Submillimeter electrodynamics of niobium carbide thin films: superconductivity and size effect

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Submillimeter spectra of conductivity and permittivity of a thin niobium-carbide, film have been measured for the first time at temperatures varying between 5 and 300 K in the 5–32 cm^{-1} frequency band. We have demonstrated that the temperature and frequency dependencies of film parameters are in a qualitative agreement with the optical characteristics of superconductors derived from the BCS theory. The superconducting energy gap and carrier relaxation time versus temperature have been calculated from the measurements. © *1996 American Institute of Physics.* [S1063-7761(96)02904-6]

Niobium carbide, NbC, is one of typical carbides of transitional metals of groups IV and V distinguished by their high mechanical strength and chemical stability.[1,2] Like most simple superconducting niobium compounds, it has a relatively high (for conventional low-temperature superconductors) superconducting transition temperature.[1,2] These properties of NbC stimulate an interest in both fundamental and applied research on this material.[3] Although the number of publications about niobium carbide is considerable, there are no data concerning its optical parameters in the submillimeter band, which is the most interesting since the superconducting gap energy is in this band.[4] Measurements in this band should yield information about the gap and its temperature dependence, residual absorption mechanisms, coherence effects and other properties of the superconducting state.[5] The aim of the reported work was to investigate in detail electrodynamic characteristics of NbC films in the frequency band of 5–32 cm^{-1} (150–960 GHz).

In our experiments we used a high-quality 1×1-cm NbC film fabricated by reactive laser deposition[6] on a plane-parallel sapphire substrate with orientation $[\bar{1}012]$ and a thickness of about 0.5 mm. The film thickness was 140 Å$\pm$10% as measured by the interference reflection technique in the *x*-ray band. The superconducting transition temperature of the film was $T_c=11.2$ K with a transition width of less than 0.1 K and a very low residual resistivity $\rho_0=14.8\ \mu\Omega\cdot$ cm due to the small defect concentration.[3]

The dynamic measurements were performed on an Epsilon laboratory submillimeter BWO-spectrometer (here BWO refers to backward-wave oscillator radiation) operating in the quasi-optical configuration and described in detail elsewhere.[7] We recorded spectra of the transmission, $Tr(\nu)$, and of the phase shift, $\varphi(\nu)$, for a wave transmitted through a sample, which consisted of the substrate and the NbC film. The spectra $Tr(\nu)$ and $\varphi(\nu)$ were processed using conventional optical formulas for the complex transmittivity of a two-layered (film plus substrate) system.[8] The film parameters, namely the indices of refraction, n, and absorption, k, were derived by numerically solving nonlinear equations for $Tr(\nu)$ and $\varphi(\nu)$ at each frequency and temperature. The resulting parameters, n and k, were used to derive other electrodynamic characteristics of the film, such as the dynamic conductivity σ, permittivity ε', penetration depth δ, surface impedance $Z=R_s+iX_s$, etc. The errors in σ and ε' in the superconducting phase were 15–20%. The substrate optical parameters, n and k, were previously determined by measuring the transmission of a sapphire plate of the same orientation without the film versus temperature.

Typical submillimeter transmission spectra $Tr(\nu)$ of the studied film on the substrate are given in Fig. 1. The spectra were recorded at temperatures when the film was in the normal (20 K) and superconducting (5 K) states. The large oscillations in the spectra are due to interference within the substrate, which was in effect an asymmetric Fabry–Perot resonator with its parallel planes—one with the deposited NbC film, the other without a film—acting as mirrors. The frequency $\Delta\nu=c/2nd$ of the oscillations is controlled by the substrate refraction index n and its thickness d (c is the speed of light in vacuum). The maximum transmission is defined by the transparency of the film. In the normal phase ($T=20$–300 K) the amplitudes of the transmission maxima are essentially equal at all frequencies. The shape of the transmission spectrum is practically constant with temperature, only the transmission is lower at lower temperatures due to the lower transparency (higher conductivity) of the film. When the film switches to the superconducting state, the spectrum shape changes considerably. At lower frequencies the transmission drops by about an order of magnitude, and at higher frequencies it increases, as shown in Fig. 2. The phase shift versus temperature is also plotted in Fig. 2. As the temperature drops from room to critical value, the phase shift is constant to within experimental accuracy. For $T<T_c$ the phase shift drops by more than 1 rad because of the superconducting transition in the film.

