

Determination of the energy gaps in metals by an optical method

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A method is proposed for separating the interband-conduction bands, and is based on the use of the analytic properties of the complex dielectric constant connected with the interband transitions. The method makes it possible to determine the number of interband conduction bands and to obtain the position of the maxima of the individual bands, and thereby determine the energy gaps in metals. The method is used to analyze the experimental results for vanadium.

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1. Measurement of the optical constants of metals yields much valuable information on their electronic structure.^[1] In particular, by studying interband transitions it is possible to determine the energy gaps produced in metals by the periodic static potential of the lattice. The structure of the interband transitions consists of a number of bands with maxima for $\epsilon_2(\omega)$ and with regions of anomalous dispersion for $\epsilon_1(\omega)$, where $\epsilon_1 = \epsilon_1 + i\epsilon_2$ is the complex dielectric constant. As a rule, the bands are quite broad and overlap each other. The positions ω_{\max} of the maxima of the bands determine the energy gaps that are present in the metal for the electronic states in the region

of the Bragg planes. It is therefore important to be able to separate the individual bands and to find ω_{\max} . The present paper is devoted to this task.

2. The main structure of the interband-conduction bands is connected with the Bragg planes. The equal-energy surfaces near the indicated planes are parallel, and this leads to maxima of the combined interband density of states and to corresponding maxima of the function $\epsilon_2(\omega)$.^[2,3] The shapes of the interband-conduction bands were calculated in^[3]. We denote by ϵ_g the contribution made to the total dielectric constant ϵ by transitions connected with physically equivalent Bragg planes, which we shall label by the index g ,

$$\begin{aligned} \epsilon_g &= \epsilon_{1g} + i\epsilon_{2g} \\ &= C_g \int_0^{\infty} \frac{dx}{(1+x^2)^{3/2}} \left[\frac{1}{\sqrt{1+x^2 - \omega'_g - i\nu'_g}} + \frac{1}{\sqrt{1+x^2 + \omega'_g + i\nu'_g}} \right], \end{aligned} \quad (1)$$

$$\omega'_g = \omega/\omega_g; \quad \nu'_g = \nu_g/\omega_g; \quad \omega_g = 2|V_g|/\hbar, \quad (2)$$

where C_g is a constant, ν_g is the effective frequency, and V_g is the Fourier component of the pseudopotential. The integral was numerically calculated in^[3] for different ω'_g and ν'_g . We shall hereafter omit the subscript g .

For the integral we can obtain an analytic expression that yields in turn the following formulas¹⁾:

$$\begin{aligned} \epsilon_1(\omega', \nu') + i\epsilon_2(\omega', \nu') &= C\pi \frac{(1 - \omega'^2 + \nu'^2 + A) + i\nu'\omega'(2 + 1/A)}{(1 - \omega'^2 + \nu'^2 + A)^2 + (\nu'\omega')^2(2 + 1/A)^2}, \quad (3) \\ A &= \left[\frac{1}{2} (1 - \omega'^2 + \nu'^2 + \sqrt{(1 - \omega'^2 + \nu'^2)^2 + 4\omega'^2\nu'^2}) \right]^{1/2} \quad (4) \end{aligned}$$

3. Independently of the shape of the interband-absorption bands, we use for our purposes only the fact that $\epsilon = \epsilon_1 + i\epsilon_2$ is an analytic complex function of the complex argument $z = \omega' + i\nu'$. We can change over from the function ϵ to the function $\epsilon^* = \epsilon - i\gamma d\epsilon/dz$. The transformation is connected with a change of the linear term in the expansion ϵ in terms of z at the point (ω', ν') . At $\gamma \ll \nu'$ the linear term decreases and at $\gamma > \nu'$ it reverses sign. The decrease of the linear term or the reversal of its sign leads to a narrowing of the bands, so that it becomes possible to separate readily the overlapping bands. By separating the real and imaginary parts and changing over from $d\epsilon/dz$ to $d\epsilon/d\omega$ we obtain

$$\epsilon_1^* = \epsilon_1 + \gamma d\epsilon_2/d\omega; \quad \epsilon_2^* = \epsilon_2 - \gamma d\epsilon_1/d\omega. \quad (5)$$

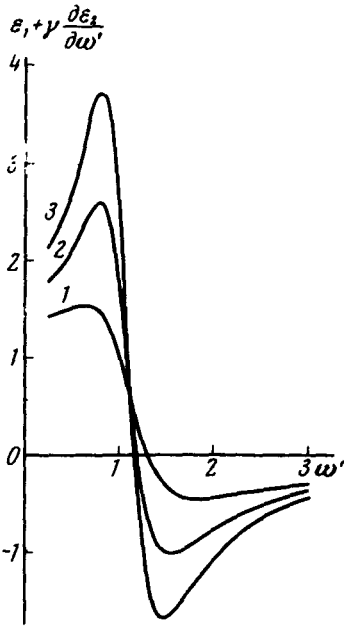


FIG. 1a. Dependence of the function $\epsilon_1(\omega') + \gamma d\epsilon_1(\omega)/d\omega'$ on ω' at $v'=0.4$: 1— $\gamma=0.2$; 2— $\gamma=0.4$; 3— $\gamma=0.8$.

