Does Strong-Coupling Theory Describe Superconducting Nb?*

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(Received 9 December 1975)

The electron-coupled phonon spectrum $\alpha^2 F$, λ, and μ^* have been determined for polycrystalline and high-purity, single-crystal niobium from tunnel junctions fabricated with three different counterelectrodes. All spectra compare well with phonon spectra extracted from neutron-scattering experiments. Values of λ are BCS-like and μ^* is always negative. Computer-modeling studies describing a niobiumlike material cannot generate an acceptable set of strong-coupling parameters.

Tunneling data determine directly the superconducting zero-frequency energy-gap edge Δ_0 and the tunneling density of states $N(E)$.[1] Fine structure in the conductance characteristics of the junction is a direct reflection of the electron-coupled phonon spectrum, $\alpha^2(\omega)F(\omega)$, of the superconductor.[2] The equations of the strong-coupling theory of superconductivity, combined with the tunneling characteristics, can be used[1,3] to obtain $\alpha^2 F$ and its associated parameters λ and μ^*.

For all simple metals and alloys studied so far,[4] self-consistency of the microsopic parameters and their agreement with the predictions of theory show that only the electron-phonon and Coulomb interactions are required to explain superconductivity.[5] Few tunneling experiments have been carried out on transition-metal compounds,[6,7] however, and most of these results have been difficult to reconcile with theory. The present analysis of both single-crystal and polycrystalline Nb tunnel junctions indicates that, in fact, strong-coupling theory, as currently formulated and which describes quite well effectively isotropic one-band materials, is not adequate for describing Nb and Nb-based *d*-band materials.

The tunnel-junction substrates used in this investigation were of two types: single-crystal Nb and polycrystalline Nb rods. The single crystals were $\frac{1}{8}$ in. in diameter, electron-beam zone grown in ultrahigh vacuum at 10^{-9} Torr. Resistivity ratios varied from 485 to 185. Each crystal was thermally oxidized *in situ*, sectioned, and masked; Au, In, or Pb thin-film counterelectrodes were then evaporated in the conventional manner. Junction resistances were 5–100 Ω. For comparison, some of the single-crystal substrates were acid etched and acid oxidized. Data from these samples were indistinguishable from those of thermally oxidized samples. The implication of this result is that no significant contamination layer caused by adsorption of residual gases from the vacuum exists on the surface of the as-grown Nb crystal.[7]

The polycrystalline Nb samples were made from commercially pure Nb rod which had been outgassed and annealed. The resistivity ratio was approximately 60. These substrates were acid etched and acid oxidized before In counterelectrode evaporation. Except for a slight increase in oxygen content (300 ppm) these samples had the same purity as the single crystals.

The sum-gap edge and the normalized first derivative of the junction I-V characteristic, from a junction bias just above the sum-gap bias to an energy greater than that of the maximum phonon-related structure, were experimentally determined.[8,9] Conventional modulation techniques[10] using an ac bridge circuit were used to measure conductance in the superconducting and normal states. Measurements from a polycrystalline-Nb–In junction are shown in Fig. 1. These data are typical of those obtained from all samples.

The normalized conductance data were used as a comparison data set for the inversion routines described by McMillan and Rowell.[1-3] The essence of the procedure is that a functional form for $\alpha^2 F$ and a value for μ^* are assumed, and then a (dI/dV)-V characteristic is calculated for comparison with the experimental data set. The mismatch between the two is used to correct the guess for the functional form of $\alpha^2 F$. After the first iteration in the numerical analysis the value of μ^* is obtained by balancing the attractive interaction represented by $\alpha^2 F$ (or λ) by the mutual repulsion represented by μ^* in such a way that the zero-frequency gap function Δ (Δ_0) equals the experimental value Δ_0. This procedure is continued until the assumed solution ($\alpha^2 F, \mu^*$) predicts a conductance characteristic with the same slope as