The electrodynamic parameters of the film derived from $Tr(\nu)$ and $\varphi(\nu)$ spectra are plotted in Figs. 3–5. Let us first discuss the parameters of the normal state.

As the temperature decreases from room temperature to

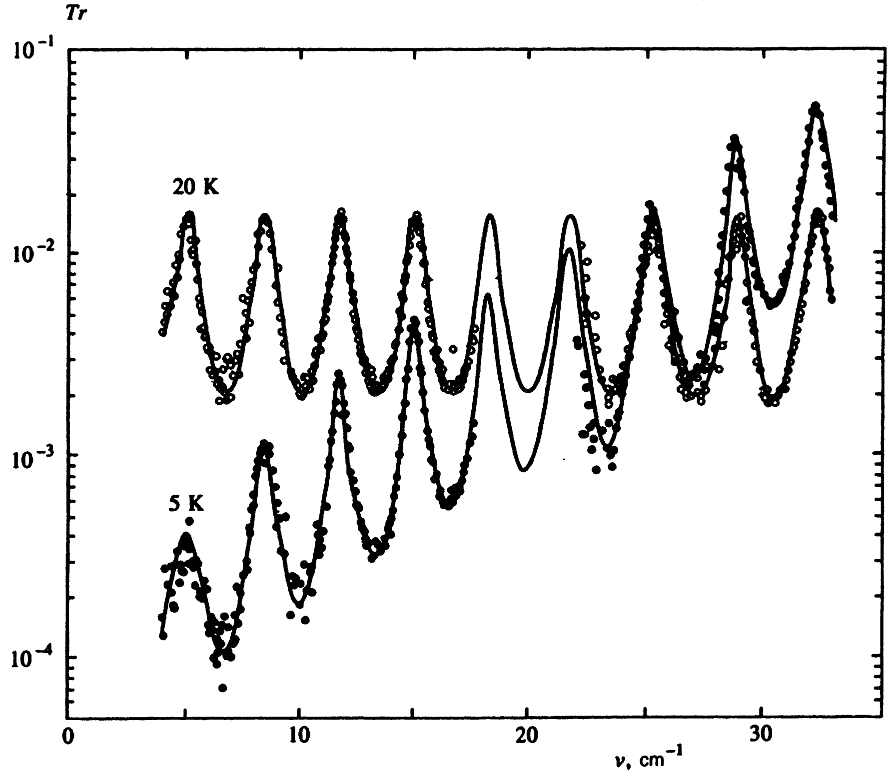

FIG. 1. Measured transmission spectra of a 140-Å NbC film fabricated on a 0.455-mm sapphire substrate at temperatures above and below the critical point $T_c = 11.2$ K.

about 20 K, the dynamic conductivity of the film increases and becomes constant at $T \leqslant 20$ K, and the permittivity remains within the experimental accuracy (Figs. 3 and 4). In the normal state for $T > T_c$ both σ and ε' are constant with frequency throughout the band ($\nu = 5-32$ cm^{-1}), the dynamic conductivity being equal to that in the dc measurement, σ_{dc} (static conductivity) within the accuracy of the measurement. The frequency dependence of the penetration depth of radiation in the film, $\delta = c/2\pi k\nu$ (skin depth) calculated the for the normal state from the measured σ and ε' is described by the function $\delta \propto \nu^{-1/2}$ (Fig. 5, $T = 300$ K). This temperature and frequency behavior of the permittivity and penetration depth is in accord with the Drude model of conductivity due to free, noninteracting carriers in the low-frequency limit $\nu \ll \gamma$, where γ is the relaxation frequency of current carriers.[9,10] In other words, our measurements in the submillimeter band indicate that the electrodynamic properties of the NbC film in the normal state can be interpreted in terms of metallic conductivity.

