Determination of electronic characteristics of niobium nitride by an optical method

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(Submitted 19 January 1983)
Zh. Eksp. Teor. Fiz. **84**, 2316–2322 (June 1983)

The dispersion of the complex dielectric constant $\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$ of niobium nitride was measured in the spectral interval 0.15–3.1 eV at temperatures 295 and 600 K. It was found that in this interval the optical properties of NbN are determined by the conduction electrons and by five interband-transition bands, to two of which correspond small gaps 0.13 and 0.27 eV. The parameters of the conduction-electron bands and of the interband-transitions are determined, as well as their temperature dependences. The following values are obtained for the conduction electrons: squared plasma frequency $\omega_{pe}^2 = 0.29$ eV^2, conduction electron density N_e 2×10^{20} cm^{-3}, reciprocal relaxation time $\nu_e = 0.325$ eV. The energy gaps, the plasma frequencies, and the reciprocal relaxation times are determined for the interband-transition bands.

PACS numbers: 71.25.Tn, 71.20. + c, 77.20. + y, 78.20.Dj

Niobium nitride is a very interesting compound. In the normal state it is a poor metal with low static conductivity that has practically no temperature dependence.[1] This indicates that the conduction-electron density is low. In the superconducting state, NbN is a superconductor with high critical parameters. In view of the indicated peculiarities it becomes quite interesting to investigate its electronic characteristics and their temperature dependences. Optical investigations yield many important electronic characteristics.[2] No such investigations were made so far to our knowledge.

We measured the complex dielectric constant $\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$ in the spectral interval 0.4–8.5 μm (3.1–0.15 eV) at 295 and 600 K.

1. EXPERIMENT

The samples were prepared by the reactive cathode sputtering method developed by E. A. Antonova and V. A. Sukhov.[3] The samples were films deposited on polished quartz substrates of area 60×20 mm. The NbN film thickness was $d\approx4000$ Å. We investigated in this paper a sample with a superconducting transition temperature $T_c = 16.1$ K, determined from the midpoint of the resistance jump ($\Delta T_c = 0.5$ K). The ratio $R_r/R_{res} = 0.93$, where R_r and R_{res} are the resistances at room temperature and near T_c, respectively. X-ray investigations have shown that the sample has a B-1 lattice (of the NaCl type) with a lattice constant $a = 4.39$ Å.

Measurements of the optical constants were made with a special setup. The mirror (sample) was in a vacuum at a pressure $p\approx10^{-5}$–10^{-6} Torr, so that the measurements could be made in the temperature interval 290–700 K. We investigated light reflected once from the sample. The light incidence angle was 60° or 80°. Ellipsometric methods were used. In the visible region the "compensator" version of the method was used (see, e.g., Ref. 2), and in the infrared region the Beattie method.[4]

Two independent quantities Δ and 2ρ were measured by a null method. Here Δ is the phase shift between the p and s components of the electric vector **R** of the wave reflected from the metal, and ρ is the angle of the reconstructed polarization ($\tan\rho = |R_p|/|R_s|$, when the plane of polarization of the incident light makes an angle 45° with the incidence plane). The complex dielectric constant $\varepsilon = \varepsilon_1 - i\varepsilon_2$ was determined from the equation

$$\frac{(\varepsilon-\sin^2\varphi)^{1/2}}{\sin\varphi\,\mathrm{tg}\,\varphi} = \frac{\cos 2\rho - i\sin 2\rho\sin\Delta}{1-\sin 2\rho\cos\Delta}. \tag{1}$$

In the Beattie method we measured four light intensities

$$I_1 = I(0, 45°);\quad I_2 = I(90°, 45°);$$

$$I_3 = I(45°, 45°);\quad I_4 = I(-45°, 45°).$$

The quantities in the parentheses are the asimuths of the polarizer and analyzer, respectively. ε_1 and ε_2 were calculated from the equations

$$n_0 = \sin\varphi\,\mathrm{tg}\,\varphi\,\frac{I_2-I_1}{I_1+I_2-2(I_1I_2)^{1/2}\cos\Delta}, \tag{2}$$

$$k_0 = 2n_0\frac{[I_1I_2(1-\cos^2\Delta)]^{1/2}}{I_2-I_1}, \tag{3}$$

$$\cos\Delta = \frac{I_3-I_4}{4(I_1I_2)^{1/2}}\left(1+\frac{I_1+I_2}{I_3+I_4}\right), \tag{4}$$

$$\varepsilon_1 = n_0^2 - k_0^2 + \sin^2\varphi, \tag{5}$$

$$\varepsilon_2 = 2n_0k_0. \tag{6}$$

The apparatus, the measurement methods, and the calculation formulas[1)] are described in greater detail in Refs. 5.

