured on identical samples. For this purpose, simultaneously with the preparation of the mirrors, a strip of indium was deposited on a glass plate (having metal contacts) through a stencil slit with a measured length-width ratio. The thickness of the deposited layer was measured by interference. The resistance of the strip was measured at room temperature and at liquid helium temperature.¹⁾ The measurements showed that the residual resistance of the indium coatings is 12.3% of that observed at room temperature; this result will be used below to determine the frequency of collisions between electrons and impurities. The conductivity of the indium coatings at 293°K was found to be 0.64×10^{17} cgs esu (64% of the bulk-metal conductivity^[2]). The density of the deposited indium was 5.9 g/cm³ (81% of the bulk-metal density^[2]).

A preliminary treatment of the experimental data, using the procedure described in $^{\lfloor 3 \rfloor}$, showed that because of the high frequency of electronphonon collisions the electron mean free path lin indium is several times smaller than the skin depth δ . Thus a normal skin-effect occurs in indium for the given spectral region. Also, in considering the appropriate formulas, it must be remembered that in our case the effective electroncollision frequency is $\nu_{\rm eff} \approx \omega$, where ω is the cyclic frequency of the light. We can therefore not use a series expansion in the parameter $\nu_{\rm eff}/\omega$. The same situation pertains to several other metals as well as to indium. We shall therefore describe the treatment of the data in somewhat greater detail.

The normal skin-effect for a metal having a spherical Fermi surface is represented by [4]

$$\varepsilon' - 1 = -4\pi e^2 N/m\omega \left(\omega - iv_{eff}\right); \tag{1}$$

here e is the electron charge, N is the concentration of conduction electrons, and m is the free-electron mass.

The Fermi surface of indium is not a sphere. However, considering that the investigated coatings have a fine-grain polycrystalline structure, we can use this relation if we are interested in the average microscopic characteristics.

For metals in the infrared region unity can be neglected compared with ϵ' . In our case this is entirely permissible, since for indium in the investigated spectral interval we have $1/|\epsilon'| \approx 10^{-2} - 10^{-4}$.

When $\nu_{\text{eff}} \approx \omega$ we consider it most convenient to use the relation between $1/\epsilon' = (n - i_{\kappa})^{-2}$ and the microscopic characteristics of the metal. By separating the real and imaginary parts we obtain the two relations

$$\begin{split} \lambda^{2} (\varkappa^{2} - n^{2}) / (n^{2} + \varkappa^{2})^{2} &= 10^{8} \cdot \pi mc^{2} / e^{2} N = 0.112 \cdot 10^{22} / N, \\ 2\lambda n \varkappa / (n^{2} + \varkappa^{2})^{2} &= 10^{4} \cdot m c v_{eff} / 2 e^{2} N = 5.93 \cdot 10^{5} \cdot v_{eff} / N. \end{split}$$

Here λ is the wavelength in microns and c is the velocity of light.

These expressions can be extended to the case of a slightly anomalous skin-effect. Equation (3) contains the effective frequency ν_{eff} of electron collisions. For the normal skin-effect it is assumed that this frequency is the sum of three frequencies:

1) the frequency ν^{ef} of electron collisions with the lattice;

2) the frequency ν^n of electron collisions with impurities;

3) the frequency ν^{ee} of electron-electron collisions.

All these frequencies result in a volume loss.²⁾ The absorption of light resulting from this loss is [4]

$$A_{v} = 3.54 \cdot 10^{-5} \cdot (v^{ef} + v^{ee} + v^{n})/\sqrt{N}.$$

$$\tag{4}$$

The calculation of the anomalous skin-effect shows that a surface loss also occurs. In the case of diffuse electron reflection from the metal surface the latter loss gives the absorption $A_{\Sigma} = 0.75/\beta$, where v is the electron velocity on the Fermi surface and $\beta = v/c$. The losses can be added in first approximation, and we shall take the surface loss into account by introducing an additional frequency $\nu^{e\Sigma}$ of electron collisions with the surface, defined by

$$A_{\Sigma} = 0.75\beta = 3.54 \cdot 10^{-5} \cdot v^{e\Sigma} / \sqrt{N}.$$

$$\tag{5}$$

Equation (3) can be generalized by including $\nu^{e\Sigma}$ in ν_{eff} :

$$\mathbf{v}_{\rm eff} = \mathbf{v}^{ef} + \mathbf{v}^{ee} + \mathbf{v}^n + \mathbf{v}^{e\Sigma}.$$
 (6)