Note that the carrier mean free path in films with a thickness of more than 500 Å is $L \approx 400$ Å (in the normal state at $T = 13$ K),[3] i.e., the thickness of the film studied in our experiment is comparable to the carrier mean free path. Under these conditions ($L \approx d$) carriers suffer additional scattering from the film boundaries,[11,12] which should be taken into account in interpreting experimental data. Assuming that the scattering from the film boundaries is diffuse,[3] we can derive parameters of a bulk NbC sample.

The conductivity σ of a thin film is related to that (σ_0) of a bulk sample through the following equation[12]:

$$\frac{\sigma}{\sigma_0} = \frac{L}{L_0} = 1 + \frac{3}{4}\left(b - \frac{b^3}{12}\right)B(b) - \frac{3}{8b}(1 - e^{-b}) - \left(\frac{5}{8} + \frac{b}{16} - \frac{b^2}{16}\right)e^{-b}, \tag{1}$$

where

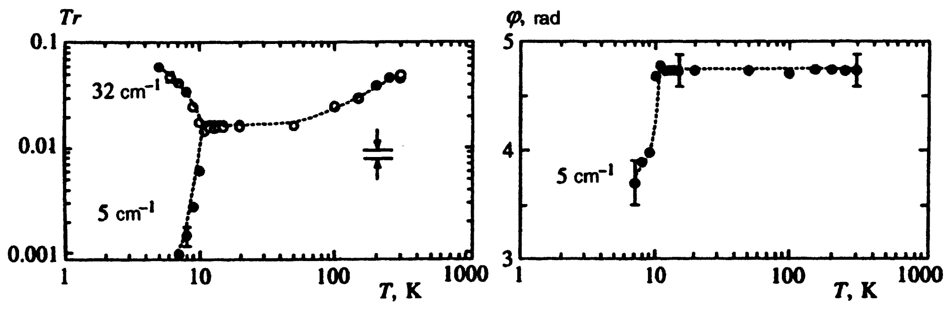

FIG. 2. Transmission and phase shift in the 140-Å NbC film on the 0.455-mm sapphire substrate at two frequencies around 5 and 32 cm^{-1}, corresponding to two interference maxima (Fig. 1).

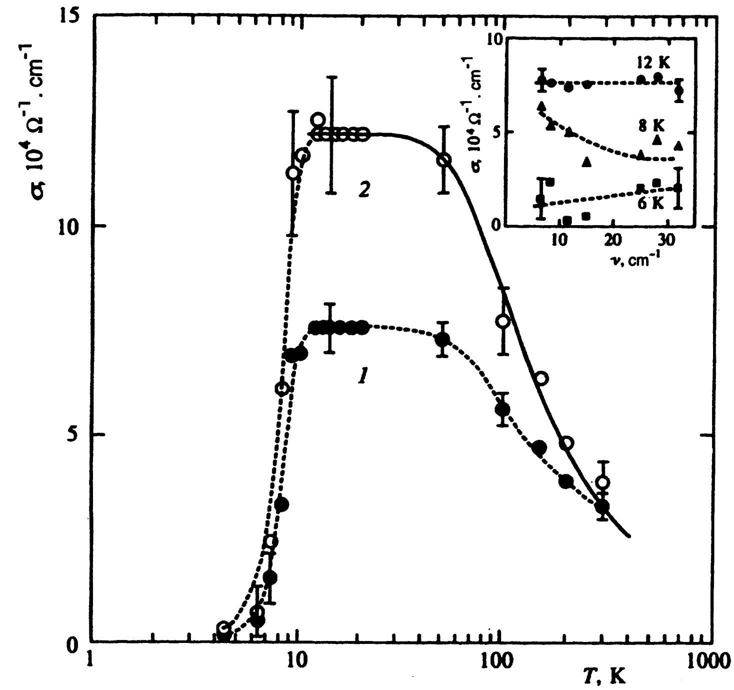

FIG. 3. Dynamic conductivity of a 140-Å NbC film (curve *1*) and bulk NbC (curve 2) in the normal and superconducting states versus temperature (see text). In the normal state the conductivity is constant with frequency, and the points show averaged values. For the superconducting state, measurements at 15 cm^{-1} are given. The solid line is a fit by the Bloch–Grüneisen equation (2). The insert shows the NbC film conductivity versus frequency at three different temperatures both above and below the critical point ($T_c = 11.2$ K).

