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Far-infrared transmission of superconducting homogeneous NbN films: Scattering time effects

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The transmission of superconducting homogeneous NbN films has been measured between 20 and 95 cm^{-1}. The results could be fitted with the Leplae extension of dirty-limit Mattis-Bardeen theory, which includes the effects of electronic scattering. The fits yield $2\Delta/k_BT_c=4.4$ and 4.1 for T_c's of 17 and 14 K, and scattering times of $(1-5)\times10^{-14}$ sec. These values are in substantial agreement with other determinations. The results, together with theoretical considerations and analysis of previous data in Pb, show that the Leplae approach simply describes optical behavior even in very strongly coupled materials. A refined description, however, probably requires consideration of both scattering and strong-coupling effects.

I. INTRODUCTION

Research in both homogeneous and granular superconducting films touches on several areas of current importance. In superconductivity itself, even the simpler homogeneous films provide new systems in which to examine basic ideas and to search for high T_c's. In them also it is possible to observe the scaling and universality associated with critical phenomena and to probe lowered dimensionality. When the films become granular there is additional potential to examine percolation behavior and the theory of inhomogeneous media, and new flexibility to tailor materials for applications. Two recent conference proceedings illustrate the complex interplay among these areas.[1,2]

NbN is a high-T_c (17 K) strong-coupling superconductor which can be made in films ranging from homogeneous to highly granular. Comprehensive dc measurements have shown a variety of interesting behavior related to many of the areas mentioned above.[3–5] In this paper we present a detailed optical analysis of homogeneous NbN films with thicknesses between 20 and 100 nm. We measure the ratio of superconducting—to—normal-state transmission T_s/T_n over the range 20 to 95 cm^{-1}. As previous work in V_3Si has shown[6,7] such far-infrared measurements give substantial insight into the superconducting behavior of the films. These measurements also provide a firm foundation for our projected far-infrared work in granular NbN which may help unravel the difficulties encountered in the few optical experiments made to date in granular superconductors.[8,9]

Our analysis of the homogeneous NbN films uses the same methods that were successful in V_3Si,[6] where the simple dirty-limit Mattis-Bardeen (MB) result[10] was inadequate to fit the data. Such a result is expected because V_3Si is a strong-coupling superconductor, but what was unexpected was the fact that it was not necessary to use the full strong-coupling theory of Nam and others. Instead the successful fit used an expanded version of MB theory, the Leplae formulation,[11] which takes into account the finite value of the electronic scattering time τ.

The measurements and analysis reported here bear directly on the properties of homogeneous and granular NbN. We also discuss the more general question of the justification of the Leplae approach, and compare the magnitude of scattering and strong-coupling effects in far-infrared analysis.

II. THEORY

The far-infrared response of superconductors near gap frequencies ($\hbar\omega_g=2\Delta$) constitutes a sensitive probe of the underlying microscopic mechanisms for superconductivity.[12,13] Early far-infrared work on superconductors culminated in a well-known study by Palmer and Tinkham.[14] Their

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transmission and reflection data on superconducting Pb implied a significant deviation of its complex conductivity function $\sigma_1^s(\omega)+i\sigma_2^s(\omega)$ from that predicted by MB (Ref. 10) for a Bardeen-Cooper-Schrieffer (BCS) superconductor. In work which unfortunately was not published, Nam reportedly[14] explained the deviations as arising from strong-coupling effects. This result was obtained from his theory on the electromagnetic properties of strong-coupling superconductors.[15] In consequence, a considerable fraction of the subsequent theoretical and experimental work in this field has involved the theory of strong-coupling superconductivity.[16–23]

The strong-coupling effects which are the focus of these works fall into two categories. The first consists of structure in the real part of the conductivity $\sigma_1^s(\omega)$ deviating from the MB result at frequencies near ω_g. For pure metals in the anomalous limit these deviations represent a few percent effect and are difficult to observe. The second category consists of effects which increase the area $\int_{\omega_g}^{\omega_D} d\omega\,\sigma_1^s(\omega)$. As the Debye frequency ω_D is much larger than ω_g, these integral effects are best studied in the low-frequency behavior of the imaginary part of the conductivity $\sigma_2^s(\omega)\sim 2A/\pi\omega$, where A is the sum-rule-determined strength[13,24,25] of the zero-frequency pole of σ_1^s. Far-infrared measurements are, in principle, a sensitive probe of both kinds of effects, but as we will see it is essential to consider scattering behavior as well.

