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Ultrasonic Evidence Against Multiple Energy Gaps in Superconducting Niobium

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The attenuation of longitudinal ultrasound along the [100] direction in Nb, resistivity ratio $R_{300}/R_0 = 5200$, has been measured with precision at low temperatures. The total attenuation in the normal state can be accurately deduced by a BCS calculation, with a single gap $2\Delta(0) = (3.52 \pm 0.02)kT_c$, from the measured superconducting attenuation. No experimental evidence has been found for the existence of either a smaller or a larger gap.

Suhl, Matthias, and Walker[1] extended the BCS theory of superconductivity to the case of two overlapping electron bands and suggested that this might apply to pure superconducting transition metals such as Nb. They postulated that each band could have distinct superconducting energy gaps and possibly different transition temperatures, depending on the strength of the interband and intraband couplings. Experimental evidence for two energy gaps in Nb came from the heat-capacity data of Shen, Senozan, and Phillips,[2] which were interpreted[3] in terms of a d-band gap $2\Delta_d(0) = 3.5kT_c$ and an s-band gap $2\Delta_s(0) = 0.32kT_c$. The ratio of the density of states at the Fermi level, N_s/N_d, depended on the purity of the sample and was 0.015 when the residual resistivity ratio (RRR) was 110. Direct evidence for the small energy gap has also come from tunneling experiments on pure Nb crystals. Hafstrom and MacVicar[4] deduced an energy gap $2\Delta(0) = 0.37kT_c$ from the tunneling characteristics along many directions (with the notable exception of the [100] direction). Thermal-conductivity measurements[5] on pure Nb were initially interpreted[5,6] on a two-gap model, but later data led Anderson, Satterthwaite, and Smith[7] to conclude that they provided no evidence for a second gap, and put an upper limit on $N_s/N_d \simeq 10^{-3}$ for a sample with an RRR of 2000.

Recently, ultrasonic attenuation measurements[8,9] on superconducting Nb have been analyzed in terms of a two-gap model. However, the energy gaps required to fit the data were quite different. At low temperatures the usual BCS gap $2\Delta_1(0) = 3.5kT_c$ applied, but near T_c a large gap $2\Delta_2(0) \simeq 10kT_c$ was used. This large gap was purity dependent, increasing as the sample RRR increased. These two gaps were associated by Lacy and Daniel[9] with the s and d bands, in contrast to the previous analyses,[3,4] where the s-band gap was very small. Here we report measurements of the electronic attenuation in the normal state, α_n, and in the superconducting state, α_s, of a very pure single crystal of Nb at low temperatures. We show that all the electronic attenuation is due to electrons with a BCS energy gap and find no evidence for either a very small or an anomalously large one.

The normalized electronic attenuation α_s/α_n is given in BCS theory by the well-known expression $2f(\Delta)$, where f is the Fermi function and $\Delta \equiv \Delta(T)$ is the temperature-dependent energy gap.

For $T_c/T > 3$, $\Delta(T)$ is independent of temperature and we deduce

$$\ln\alpha_s(T) = -\Delta(0)/kT + \ln 2\alpha_n. \quad (1)$$

At these low temperatures, therefore, measurements of only $\alpha_s(T)$ can be used to deduce *both* $\Delta(0)$ *and* α_n, the normal-state electronic attenuation due to excitations which have an energy gap $2\Delta(0)$ when in the superconducting state. In this temperature range α_s/α_n is very small, so that accurate measurements require a long, pure sample and high ultrasonic frequencies. Previous measurements in this temperature range have not been of sufficient accuracy for this analysis to be performed.

We used a Nb rod 10 mm long by 5 mm diam., cut from a single crystal[10] so that its axis was parallel to a $\langle 100\rangle$ direction. Its resistivity ratio $R_{300}/R_{9.3}$ was measured to be 2100, corresponding to $R_{300}/R_0 = 5200$. Longitudinal phonons were generated and detected by thin-film CdS transducers[11] grown on the polished end faces of the sample. The attenuation was measured using standard pulse-echo techniques. The sample was cooled in a glass ^{4}He cryostat for temperatures between 1 and 4.2 K and in a ^{3}He-^{4}He dilution refrigerator[12] for the range 0.15 to 1 K. An accuracy of ± 0.003 dB cm^{-1} in α_s was achieved by measuring the amplitude of echoes up to the eighth, relative to their amplitude in the temperature-independent region below 1 K, to ± 0.05 dB. The results at 365 MHz as a function of T_c/T are shown in Fig. 1.