2. MEASUREMENT RESULTS

The experimental values of ε_1 and ε_2 of NbN were smoothened beforehand with a computer. The smoothening was by least squares using third-degree polynomials at seven nonequidistant experimental points. Six points (three each at the ends of the spectral interval) were left unsmoothened. Figures 1a, 1b, 2a, and 2b show the variances of the smoothened values of ε_1 and ε_2. The measurements errors were 2–4% in the spectral region 0.4–0.75 μm; 5–7% in the 0.75–1

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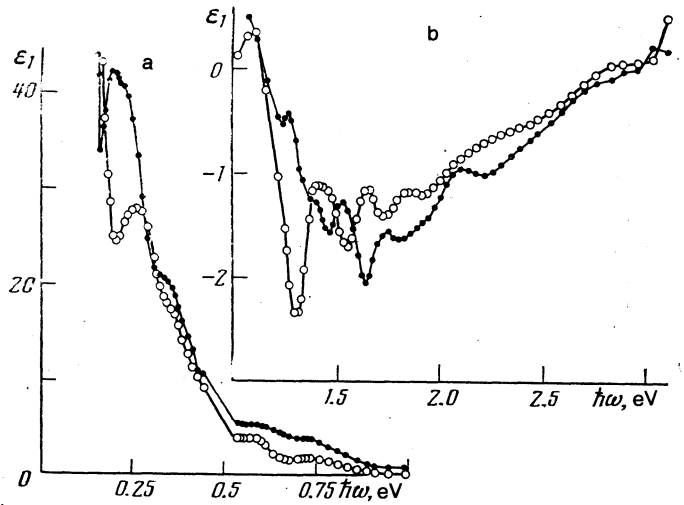
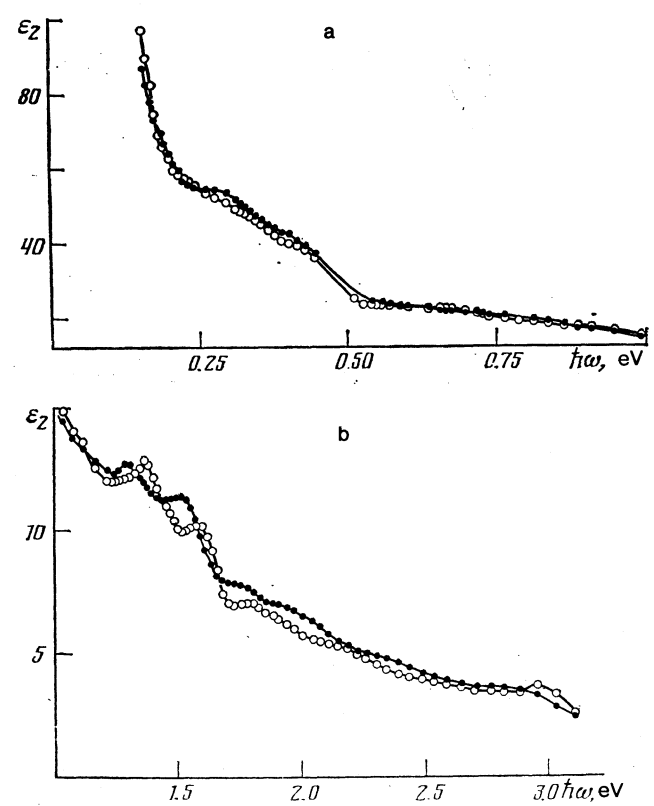


FIGS. 1a, b. Real part $\varepsilon_1(\omega)$ of the dielectric constant of NbN: ● —$T \approx 295$ K, ○ —$T \approx 600$ K.

μm region, 3–5 at 1–2.4 μm, and 6–8 in the 2.8–8.5 μm region. Altogether we obtained 118 values each for ε_1 and ε_2 at room temperature and 117 each at 600 K.