As a framework within which to interpret the optical properties of an ever growing number of new superconducting materials, the strong-coupling theories suffer two major drawbacks. First, they require accurate knowledge of the frequency-dependent complex gap function $\Delta_1(\omega)+i\Delta_2(\omega)$ which replaces the single gap parameter Δ of the BCS (Ref. 26) theory. This requires a preliminary set of tunneling measurements or other experiments. Second, at present detailed calculations have been done for the extreme anomalous and extreme local limits only. These limits are often inapplicable to the materials of current interest.

An approach which avoids these difficulties and yet begins to describe strong-coupling materials has been developed by Leplae[11] and used with good results by a few authors.[6,27,28] It is surprising that Leplae's method has received such little attention, especially in view of the limitations to the complete strong-coupling treatment. In Leplae's development σ_1^s (at $T=0$) is given by

$$\sigma_1^s(\omega,q)=\frac{1}{2\hbar\omega}\int_{\Delta}^{\hbar\omega-\Delta} dE\{[g(E,E')-1]\sigma_1^n(|\epsilon'|-|\epsilon|,q)+[g(E,E')+1]\sigma_1^n(|\epsilon'|+|\epsilon|,q)\}\,, \tag{1}$$

where

$$\begin{aligned} g(E,E')&=(EE'-\Delta^2)/|\epsilon\epsilon'|\,,\\ \epsilon^2&=E^2-\Delta^2\,,\\ \epsilon'^2&=E'^2-\Delta^2\,,\\ E'&=\hbar\omega-E\,. \end{aligned} \tag{2}$$

Here q is the radiation wave vector and $\sigma_1^n(\omega,q)$ is the real part of the normal-state conductivity. A Kramers-Kronig integration yields

$$\sigma_2^s(\omega,q)=\frac{2A}{\pi\omega}+\frac{2\omega}{\pi}\mathscr{P}\int_{0+}^{\infty} d\omega'\frac{\sigma_1^s(\omega',q)}{\omega^2-\omega'^2} \tag{3}$$

with A given by

$$A=\int_{0+}^{\infty} d\omega[\sigma_1^n(q,\omega)-\sigma_1^s(q,\omega)]\,. \tag{4}$$

A simple function to use for σ_1^n is the Drude form in the local limit

$$\sigma^n=\sigma_1^n+i\sigma_2^n=\frac{\sigma_0}{1+i\omega\tau}\,, \tag{5}$$

where σ_0 is the dc conductivity. This assumption worked well in explaining the earlier results in V_3Si. The MB theory in the extreme dirty limit gave too broad a curve width for T_s/T_n, but the inclusion of a finite τ gave a good fit except at low frequencies. Therefore, despite the strong-coupling nature of V_3Si ($2\Delta/k_BT_c=3.8$) a fit was possible without recourse to Nam's full strong-coupling treatment.

It is not obvious why the Leplae approach should be able to accommodate a strong-coupling system since it is derived within the framework of the BCS theory. It is helpful to observe that Leplae's development requires no statement concerning normal-state properties and requires only that the superconductivity be "BCS type." Leplae's method thus represents a way to consider systems whose normal-state behavior is dominated by strong-coupling effects[29] yet whose superconductivity is not. There is also evidence that at least in some appropriate limit the Leplae and Nam approaches give the same result, despite their conceptual differences. Our calculations show that both theories yield identical results for the sum rule strength A over the range $0.05 < \omega_g \tau < 10$ which includes all the previous V_3Si data and the NbN results presented here.

To show even more clearly that the Leplae method can successfully fit data for a very strongly coupled material, we examined Palmer and Tinkham's results for Pb. With the assumption of a Drude form for σ^n, it was possible to fit the T_s/T_n data very nearly as well as Nam did. The fit (shown in the Appendix) required a scattering time of 4.8×10^{-14} sec, a reasonable value for a pure metal film about 0.1 nm thick which is expected to be dominated by surface scattering effects.