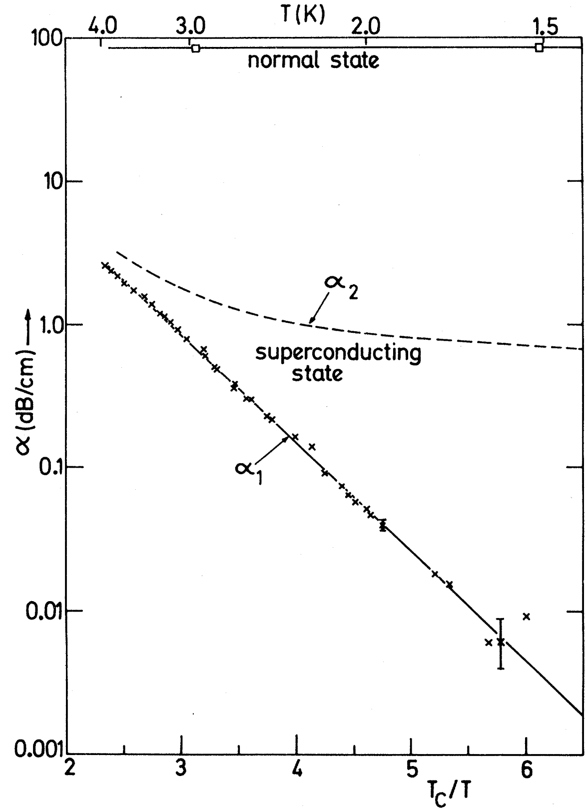

FIG. 1. Attenuation of 365-MHz longitudinal waves in normal Nb (squares) and superconducting Nb (crosses); RRR, 5200, $T_c = 9.25$ K, $q \parallel \langle 100\rangle$. Solid line, α_1, and dashed line, α_2, are theoretical curves from BCS theory, which for $T_c/T > 3$ are given by $\alpha_1 = 170/[\exp(1.76T_c/T)+1]$ and $\alpha_2 = \alpha_1 + (0.015\times 170)/[\exp(0.16T_c/T)+1]$. The experimental points show no evidence of the smaller energy gap.

The superconducting energy gap that fits our data (line marked α_1 in Fig. 1) is $2\Delta(0) = (3.52 \pm 0.02)kT_c$, in agreement with that found previously[13] on a less pure sample and in reasonable agreement with an extrapolation of the results by Lacy and Daniel,[9] for propagation along the [100] direction. With the use of Eq. (1) the corresponding value of α_n is derived to be 85 ± 2 dB cm^{-1} for $T < 3$ K. Direct measurements of the total electronic attenuation in this region in the normal state were made by applying a magnetic field greater than $H_{c2} = 0.27$ T parallel to the direction of sound propagation. Longitudinal magnetoacoustic effects in Nb are small, and by measuring the attenuation as a function of frequency and magnetic field, we found that the total normal-state attenuation was 85 ± 2 dB cm^{-1} at 365 MHz in our sample and was independent of temperature below 3 K. Thus, *all* the electronic attenuation measured at this frequency can be accurately deduced from the measured superconducting attenuation at low temperatures by a BCS calculation with a single gap $2\Delta(0) = 3.52kT_c$.

Fal'ko[14] has suggested that for a two-band superconductor the attenuation in the superconducting state is of the form

$$\alpha_2 = 2\alpha_n^1 f(\Delta_1) + 2\alpha_n^2 f(\Delta_2), \quad (2)$$

where α_n^1 is the normal-state attenuation due to electrons which have the energy gap Δ_1 when superconducting. From this we can estimate the magnitude of the ultrasonic attenuation α_2 that might be expected if 0.015 of the electrons in niobium has an energy gap $2\Delta(0) = 0.32kT_c$ as suggested by the specific-heat[2] and tunneling[4] data. We assume, as found by Hafstrom and MacVicar,[4] that this small gap is temperature independent below 4.2 K. There is no simple relation between the density of states and the electronic attenuation, unless the relevant Fermi surface geometry is known. Acoustic phonons of wave number q interact most strongly with electrons (of mean free path l) moving perpendicular to the sound propagation direction on an "effective zone" when $ql \gg 1$. We estimate that $ql = 6.8 \pm 0.5$ at low temperatures, for 365-MHz phonons in our sample; the effective electrons are those moving perpendicular to the [100] direction, whereas in tunneling measurements the electrons sampled are those moving parallel to the tunneling direction. This effective zone includes many orientations along which the small energy gap was observed by tunneling, including the [011] direction. On the Fermi surface of Nb computed by Mattheiss,[15] the most unusual group of electrons lie on the ΓN line ($\langle 011 \rangle$ direction) and are included in our effective zone. These electrons have very low velocities and so might be expected to contribute significantly to the attenuation. Therefore, the small-gap electrons previously proposed ought to contribute to the attenuation of longitudinal ultrasound propagating along the [100] direction in niobium.

The simplest assumption is that these electrons contribute 0.015 of the electronic attenuation in the normal state. Hence from Eq. (2)

$$\alpha_2 = \frac{2\alpha_n}{\exp(1.76T_c/T)+1} + \frac{0.015\times 2\alpha_n}{\exp(0.16T_c/T)+1}, \qquad (3)$$

as shown in Fig. 1. It is obvious that attenuation of this magnitude would easily have been detected. The amplitude of the eighth echo at 365 MHz was monitored down to 0.15 K, but it changed by less than 0.05 dB between 1.2 and 0.15 K. Since the total normal electronic attenuation at 0 K in the eighth echo is estimated as 1380 ± 25 dB, we can conclude that if electrons with a small gap exist in pure Nb, they are responsible for less than 10^{-4} of the normal electronic attenuation of longitudinal phonons propagating along the [100] direction. If it is further assumed that the normal-state electrons associated with the two gaps contribute the same acoustic attenuation per electron, we can deduce an upper limit of 10^{-4} for N_s/N_d. We conclude that if this small energy gap exists, we should have been able to detect it, and that its absence reinforces the conclusion of Anderson, Satterthwaite, and Smith[7] from thermal-conductivity data that a single-gap model satisfactorily accounts for the superconducting state of Nb.