$$B(x) = \int_x^{\infty} \frac{e^{-z}}{z} dz, \quad b = d/L.$$

Equation (1) was derived using the formula $\sigma = ne^2 L/m^* v_F$ assuming that the effective mass m^* and the Fermi velocity v_F are independent of the film thickness. A numerical solution of Eq. (1) yields the mean free path in bulk NbC, hence its conductivity. The resulting conductivity as a function of temperature is plotted in Fig. 3. At high temperatures the conductivity (and free path) are proportional to $1/T$, which is due to the scattering of carriers from phonons.[10] For $T < 20$ K both σ and L are no longer functions of temperature and are controlled by the scattering of carriers from impurities and defects. The conductivity σ_0 versus temperature can be described by the Bloch–Grüneisen formula:[13]

$$\rho_{ph} = \frac{CT}{\Theta_D^2} G\left(\frac{T}{\Theta_D}\right), \quad G\left(\frac{T}{\Theta_D}\right)$$

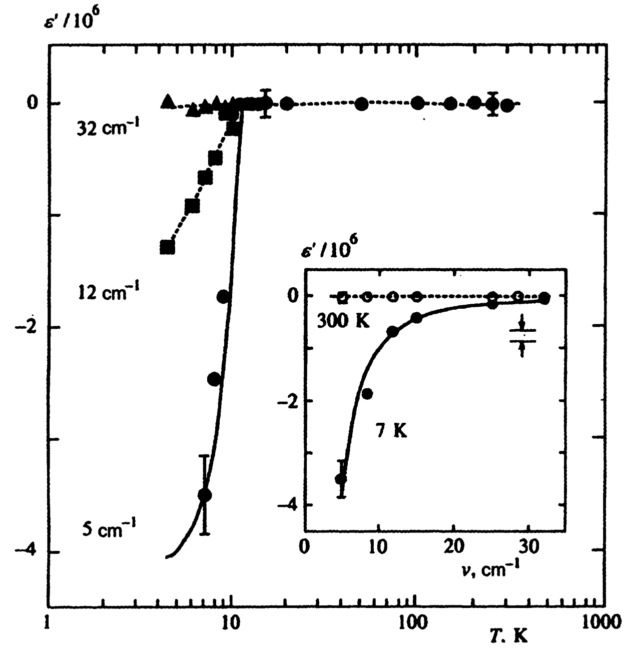

FIG. 4. Permittivity ε′ for the NbC film measured at three frequencies versus temperature. In the insert the permittivity at two temperatures above and below the transition point ($T_c = 11.2$ K) is plotted against frequency. The solid lines are calculations from the two-fluid model of the superconducting state:[5,14] $\varepsilon' \propto \nu^{-2}[1-(T/T_c)^4]$.

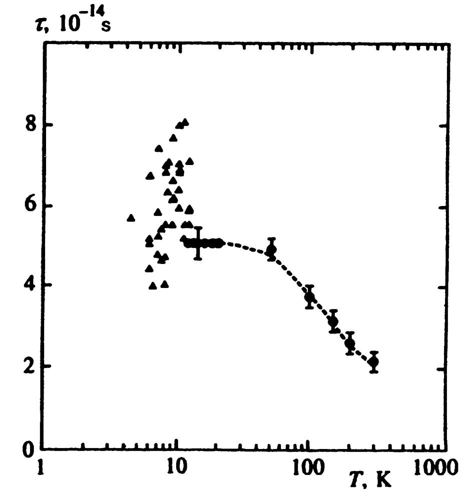

FIG. 5. (a) Penetration depth δ for the NbC film versus frequency measured at temperatures higher and lower than the transition point $T_c = 11.2$ K. The solid line is a fit to the Drude conductivity model. (b) Penetration depth for the NbC film at a frequency of 5 cm^{-1} versus temperature.