There is thus ample evidence that the Leplae approach is a useful one for determining much about the optical properties of strong-coupling superconductors. This method promises a partial theory of the electromagnetic behavior of strong-coupling materials within the BCS framework but without the usual weak-coupling assumption $\lambda = N(0)V << 1$. That the Leplae method can be used for any value of λ is evident from the Bogoliubov-Valatin approach[30,31] to superconductivity. There the BCS problem is solved by exact diagonalization of the "model Hamiltonian" requiring no assumption on the strength of the pairing potential $V_{kk'}$ between time-reversed single-electron states. Upon diagonalization the usual assumption $V_{kk'} \rightarrow V$ is made for a limited energy range about the Fermi surface. The usual self-consistent gap equation is obtained which may be solved for $2\Delta(0)$ at $T=0$ and for $k_B T_c$ at $\Delta = 0$. If no restriction is placed on the magnitude of λ one obtains

$$\frac{2\Delta(0)}{k_B T_c} = \frac{3.53}{1 - e^{-2/\lambda}}, \quad \lambda > 0 \tag{6}$$

a result infrequently found in print. This equation gives the usual weak-coupling result $2\Delta(0)/k_B T_c = 3.53$ at small λ. For larger λ, $2\Delta(0)/k_B T_c$ becomes greater than 3.53, a standard indication of strong-coupling behavior. Hence, in principle, a Leplae analysis of materials with large values of $2\Delta(0)/k_B T_c$ is justified.

III. EXPERIMENT

The three samples denoted by A, B, and C were prepared at the Naval Research Laboratory by reactively sputtering NbN onto sapphire substrates 0.043-cm thick.[32] Their nominal film thicknesses d are given in Table I. The sheet resistance $R_\square$ $(= 1/\sigma_0 d)$ of the films was measured at 300 and 22 K using the standard van der Pauw method. As the samples were cooled, the resistance of the thickest film changed by less than 2% before going superconducting, while for the thinner films it increased to a peak value just before the transition. This is the same dc behavior seen by Gubser *et al.*[5]

TABLE I. Measured and derived parameters for the three NbN samples. All the quantities are defined in the text, except for f_{max}, the frequency at which the peak value $(T_s/T_n)_{max}$ occurs. The quoted values of 2Δ are the fit values slightly corrected to 0 K.

Sample	A	B	C
Experimental parameters			
d (nm)	100	30	20
$R_\square$ (300 K) (Ω)	8.0	52	65
$R_\square$ (22 K) (Ω)	8.0	79	87
T_c (K)	17	15	14
f_{max} (cm^{-1})	58	42	41
$(T_s/T_n)_{max}$	4.4	2.8	2.6
Derived parameters			
2Δ (meV)	6.45	5.00	4.89
τ (10^{-14} sec)	4.7	1.2	1.0
$\omega_g \tau$	0.46	0.09	0.07
$2\Delta/k_B T_c$	4.4	3.9	4.1

The values of the transition temperature T_c as determined by this measurement are given in Table I along with the measured values of $R_\square$. All the dc results for $R_\square$ and T_c (including the high value $T_c = 17$ K for the thickest sample) were closely confirmed by optical measurements to be described later.

The samples were pressed between 1-mm-thick indium sheets for good thermal contact and were mounted on a cold finger. The sample temperature was monitored by a Si diode sensor. The lowest attainable sample temperature was 4.5 K. A heater and temperature controller could maintain steady temperatures above this value.

A Grubb-Parsons Cube Interferometer was used to measure the sample transmission. Broadband radiation from the Hg arc was focused onto the 4-mm input aperture of the detector using a 7.6-cm-diam. mirror with a focal length of 20 cm. The sample was mounted in the converging beam 10 cm in front of the detector, a composite Si bolometer operating near 1.7 K. A cooled 100-cm^{-1} low-pass filter was inserted into the beam in front of the detector. Stray light as measured by blocking the sample aperture with an Al sheet was found to be only a few percent of the light transmitted in the normal state. This spectrometer system is sufficiently sensitive to measure a transmission of 0.001 (0.1%) through a 1-cm-diam. sample in the spectral range 20 – 95 cm^{-1}.