It can be seen from Figs. 1 and 2 that $|\varepsilon_1(\omega, 295\ \text{K})| > |\varepsilon_1(\omega, 600\ \text{K})|$ and $\varepsilon_2(\omega, 295\ \text{K}) > \varepsilon_2(\omega, 600\ \text{K})$, except for the region near 1 eV and at the ends of the spectral interval. From there on $\varepsilon_2(\omega)$ is a decreasing function. The plot of $\varepsilon_1(\omega)$ has decreasing and increasing regions. Against the background of the general structure, a number of maxima



FIGS. 2a, b. Imaginary part $\varepsilon_2(\omega)$ of the dielectric constant of NbN: ● — $T \approx 295$ K, ○ —$T \approx 600$ K.

are observed in $\varepsilon_2(\omega)$ and a continuous structure in $\varepsilon_1(\omega)$. In turn, the s structure of the maxima of $\varepsilon_2(\omega)$ consists of basic broad maxima against the background of which there appears a fine structure. The function $\varepsilon_1(\omega)$ vanishes twice. When the temperature is raised, the main structure of $\varepsilon_2(\omega)$ and $\varepsilon_1(\omega)$ remain the same. The positions of the maxima of the fine structure of $\varepsilon_2(\omega)$ shift in the main towards higher energies. The same is observed for the positions of the extrema of $\varepsilon_1(\omega)$.

It is important that $\varepsilon_1(\omega)$ is a large positive quantity at $\omega > 1$ eV. This indicates predominance of the interband-transition contribution over the contribution of the conduction electrons. It follows from Figs. 2a and 2b that in our spectral interval one can single out four main broad interband-transition bands. The first is at energies ~ 0.26 eV, the second at ~ 0.74 eV, the third at ~ 1.3 eV and the fourth at ~ 2 eV. In addition, the behavior of the functions in the spectral region $\omega < 0.25$ eV at both temperatures points to the presence of a fifth band at energies ~ 0.15 eV. The contribution to $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ from the conduction electrons is much smaller than the contribution from the interband transitions. In other words, the density of the conduction electrons in NbN is low, in agreement with data on the static conductivity.[1]

3. DISCUSSION OF EXPERIMENTAL RESULTS

It was shown in Ref. 2 that for transition metals the main contribution to $\varepsilon(\omega)$ at frequencies $\omega \ll \Omega_p$ is made by conduction electrons and interband transitions connected with Bragg planes. Here $\Omega_p^2 = 4\pi e^2 N_{\text{val}}/m$, is the density of the valence electrons, e and m are the charge and mass of the free electron. We assume that the same conclusion holds for NbN. The compound NbN has B-1 lattice (of the NaCl type). The unit cubic cell with lattice constant $a = 4.39$ Å contains 40 valence electrons $\Omega_p^2 \approx 656\ \text{eV}^2$ ($\Omega_p = 25.6$ eV). The upper limit of our spectral interval is $\omega_{\max} = 3.1$ eV, i.e., $\omega_{\max} \ll \Omega_p$.

We have noted above that five interband-transition bands and a conduction electron band can be separated in

the experimental relation. We have thus considered the theoretical model

$$\varepsilon(\omega)=1+\sum_{m=1}^{6}\varepsilon^{(m)}(\omega), \tag{7}$$

where the first term of the right-hand side is the contribution of the vacuum, the exponent $m=1$ pertains to the conduction electrons and $m>1$ to the electrons that take part in the interband electrons (the "Bragg" electrons). For the conduction electrons we used the Drude form

$$\varepsilon^{(1)}(\omega)=-\omega_{p1}^2/\omega(\omega-i\nu_1). \tag{8}$$

The form of the Bragg-electron bands was obtained in Refs. 6. In our study we used the simplest analytic expression

$$\varepsilon^{(m)}(\omega)=\varepsilon_1^{(m)}(\omega)-i\varepsilon_2^{(m)}(\omega)$$

$$=\frac{\omega_{pm}^2}{(\omega-i\nu_m)^2}\left(\frac{\omega_{0m}}{[\omega_{0m}^2-(\omega-i\nu_m)^2]^{1/2}}-1\right). \tag{9}$$

Here $\hbar\omega_{0m}=\Delta_m$, $1/\nu_m$, and ω_{pm}^2 are respectively the energy gap, the relaxation time, and the square of the plasma frequency of Bragg electrons with index m. It follows from (9) that

$$\int_0^\infty \omega\varepsilon_2^{(m)}(\omega)\,d\omega=\frac{\pi}{2}\omega_{pm}^2. \tag{10}$$

Equation (10) coincides with the sum rule. Thus, the oscillator strength is ω_{pm}^2/Ω_p^2. The conduction-electron band is described by the two parameters ω_{p1}^2 and ν_1. Each band of Bragg electrons is described by the three parameters ω_{0m}, ω_{pm}^2, ν_m. To estimate the parameters we used the method of least squares. We obtained the minimum of the function F:

$$F=\sum_{k=1}^{N}[\varepsilon_2(\omega_k)-\varepsilon_2^{T}(\omega_k)]^2. \tag{11}$$

Here $\varepsilon_2(\omega_k)$ is the experimental value of the imaginary part of the dielectric constant at the point ω_k,

$$\varepsilon_2^{T}(\omega_k)=\sum_{m=1}^{6}\varepsilon_2^{(m)}(\omega_k)$$

is the theoretical value of the imaginary part of the dielectric constant obtained at the point ω_k from expression (9). All the calculations were made with a computer.