A quantum-mechanical calculation of ν^{ee} yields the equation^[5]

$$v^{ee} = v^{ee}_{c1} [1 + (\hbar \omega/2\pi kT)^2],$$
 (7)

where ν_{cl}^{ee} is the classical frequency of electron-

electron collisions. Substituting (6) and (7) in (3), we find that $2\lambda n_{\mathcal{K}}/(n^2 + \kappa^2)^2$ has the form $a + b/\lambda^2$, where a and b are independent of λ .

The experimental results are treated as follows. First Eq. (2) is used to determine N; the left member of this equation should not depend on λ . Equation (3) is then used to plot the dependence of

¹⁾The intermediate lead coating was too thin to contribute to the conductivity.

²⁾The volume loss should also include the frequency of collisions between electrons and optical lattice vibrations, but we do not know the magnitude of this frequency for metals. The role of interactions between electrons and optical lattice vibrations in metal optics will be studied separately.

 $2\lambda n\kappa/(n^2 + \kappa^2)^2$ on $1/\lambda^2$. The slope of the resulting straight line determines ν_{cl}^{ee} , and the intercept on the ordinate axis gives the sum $\nu^{ef} + \nu_{cl}^{ee} + \nu^n + \nu^{e\Sigma}$. When the optical measurements are combined with measurements of the static conductivity performed on the same specimens at the same temperature, we determine

$$v_{c1}^{ef} + v_{c1}^{ee} + v^n = 2.53 \cdot 10^8 \cdot N/\sigma,$$
 (8)

where ν_{cl}^{ef} is the classical frequency of electron

collisions with the lattice. By measuring the residual resistance we obtain ν^{n} . Finally, using the quantum-mechanical calculation of $\nu^{ef, [6]}$ we obtain $\nu^{ef} = \nu^{ef}_{cl} \varphi$ (the function φ is given in [6]). The entire set of measurements enables the separate determination of ν^{ef} , ν^{ef}_{cl} , ν^{ee}_{cl} , ν^{n} , and $\nu^{e\Sigma}$;

the last quantity is used to calculate v from (5).

The foregoing calculating procedure will now be applied in determining the microscopic characteristics of indium. Figure 1 shows the relationship between $\lambda^2 (\kappa^2 - n^2)/(n^2 + \kappa^2)^2$ and λ ; the practical absence of dependence on λ is observed, with the exception of points in the short-wave region. To account for this effect measurements should be performed in the visible region. Using (2), we obtain N = $6.2 \times 10^{22} \text{ cm}^{-3}$.



FIG. 1. $\lambda^2 (n^2 - \kappa^2)/(n^2 + \kappa^2)^2$ vs. λ for indium.



FIG. 2. $2\lambda n_{\varkappa}/(n^2 + \kappa^2)^2$ vs. $1/\lambda^2$ for indium.

Figure 2 shows the dependence of $2\lambda n\kappa/(n^2 + \kappa^2)^2$ on $1/\lambda^2$; the relation is actually a straight line.³⁾ The parameters of the line give

$$v_{c1}^{ee} = 0.08 \cdot 10^{14} \text{ sec}^{-1},$$

 $v^{ef} + v_{c1}^{ef} + v^n + v^{e\Sigma} = 2.69 \cdot 10^{14} \text{ sec}^{-1}.$