Double-sided interferograms were taken over a limited range of mirror travel in order to restrict spectral resolution to 11 cm^{-1}. This prevented the appearance of interference fringes (channel spectra)

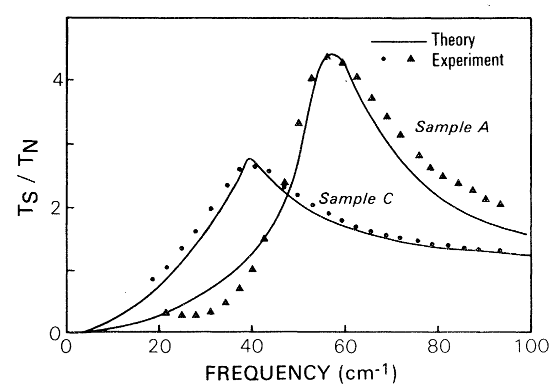

FIG. 1. Ratio of superconducting – to – normal-state transmission T_s/T_n vs frequency for two NbN films on sapphire substrates. The solid lines are the best fits derived from the Leplae theory, with the parameter values given in Table I.

from the sapphire substrates, but it eliminated the possibility of examining fine structure. Data acquisition and Fourier transformation were carried out by a dedicated microcomputer.[33]

Transmission spectra were taken at 4.5 K, well below the critical temperature for each sample. Upon heating, the transmission through each sample decreased gradually until it reached a plateau value. The temperature at which the plateau just began was taken as T_c. This agreed with T_c from the dc measurements to within 3%. Since the dc measurements were taken with the apertures on the heat shield surrounding the sample blocked off, external radiation was not a factor in heating the films above the temperature of the Si diode sensor. The spectra taken at 4.5 K were divided by those taken at 22 K to produce the ratio T_s/T_n shown in Fig. 1. This ratio tends to eliminate undesirable frequency dependent factors such as the beam-splitter characteristic of the spectrometer. As would be expected from the similarity in the $R_\square$ values, the results for samples B and C are virtually identical and only the data for C are shown for clarity. With its very different value of $R_\square$, sample A yields an entirely distinct curve as shown.

It was useful to separately measure T_n. To accomplish this the intensity transmitted through the sample at 22 K was ratioed against the intensity transmitted through the empty sample aperture. For the normal-state Drude model T_n should be constant or increase with frequency, depending on the value of τ. The observed T_n spectra were nearly flat but sloped in the wrong direction for explanation by the Drude model. Heating in the low-pass filter or in the detector due to the larger input from the reference beam could have been responsible for this discrepancy. The very-low-frequency results are independent of the conductivity model, and values of $R_\square$ (22 K) found from the zero-frequency intercept of T_n agreed with the dc values to within 3%.

IV. ANALYSIS AND DISCUSSION

The data in Fig. 1 were fitted by means of the Leplae equations (1) – (4), with σ_1^n taken in the local Drude form given by Eq. (5). σ_1^s and σ_2^s were calculated by computer as described elsewhere.[6] They were used in turn to calculate T_s/T_n according to the equation of Glover and Tinkham,[34] which averages over fringes as we did in our experiment. The calculation of transmission requires the sheet resistance, which we took as a nonadjustable parameter with the measured value $R_\square$ (22 K). The parameters 2Δ and τ were adjusted to give the best fit to the data.

It was impossible to make a remotely satisfactory fit for any of the samples under the dirty-limit assumption $\tau=0$, which gave low values for T_s/T_n. This deviation was especially striking for sample A, where the calculated peak height was only 2.8 as compared to a measured height of 4.4. The half-widths of the theoretical curves were also too large. The introduction of a finite τ improved the situation substantially. For samples B and C the fit became excellent, with some mismatch in the half-width which is more pronounced on the low-frequency side of the peak. For A it became possible to match the peak height and the agreement in half-widths improved, but there is a noticeable departure on both the low- and the high-frequency sides. The low-frequency deviation may be significant, since it was observed also in our fits to V_3Si and to Palmer and Tinkham's data for Pb.

The fit results for 2Δ and τ are given in Table I, as are the quantities $\omega_g\tau$ and $2\Delta/k_BT_c$. The typical uncertainty in the scattering time is 20%. The gap energy is determined largely by the clear-cut peak position and our determination of 2Δ carries an uncertainty of only 2%. As a result the uncertainty in $2\Delta/k_BT_c$ is only about 5%. The quantity $\omega_g\tau$ is a measure of the deviation from the dirty limit, and it is clear that, like V_3Si, the alloy NbN lies in an intermediate region between the extreme dirty and the extreme anomalous limits.