It must be noted that Eq. (9) does not take into account the interband transitions connected with the lines and points of intersection of the Bragg planes. The latter are of substantially lower intensity and usually manifest themselves in the form of a fine structure.

The results are listed in Table I. The agreement between the experimental $\varepsilon_2(\omega)$ and the theoretical $\varepsilon_2^T(\omega)$ dependence at $T=295$ K is shown in Fig. 3. It can be seen from the figure that the theoretical curve describes well the main structure of the dispersion of ε_2 and does not describe the fine structure. It is impossible to describe the fine structure with the aid of the Bragg-band shape [Eq. (9)].[2] The least-squares method averages this structure.

A theoretical calculation of $\varepsilon_2(\omega)$, using the empirical-pseudopotential method, was carried out in Ref. 7. The results are shown in Fig. 4. Two principal maxima are seen. The text places them at $\sim$0.1 and $\sim$0.6 eV (the calculation yields $\sim$0.2 and $\sim$0.8 eV). Besides these maxima one can see in the figure maxima at $\sim$1.5 eV, $\sim$4 eV, and $\sim$7 eV. The data in the table indicate that the theory is on the whole in agreement with experiment.

It can be seen from the table that NbN has two interband transition bands with small gaps $\sim$0.13 and $\sim$0.27 eV. It is seen furthermore that for the conduction electrons ω_p^2 is a small quantity. Its large temperature dependence indicates that account must be taken of electron jump-overs through the second and third gaps. Allowance for this circumstance has made it possible to estimate the square ω_{pe}^2 of the conduction-electron plasma density at $T=0$ K, which was found to be 0.29 eV^2. The corresponding conduction electron density[3] is $N_e=2\times10^{20}$ cm^{-3}, which is lower by two orders of magnitude than the conduction-electron density of ordinary metals. NbN is thus a semimetal.

The parameter ν_1 increases very weakly with increasing temperature, i.e., the main contribution to ν_1 is made by electron collisions with the grain boundaries and with the defects. As $T\to0$ the parameter $\nu_1\to0.320$ eV. We estimate the ratio

$$R_r/R_{\text{res}}=\frac{\omega_{p1}^2(0\text{ K})}{\omega_{p1}^2(295\text{ K})}\frac{\nu_1(295\text{ K})}{\nu_1(0\text{ K})}=0.935,$$

which agrees very well with the experimental value 0.93 cited in Sec. 1.

We proceed now to the second band. Transfer of electrons from the second band to the conduction band decreases ω_{p2}^2. It must be noted that the sum $\omega_{p1}^2+\omega_{p2}^2$ equals

TABLE I.

Band number	$T\approx295$ K						$T\approx600$ K					
	1	2	3	4	5	6	1	2	3	4	5	6
Δ, eV	0	0.134	0.271	0.735 ±0.001	1.28	2.1	0	0.142	0.249	0.743 ±0.001	1.28	2.1
ν, eV	0.325 ±0.005	0.027	0.150	0.214 ±0.001	0.266 ±0.001	0.90 ±0.05	0.33 ±0.005	0.008	0.174	0.217 ±0.001	0.261 ±0.001	0.90 ±0.05
ω_p^2, eV^2	0.315 ±0.005	1.31	6.9	7.1	11.6	18	0.756 ±0.005	0 858 ±0.005	7.2	7.7	10.3	17

Note. Unless indicated in the table, the error of the parameters in the employed model is less one significant figure.