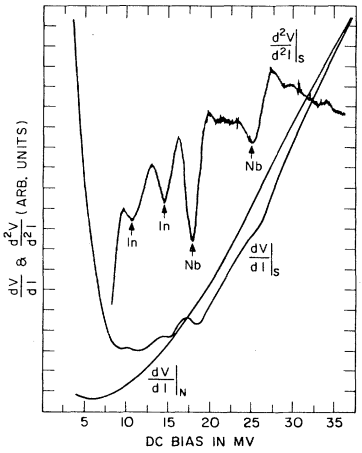

FIG. 1. Tunneling characteristics from an annealed polycrystalline-Nb–In junction of area 0.3 mm^2, Δ_{Nb} = 1.51 meV, Δ_{In} = 0.55 meV, Nb resistivity ratio of 57, and T_c of 9.05 K. (The second derivative in the normal state, not shown, is a smooth parabolic curve following the general shape of the superconducting d^2I/dV^2 curve shown. Such a shape could be indicative of up-to-now unidentified normal-state emission processes in Nb.)

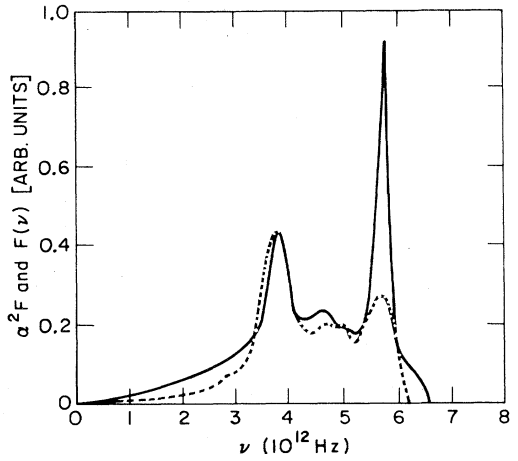

FIG. 2. Comparison of $\alpha^2(\omega)F(\omega)$ from a polycrystalline-Nb–In junction (---) with $F(\omega)$ from neutron scattering (——) (Ref. 13). (The heights of the two spectra at the transverse peak are arbitrarily set equal.)

the experimental data set. This solution is also self-consistent.

It is commonly believed that when very reasonable values of μ^* (~0.1–0.2) are obtained, the junction data are of high quality.[1,6,7,11] In cases where λ and μ^* are not those predicted by theory,[5] it has been thought that the data were not representative of the bulk material[11] (which has often been the case[1,6,7]). However, if an (additional) attractive coupling mechanism were partially responsible for the superconductivity in a material, phonon structures in the tunneling characteristics would be too weak to give a correct value for Δ_0 and the computer code would compensate by adjusting μ^* and/or λ to anomalously low values.[12] Similarly, if the equations derived in the Eliashberg theory are too oversimplified to handle differences in coupling due to localized electrons, values of λ and μ^* could easily be anomalous because the deconvolution is specifically designed for an effectively isotropic single-band material.

Electron-coupled phonon spectra typical of the Nb junctions investigated are plotted in Figs. 2 and 3 for In counterelectrodes. A comparison of α^2F and the neutron-scattering spectrum from polycrystalline Nb at room temperature[13] is shown in Fig. 2. Their agreement is striking; only the longitudinal peak heights are different. Although suppression of the longitudinal peak of α^2F has often been observed even in the simple metals,[1,4,11] for Nb there is a one-to-one correspondence between α^2F and the phonon spectrum right up to the peak position where the tunneling spectrum falls off sharply. Two typical spectra deduced from single-crystal junctions are given in Fig. 3. Spectra, irrespective of counterelectrode, were found to overlie one another with only minor differences in longitudinal peak height and shoulder structure.[14]

Although the shape of α^2F is clearly accurate, the values of λ and μ^* associated with these α^2F

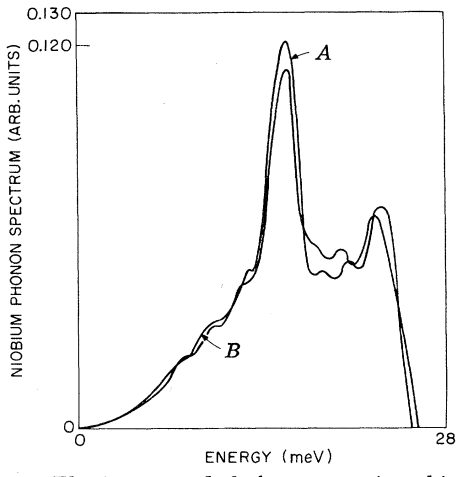

FIG. 3. Electron-coupled phonon spectra obtained from two different single-crystal-Nb–In junctions (areas ~0.5 mm^2). The measured T_c of both crystals was 9.22 K; the resistivity ratio of sample *A* was 483; of sample *B*, 186.