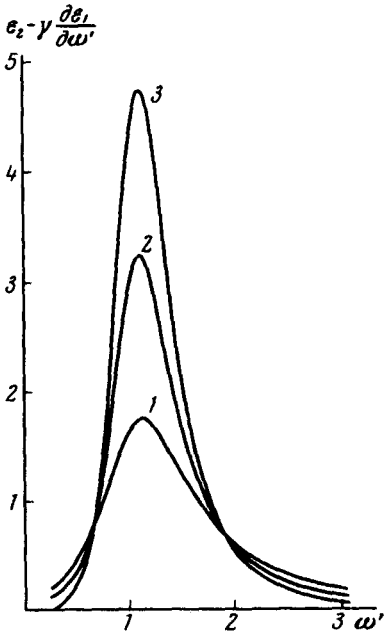


FIG. 1b. Dependence of the function $\epsilon_2(\omega') - \gamma d\epsilon_2(\omega)/d\omega'$ on ω' at $v'=0.4$: 1— $\gamma=0$; 2— $\gamma=0.4$; 3— $\gamma=0.8$.

We shall illustrate this method for interband transitions described by Eq. (3). Figures 1a and 1b show the functions $\epsilon^*_1(\omega')$ and $\epsilon^*_2(\omega')$ at $v'=0.4$ and for different γ . Figures 1a and 1b show the extent to which the resolution of the individual bands is substantially improved.

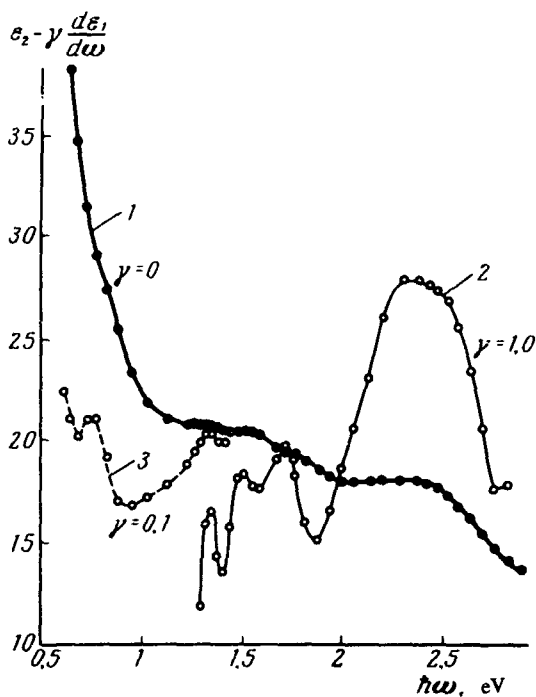


FIG. 2 Separation of the interband-conduction bands of vanadium. Ordinates—experimental values of the function $\epsilon_2(\omega) - \gamma d\epsilon_1(\omega)/d\omega$; 1— $\gamma=0$; 2— $\gamma=1.0$ eV; 3— $\gamma=0.1$ eV.

4. When the proposed method is used to reduce experimental results, it must be borne in mind that the method presupposes the existence of sufficiently detailed and exact measurements and requires of necessity a preliminary smoothing out of the experimental functions $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$. The larger the coefficient γ , the larger the influence of the term with the derivative and the more stringent the requirements imposed on the measurement intervals and on the degree of smoothing. For each region of the spectrum it is necessary to choose the optimal value of γ .

Next, the energy gaps can be determined by using the relation $\Delta \approx \hbar\omega_{\max}$, where Δ is the corresponding energy gap and ω_{\max} is the position of the maximum of the function $\epsilon_2(\omega)$. If Δ must be known with high accuracy, it is necessary to take into account the small difference between these quantities, brought about by the quantity ν' . This question is discussed in^[3].

5. The proposed method was used to analyze the optical constants of vanadium.^[5] We have changed over from the dimensionless ω' and γ to ω and γ in units of eV. The experimental functions $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ were smoothed beforehand by means of an algorithm that uses third-degree polynomials.^[6] Figure 2 shows the function $\epsilon_2(\omega)$ (curve 1) and the functions $\epsilon_2(\omega) - \gamma d\epsilon_1(\omega)/d\omega$. In the visible region $\gamma=1.0$ eV (curve 2), and in the infrared $\gamma=0.1$ eV (curve 3). It is also seen from Fig. 2 that the resolution of the interband-conduction bands is substantially improved. In the spectral region 0.5–2.8 eV, five bands were observed for vanadium with maxima at 0.75, 1.35, 1.51, 1.72, and 2.30 eV. Thus, vanadium has in the indicated region five energy gaps, whose values are close to the cited values of ω_{\max} . Further refinement of the values of Δ call for the knowledge of ν' . Identification of the bands calls for additional research.

¹Equivalent expressions were obtained in^[4], where, however, a misprint appeared in the real part of the integral. The correct formulas are

$$\epsilon_2 = \frac{2\pi C \omega' / \nu'}{(\omega'^2 + \nu'^2)^2} \left[\frac{\omega'^2 - \nu'^2 - 1/2}{b(a^2 + b^2)} - \frac{1}{2b} + 1 \right];$$

$$\epsilon_1 = \frac{\pi C}{2(a^2 + b^2)b} - \frac{\omega'^2 - \nu'^2}{2\omega' \nu'} \epsilon_2; \quad a^2 + b^2 = [(1 - \omega'^2 + \nu'^2)^2 + 4\omega'^2 \nu'^2]^{1/2};$$

$$b^2 = \frac{1 - \omega'^2 + \nu'^2}{2} + \frac{1}{2} [(1 - \omega'^2 + \nu'^2)^2 + 4\omega'^2 \nu'^2]^{1/2}.$$

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