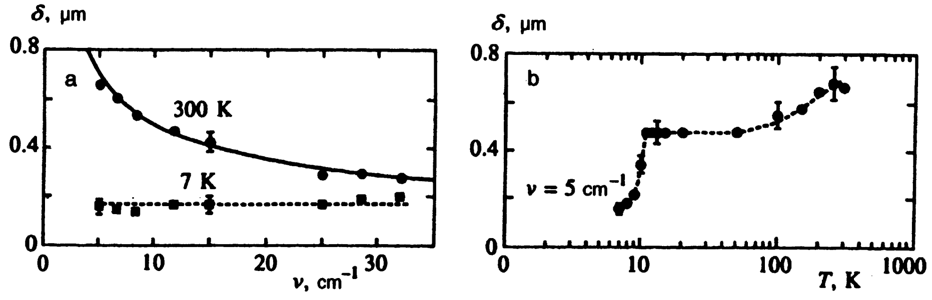

FIG. 6. Superconducting-gap energy $2\Delta(T)$ for the NbC film versus temperature derived from submillimeter measurements of the conductivity and dielectric permittivity using the BCS formulas.[15,20] Different points corresponding to one temperature were measured at different frequencies. The solid line is the least-square fit of the BCS formula for $2\Delta(T)$ to the experimental data.

$$=\left(\frac{T}{\Theta_D}\right)^4\int_0^{\Theta_D/T}\frac{z^5dz}{(e^z-1)(1-e^{-z})}, \qquad (2)$$

where $1/\sigma=\rho=\rho_0+\rho_{\rm ph}$, $\rho_{\rm ph}$ is the lattice resistivity due to scattering by phonons, ρ_0 is the residual resistivity, C is the empirical constant, and Θ_D is the Debye temperature. Figure 3 demonstrates that Eq. (2) approximates the experimental data well and yields the Debye temperature of bulk NbC: $\Theta_D=400\pm100$ K at $\rho_0=0.82\cdot10^{-5}\Omega\cdot$cm and $C=1.3\cdot10^{-2}\Omega\cdot$cm$\cdot$K. The resulting parameters Θ_D and ρ_0 are in a good agreement with the published data for single-crystal samples.[1,2]

Now let us discuss the parameters of the NbC film in the superconducting state. For $T<T_c$ the conductivity monotonically drops with decreasing temperature at all the frequencies (see insert in Fig. 3). After the transition to the superconducting state submillimeter spectra of the permittivity of NbC also change radically. Instead of ε' constant with frequency for $T>T_c$, we have a strong dependence $\varepsilon'\propto\nu^{-2}$ (insert in Fig. 4), as a result, ε' drops from zero to about -10^6 at frequencies below 10 cm^{-1} (Fig. 4). The penetration depth $\delta(\nu,T)$ also changes: for $T<T_c$ it drops by a factor of more than two at 5 cm^{-1} and at lower temperatures it is constant with frequency (Fig. 5).

All in all, the recorded curves of the conductivity and permittivity of the NbC film as functions of temperature and frequency conform well to the picture of the optical properties of superconductors derived from the BCS theory.[5,14,15] The drop in the conductivity, which is proportional to the absorption of radiation, at $T<T_c$ is caused by the superconducting-gap opening in the spectrum of elementary excitations at $\nu<2\Delta/h$, where 2Δ is the superconducting-gap energy. The dispersion of the dielectric permittivity, $\varepsilon'\propto\nu^{-2}$, is due to the condensation of electrons in Cooper pairs, which allows electric transport without losses at low frequencies (zero dc resistivity). The spectral response of electrons in the superconducting state is a delta-function in $\sigma(\nu)$ at zero frequency.[16,17] According to the causality principle that leads to the Kramers–Kronig relations,[18] this delta-function in the conductivity spectrum yields the function $\varepsilon'\propto\nu^{-2}$ in the permittivity spectrum which was recorded in our experiments. The increase in the absolute value of ε' with decreasing temperature (Fig. 4) is due to the rise in the density of superconducting electrons, i.e., the spectral weight of the delta-function.