are in total disagreement with theoretical predictions[5,15]: typically, $\mu^* = -0.11$ and $\lambda = 0.39$, compared to the theoretical values of $+0.13$ and 0.82, respectively. In fact, a negative μ^* has no meaning within the strong-coupling theory unless it is taken to mean either that there exists some other attractive electron interaction besides electron-phonon coupling,[12] or that theory is inadequate to explain simultaneously the weak phonon structure and a high gap value (1.56 meV for Nb).

In order to determine if low-bias data inaccuracy was the cause of these anomalous values of μ^* and λ, careful measurements from 2 meV above the gap edge outward were made on a single-crystal-Nb–Au junction. Although the normalized conductance data varied only slightly from those previously taken from 3 to 5 meV (far below structure in α^2F for Nb), μ^* was raised by only $+0.02$ and λ increased by only 0.05.[16] Thus, even by extending that data set to very low biases, it is clear that μ^* will never become positive. A second approach to "improving" the values of λ and μ^* is to lower the gap value. To obtain a value of μ^* comparable to theory by varying the gap of Nb, Δ_0 has to be lowered to ~ 1.3 meV from the experimentally determined value of 1.56 meV; even then, λ is far too small (~ 0.75) compared to theoretical predictions.

Although acid-etch treatment of the Nb junctions indicated that no contamination existed at the surface, and the good agreement of α^2F with neutron-scattering data reinforces this conclusion, a more explicit means of determining if there was a surface problem is to amplify artificially the observed tunneling structures and deconvolute the resulting data set. Various amplification techniques were applied to the single-crystal-Nb–Au conductance data. In all cases, as μ^* increased toward theoretically acceptable values, λ grew to a value of 2 or greater, and the associated T_c values grew to values between 15 and 27 K.[5,17] In fact no amount of "playing" with the Nb experimental data set reproduced currently accepted values for the microscopic parameters of Nb.

In order to understand more clearly the related behaviors of λ and μ^* as a function of α^2F for a given Nb gap edge, computer modeling studies were carried out. Three different spectral shapes for α^2F were assumed (double Gaussians as in the Nakagawa-Woods spectrum, an equal-peaked spectrum, and the experimentally observed spectrum) and μ^* was set at various values; the resulting λ and T_c were then calculated. Surprisingly, as μ^* varies from $+0.15$ to -0.11, T_c goes through a maximum for all three shapes while λ steadily decreases. For $\mu^* = -0.11$, all models yield a calculated T_c close to that for Nb. When μ^* is positive and ~ 0.15, only the Nakagawa-Woods spectrum reproduces McMillan's original calculation; the other spectra require λ between 1.5 and 2.0 to obtain a T_c close to 9.2 K. The structures in the experimental density of states are compatible only with the model spectrum based on the deconvoluted spectra shown in Fig. 3.

Although the junctions in this investigation are still not perfect, they are clearly of a previously unobtained high quality. Fifteen junctions having either polycrystalline or single-crystal Nb substrates with three different counterelectrodes give similar Nb electron-coupled phonon spectra. Careful and accurate measurements of the superconducting density of states near the Nb gap edge indicate that the values of λ and μ^* characteristic of these junctions are ~ 0.58 and -0.05, respectively.[15] Considering the quality of the experimental data, the results of computer modeling, and the agreement between tunnel-junction and neutron-scattering phonon spectra, it appears that the currently accepted formalism for strong-coupling superconductivity is inadequate for describing Nb.

We would like to thank Mr. Keith Milkove for valuable assistance in the tunneling measurements and Dr. W. L. McMillan for stimulating conversation.

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*This work supported by U. S. Army Research Office (Durham), Advanced Research Projects Agency, and U. S. Office of Naval Research.

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[1]W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), p. 561.

[2]J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Lett. 10, 336 (1963); D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. 148, 263 (1966).