Near T_c, several authors[8,9,13] have observed large deviations from the BCS temperature dependence. Lacy and Daniel[9] have recently interpreted such deviations in Nb with an RRR of 6500 on a two-gap model with 25% of the attenuation from electrons with a gap $2\Delta(0) = 3.5T_c$ and 75% from electrons with a gap $2\Delta(0) = 10kT_c$. The temperature variation of the attenuation was independent of ql, for $ql \lesssim 1$, and, for this two-gap model, should persist for $ql > 1$. Similar deviations from BCS behavior near T_c have been found in Tl,[16] Pb,[17] and Hg,[18] which are all, like Nb, superconductors for which $T_c/\Theta > 0.02$. When ultrasonic measurements of α_s are made near T_c in these superconductors with $ql < 1$, the deviations from BCS can be due to different phonon-limited free paths in the normal and superconducting states.[17] On the other hand, when $ql \gg 1$, the attenuation is independent of l, yet the data on Hg in this region show clearly that these deviations are still large. Our measurements on Nb show that, within our experimental error of 3%, all the electronic attenuation at low temperatures can be accounted for by a BCS calculation with a single gap $2\Delta(0) = 3.52kT_c$, for $ql = 6.8$. Thus if any electrons have a large gap, $2\Delta(0) \sim 10kT_c$, in Nb they are responsible for less than 3×10^{-2} of the normal electronic attenuation of longitudinal phonons propagating along the [100] direction. Following the assumptions made in the discussion on the small gap, we suggest an upper limit of 3×10^{-2} for the relative density of states of electrons with a very large energy gap. Hence, any deviations from BCS behavior near T_c when $ql \gtrsim 1$ in Nb, like those in Hg, require a further refinement of the theory for their explanation and cannot be attributed to the presence of exceptionally large energy gaps.

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Nonlinear Response in the Metallic Field Effect*

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We observe that charging the interface of a silver film on mica at a frequency ω modulates the conductance of the film at both ω and 2ω. Relative magnitudes and phases of the observed modulations, and their dependence on a superimposed dc charge, are consistent with a field-effect model assuming scattering of conduction electrons by surface charges, if the latter occur in patches that scatter the electrons coherently.

Recently, Berman and Juretschke[1] concluded that the metallic field effect in thin films of silver on mica results from the change of scattering of conduction electrons at the silver-mica interface caused by the applied surface charge. Surface scattering by localized charges should give a field effect proportional to Nz^2, where N is the number of scattering centers and z is the number of elementary charges of each center. The observed field effect $\delta\Sigma/\delta q$ in silver is negative and reverses with the sign of the applied charge. This behavior implies that for scattering of conduction electrons the silver-mica interface appears normally positively charged and to a level much larger than the charge that can be applied externally. The experiment also indicated that the normally present positive charge increases with increasing temperature.[2]

Further experiments[3] on the same system have provided the following new information:

(1) A field voltage $V_1(\omega)$ at frequency ω produces field-effect signals at ω and 2ω for frequencies ω around a few hundred hertz.

(2) The field-effect signal at ω is proportional to V_1. The signal at 2ω is proportional to V_1^2, and 90° out of phase.

(3) At a given temperature, a dc field voltage V_0 superimposed on $V_1(\omega)$ causes a linear change in the amplitude of the field effect signal at ω, but has no effect on the second-harmonic amplitude. A positive dc bias increases the field-effect amplitude.

(4) The response to dc bias is slow and equilibrium may be reached only after several minutes.

These facts support our basic interpretation of the metallic field effect. Furthermore, they allow identifying some specific aspects of the operative mechanism.

Surface scattering by charged centers can give rise to harmonics in the conductance Σ in two simple ways. First of all, surface charging can change N. Since N is always positive, harmonics are generated if the ac amplitude sweeps through the condition corresponding to a neutral surface. Alternatively, harmonics appear if the applied ac charge changes the occupation z of each center while N stays fixed. In this case we expect a change of conductance of the sample

$$\delta\Sigma \propto -N(z_0+z_1\sin\omega t)^2+Nz_0^2 = -2Nz_0z_1\sin\omega t+\tfrac{1}{2}Nz_1^2(\cos 2\omega t-1), \qquad (1)$$

where the ac and dc charges per unit surface are Nez_1 and Nez_0, respectively. Equation (1) has all the dependences listed above under observations (1) and (2). Furthermore, it predicts that the fundamental signal amplitude varies linearly with V_0 (or z_0) while the second-harmonic amplitude is