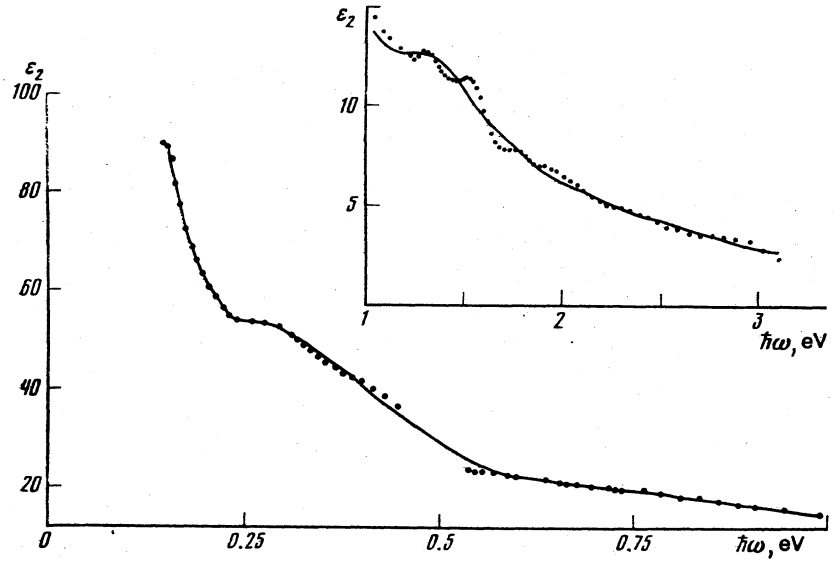


FIG. 3. Comparison of the experimental $\varepsilon_2(\omega)$ with the theoretical function $\varepsilon_2^T(\omega)$: solid curve—$\varepsilon_2^T(\omega)$, ● —$\varepsilon_2(\omega)$.

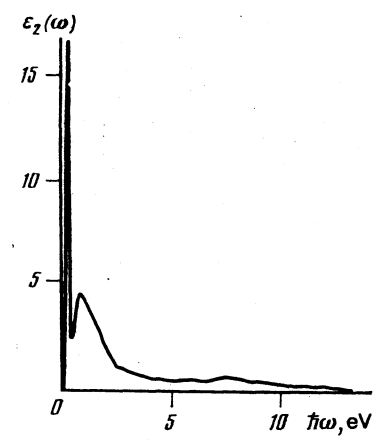


FIG. 4. Plot of $\varepsilon_2(\omega)$ of NBN calculated by the Fong and Cohen empirical-pseudopotential method. The figure is taken from Ref. 7.

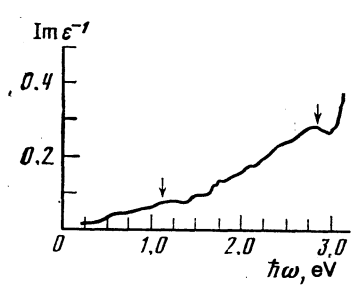


FIG. 5. Loss function of niobium nitride at $T = 295$ K. The arrows mark the positions of the zeros of $\varepsilon_1(\omega)$.

1.625 and 1.614 at $T = 295$ and 600 K, and is thus constant within the limits of errors. With increasing temperature, Δ_2 increased somewhat but ν_2 decreased substantially. This is apparently due to the appreciable increase of the population of the upper level of the second band at $T = 600$ K. The ratio of the populations of the upper and lower levels increases to 0.51.

We consider now the remaining bands. When the temperature increases, the values of ν_3 and ν_4 increase, as expected. ω_{p3}^2 and ω_{p4}^2 also increase. The temperature dependences of Δ_3 and Δ_4 have opposite signs. The low sensitivity of the sum F to the values of the parameters of the fifth and sixth bands prevents us from determining their temperature dependence. The sum of the squares of the plasma frequencies $\Sigma_{m=1}^{6}\omega_{pm}^2$ for $T = 295$ and 600 K is respectively 45.7 and 43.7 eV^2. At both temperatures

$$\sum_{m=1}^{6}\omega_{pm}^2 \ll \Omega_p^2.$$

NbN should thus have substantial interband-transition bands at $\omega > \omega_{\max}$. It follows from Table I that ω_p^2 increases with increasing Δ.

We have mentioned above that at both temperatures $\varepsilon_1(\omega)$ vanishes twice in our interval, i.e., plasma oscillations are possible and should manifest themselves in the loss function $\mathrm{Im}[\varepsilon(\omega)]^{-1}$. The loss function of niobium nitride at $T = 295$ K is shown in Fig. 5. The arrows mark the positions of the zeros of the function $\varepsilon_1(\omega)$. It can be seen that the zeros of $\varepsilon_1(\omega)$ correspond to the largest maxima of the function $\mathrm{Im}[\varepsilon(\omega)]^{-1}$. The small value and the large width of the maxima is due to the large value of $\varepsilon_2(\omega)$, which leads to a strong damping of the plasma oscillations. The maximum manifests itself most strongly at $\omega = 2.87$ eV.

In conclusion, we thank E. A. Antonova, D. R. Dzhuraev, and V. A. Sukhov for producing the sample.

[1)]Equation (4) was obtained by averaging the three equations given in Ref. 4 for $\cos \Delta$.
[2)]It is possible that the fine structure is connected with interband transitions in the region of intersection of several Bragg planes.
[3)]It is assumed that in the conduction band the effective conduction-electron mass is equal to that of the free electron.

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Translated by J. G. Adashko