The results show that all the samples are in the strong-coupling regime. As expected the highest value of $2\Delta/k_BT_c$, 4.4 ± 0.2, occurs for the highest T_c, 17 K. Both numbers agree very well with the results of Saito *et al.*,[35] who found a maximum T_c of 17.3 K and whose data extrapolated to 17 K yields $2\Delta/k_BT_c=4.5$. The gap energy for sample C also agrees within experimental error with the results of Saito *et al.* at 14 K, while the energy for sample B is a few percent low.

Our values of τ reflect impurity scattering and perhaps surface scattering as well. They decrease with increasing dc resistivity as they should, and are comparable to values obtained from Leplae fits and an independent determination in V_3Si.[6] The scattering times also agree with values we obtain from the estimated dc resistivities, using the NbN Fermi velocity of 0.9×10^8 cm/sec found by Papaconstantopoulos[36] from an augmented-plane-wave (APW) band-structure calculation. They are, however, considerably larger than the values quoted by Hechler *et al.*[37] and Mathur *et al.*[38] for NbN films of about the same resistivities as ours. These numbers are derived from a carrier concentration nearly 100 times larger than the value implied by our results and those of Papaconstantopoulos. Since our values of τ are direct-fit parameters and involve no band-structure assumptions, they independently support the APW results. It is also possible, however, that both scattering and strong-coupling behavior must be invoked to fully understand our optical data. The inclusion of significant coupling effects would lower the fit values of τ.

V. CONCLUSIONS

Our analysis of homogeneous NbN has shown that the Leplae theory does well in fitting far-infrared data even in a very strongly coupled material. We obtained the correct gap energy for two of the three samples, and the very slightly low value for the third sample may represent a materials problem. Our fit values of τ agree with experimental values for another strong-coupled alloy superconductor and with a recent APW band-structure calculation. The fit to the thickest, most conductive sample is not ideal, but the fits to the more resistive samples are of good quality. The latter begin to be representative of granular NbN, and the Leplae method appears to provide an excellent starting point for further optical analysis of the granular system. Since $R_\square$, T_c, 2Δ, and τ can all be found optically without any dc data, such analysis gives a completely independent way to probe granular films.

The Leplae theory and Nam's full strong-coupling approach were almost equally successful in fitting T_s/T_n data, as was illustrated when both methods gave nearly the same quality of fit for Pb. The Leplae approach, however, is never quite as satisfactory on the low-frequency side of the peak. At frequencies below ω_g the transmission is determined by σ_2^s (since σ_1^s is zero) and the low-frequency deviations may represent integral strong-coupling effects. Thus for many alloy superconductors of current interest a full description of far-infrared behavior requires consideration of both strong-coupling and scattering effects. The Leplae theory alone, however, simply describes a large part of what is observed.

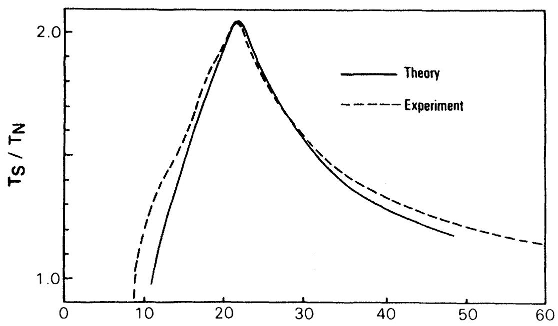

FIG. 2. Experimental values of T_s/T_n for Pb compared to the best fit from the Leplae theory. The dashed line is fitted by eye to the data of Palmer and Tinkham (Ref. 16). See Appendix.

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APPENDIX: LEPLAE FIT TO DATA FOR Pb

Figure 2 shows the best Leplae fit to Palmer and Tinkham's T_s/T_n data for a Pb film.[14] It was obtained using their experimental values $R_{\square}=252\Omega$ and $\omega_g=22.5$ cm^{-1}, and yields $\tau=4.8\times10^{-14}$ sec ($\omega_g\tau=0.2$). The goodness of the fit is comparable to that reported[14] for Nam's unpublished full strong-coupling calculation. This success suggests that transmission data in strong-coupling thin films cannot be fully understood without a consideration of scattering. A finite scattering time can influence the optical response of a superconductor as much as strong electron-phonon coupling does.

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