From the value of the static conductivity we obtain $\nu_{cl}^{ef} + \nu_{cl}^{ee} + \nu^n = 2.44 \times 10^{14} \text{ sec}^{-1}$. According to ^[6], for T $\gg \oplus$ we have $\varphi = 1$. For indium $\oplus = 111^{\circ}$ K; for room temperature $\varphi = 1$ and we have $\nu^{ef} = \nu_{cl}^{ef}$. Hence $\nu^{e\Sigma} = 0.25 \times 10^{14} \text{ sec}^{-1}$ and $v = 1.5 \times 10^8 \text{ cm/sec.}^{4}$ In indium $\nu^{e\Sigma}$ and v are determined with very low accuracy, since the surface loss constitutes only a small fraction of the total loss. Measurements of the residual conductivity give $\nu^n/(\nu_{cl}^{ef} + \nu_{cl}^{ee} + \nu^n) = 0.123$; hence $\nu^n = 0.30 \times 10^{14} \text{ sec}^{-1}$ and $\nu^{ef} = \nu_{cl}^{ef} = 2.06 \times 10^{14} \text{ sec}^{-1}$, The microscopic characteristics of indium can now be summarized as follows:

$$\begin{array}{cccc} N & 6.2 \cdot 10^{22} \text{ cm}^{-3} \\ N/N_a & 2.0 \\ \varepsilon' = \mathbf{v}_{c1}^{ef} & 2.1 \cdot 10^{14} \text{ sec}^{-1} \\ \mathbf{v}^n & 0.30 \cdot 10^{14} \text{ sec}^{-1} \\ \mathbf{v}_{c1}^{ee} & 0.08 \cdot 10^{14} \text{ sec}^{-1} \\ \varepsilon & 1.5 \cdot 10^8 \text{ cm/sec} \end{array}$$

Here N_a is the concentration of indium atoms. Using the values of ν_{eff} and v, we calculate the mean free electron path $l = v/\nu_{eff} = 0.5 \times 10^{-6}$ cm (for $\lambda = 4 \mu$). The skin depth for the same wavelength is $\delta = \lambda/2\pi_{K} = 2.4 \times 10^{-6}$ cm. It is thus seen that δ is 5 times larger than l; therefore the foregoing formulas can be used for indium.

It is easy to compute the size L of the small crystals in the evaporated indium coatings: L = $v/\nu^n = 5 \times 10^{-6}$ cm.

It is interesting to compare the microscopic characteristics of indium with those of other metals. The electronic structure of indium is very similar to that of aluminum. Both metals belong to the same group. Aluminum has a facecentered cubic lattice, while indium has a facecentered weakly tetragonal lattice. The axial ratio for indium is 1.08; thus the band structures of the two metals are similar. Comparing the microscopic characteristics of these metals,^[8] we find close values of the conduction electron concentrations:

$$N_{\rm In} = 6.2 \cdot 10^{22} {\rm \ cm}^{-3}, \quad N_{\rm Al} = 7.4 \cdot 10^{22} {\rm \ cm}^{-3}.$$

The collision frequencies differ considerably:

³⁾The figure does not show the point for $\lambda = 0.71 \ \mu$, which lies off the straight line exactly as in Fig. 1.

⁴⁾Indium has a face-centered tetragonal lattice containing 4 atoms in each cell. The vibrations of this lattice should include optical branches, whose role in metal-optical measurements is still not entirely understood. This effect should result in a decrease of v.

$$\begin{split} \nu_{In}^{e\!f} &= 21 \cdot 10^{13} \; \text{sec}^{-1}, \; \nu_{AI}^{e\!f} &= 7.7 \cdot 10^{13} \; \text{sec}^{-1}, \\ (\nu_{cl}^{e\!e})_{In} &= 8 \cdot 10^{12} \; \text{sec}^{-1}, \quad (\nu_{cl}^{e\!e})_{AI} &= 3.8 \cdot 10^{12} \; \text{sec}^{-1}. \end{split}$$

With regard to the collision frequencies indium resembles lead,⁵⁾ which is in the fourth group: $\nu_{Pb}^{ef} = 24 \times 10^{13} \text{ sec}^{-1}$, $(\nu_{cl}^{ee})_{Pb} = 8 \times 10^{12} \text{ sec}^{-1}$. The Debye temperatures of the two metals are fairly close: $\Theta_{Pb} = 86^{\circ}$ K, $\Theta_{In} = 111^{\circ}$ K.

From the foregoing it can be concluded that the band structure of a metal determines the concentration of conduction electrons, while the Debye temperature determines the frequency of electron collisions with the lattice. This correlation will be examined in greater detail in the future.

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Translated by I. Emin

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⁵⁾Detailed results obtained in investigations of the microscopic characteristics of lead will be published separately.