Measurements of the penetration depth yield the plasma frequency ω_p or, more exactly, its lower limit because in our case the penetration depth, electron mean free path, and the coherence length $\xi_0=240$ Å are comparable ($\delta\approx L\approx\xi_0$), and the real penetration depth of radiation, $\delta(T=0)$, is larger than its London limit $\lambda_L(T=0)=c/\omega_p$.[19] Extrapolating of $\delta(T)$ to $T=0$ yields $\delta(0)\approx1200$ Å and $\omega_p>1.6$ eV, which does not contradict the value $\omega_p=3.6$ eV derived from measurements of the upper critical magnetic field.[3]

The temperature dependence of the superconducting gap and relaxation time of carriers can be derived from measurements of the conductivity and dielectric permittivity. The conventional integral formulas of the BCS theory,[15,20] which are valid in the case of weak coupling at all ratios of ξ_0 to L, have been used. The calculations in the 4–12 K temperature range and the 5–32 cm^{-1} frequency band are given in Figs. 6 and 7. One can see that the superconducting-gap energy in NbC drops with the temperature from $2\Delta\approx20$ cm^{-1} at 4–5 K to zero at 11–12 K. The solid line in Fig. 6 shows a least-squares fit of the function $2\Delta(T)$ from the BCS theory to the experimental data. This fit yields $2\Delta(0)=23\pm4$ cm^{-1} and $2\Delta(0)/k_BT_c=3.0\pm0.5$. This result is slightly smaller than that derived from tunneling measurements in NbC: $2\Delta(0)/k_BT_c=3.72\pm0.04$.[4] The discrepancy may be caused by neglecting the effect of strong

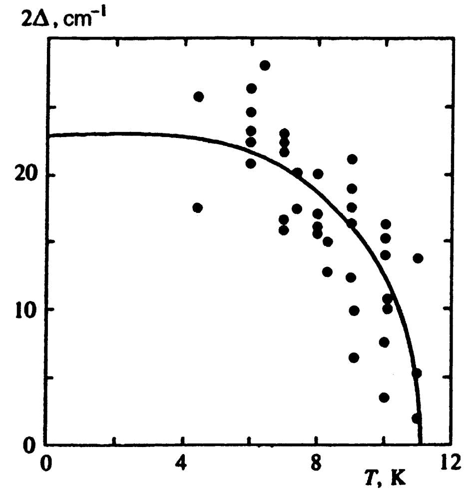

FIG. 7. Relaxation time τ of current carriers in the NbC film versus temperature derived from submillimeter spectra of conductivity and dielectric permittivity using the BCS formulas[15,20] below T_c and Drude model above T_c. In the normal state the conductivity is constant as a function of frequency and the points show averaged values. In the superconducting state the different points corresponding to one temperature are measurements at different frequencies.

coupling in this material, in which the coupling constant is 0.9 (Ref. 4).

As can be seen in Fig. 7, the carrier relaxation time τ in the superconducting state is practically independent of temperature. The relaxation time in the superconducting state is equal within the experimental accuracy to that in the normal state at a temperature slightly higher than the critical one (12–15 K). This indicates that τ in the superconducting state is controlled by the scattering of normal carriers from impurities and other defects. Therefore the size effect can be adequately taken into account for $T<T_c$, i.e., the conductivity of a bulk NbC sample in the superconducting state can be calculated. Given the carrier relaxation time and Fermi velocity, one can calculate the bulk relaxation time by Eq. (1), and then the complex conductivity of bulk NbC in the superconducting state can be derived using conventional formulas,[15,20] provided that the gap 2Δ in the spectrum of excitation is independent of the film thickness. The resulting real component of bulk NbC conductivity in the superconducting state versus temperature is shown in Fig. 3. It can be seen that, as in a thin film, the conductivity of bulk NbC drops with the decreasing temperature, which is due to the superconducting-gap opening.

To sum up, their paper reports the first measurements of electrodynamic parameters of a thin niobium carbide film in the 5–32 cm^{-1} frequency band at temperatures of 5–300 K. Electrodynamic parameters of bulk NbC and the Debye temperature have been calculated under the assumption that scattering of current carriers on the boundary is diffuse. Fairly good agreement of measured optical parameters of the film and bulk material versus temperature and frequency with the optical characteristics of conventional (low-temperature) superconductors derived from the BCS theory[5,15,20] has been demonstrated. The energy of the gap in the spectrum of elementary excitations and the carrier relaxation time in both normal and superconducting state as functions of temperature have been calculated.

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