[3]W. Hubin, Department of Physics, University of Illinois at Urbana, Technical Report No. 182, 1970 (unpublished). This program has been modified to accept data from all types of junctions including those having strong-coupling superconductors on both sides of the barrier. Data from the following papers were used to

debug the final inversion algorithms: J. M. Rowell, W. L. McMillan, and R. C. Dynes, "A Tabulation of the Electron-Phonon Interaction in Superconducting Metals and Alloys: Part I" (unpublished); R. C. Dynes, Solid State Commun. 10, 615 (1972); P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).

[4]Rowell, McMillan, Dynes, Ref. 4; Dynes, Ref. 4; Allen and Dynes, Ref. 4.

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[6]L. Y. L. Shen, Phys. Rev. Lett. 24, 1104 (1970).

[7]L. Y. L. Shen, *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass, AIP Conference Proceedings No. 4 (American Institute of Physics, New York, 1972), p. 31, and Phys. Rev. Lett. 29, 1082 (1972); L. F. Lou and W. J. Tomasch, Phys. Rev. Lett. 29, 858 (1972).

[8]M. H. Frommer, J. Bostock, K. Agyeman, R. M. Rose, and M. L. A. MacVicar, Solid State Commun. 13, 1357 (1973); J. Bostock, Kofi Agyeman, M. H. Frommer, and M. L. A. MacVicar, J. Appl. Phys. 44, 5567 (1973).

[9]The bias region just above the sum gap determines the low-energy region of α^2F which strongly affects the determination of λ and $\langle\omega\rangle$, the average phonon frequency of α^2F. If this region is not accurate, although the general shape of α^2F may be correct, the numbers representing μ^*, λ, and $\langle\omega\rangle$ may not be representative.

[10]R. V. Coleman, R. C. Morris, and J. E. Christopher, in *Methods of Experimental Phyiscs*, edited by R. V. Coleman (Academic, New York, 1974), Vol. 11.

[11]J. M. Rowell, W. L. McMillan, and W. L. Feldman, Phys. Rev. B 3, 4065 (1971); R. C. Dynes and J. M. Rowell, Phys. Rev. 187, 821 (1969).

[12]There is no *absolute* way to determine whether the junction is, with anomalous values of λ and μ^*, dirty and/or contaminated or whether there is a second attractive mechanism operating in the material being investigated.

[13]Y. Nakagawa and A. D. B. Woods, Phys. Rev. Lett. 11, 271 (1963).

[14]Single-crystal junctions: three Nb-Au, one Nb-Pb, and eight Nb-In. For the polycrystalline rods, three Nb-In junctions.

[15]Shen, Ref. 7, also reports a negative μ^* for preliminary data on Nb junctions.

[16]A comparison study of Al-In data versus Nb-In data showed that equally small changes in the In density of states in the region between 2 and 4 meV resulted in a change of μ^* from 0.116 ($\lambda = 0.81$) to 0.51 ($\lambda = 0.66$). Such high sensitivity of the program renders absolute numbers obtained in any study almost meaningless; only the positive or negative character has significance.

[17]Since the experimental values of λ and μ^* are determined from a self-consistent colution, it is almost guaranteed that the calculated T_c agrees with the measured T_c (as it does). Agreement of T_c values is *not* a sufficient condition for the uniqueness of the solution; it is only a manifestation of self-consistency.

Magnetoelastic Excitations in Single-Crystal Gadolinium*

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(Received 24 November 1975)

We show that parallel static and rf magnetic fields applied in the basal plane of single-crystal gadolinium samples excite phonons having a frequency equal to that of the rf field. These results, including measurements of the phonon signal as a function of angle between the rf and dc fields and as a function of the power input to the cavity, are shown to be inconsistent with current magnetoelastic theory.

A tunable spin-phonon spectrometer[1] has been used to investigate the excitation of microwave (10–24 GHz) phonons in single crystals of gadolinium. Gd single-crystal c-plane disks with diameters of 2–3 mm and thicknesses of 20–50 μm were polished, and bonded to one end of the phonon detector, a rectangular rod of SrF_2 doped with Tm^{++}. The c axis of the Gd crystal was parallel to the axis of the detector. The ground state of Tm^{++} in SrF_2 is a Kramers doublet with an effective g factor of 3.445. At sufficiently low temperatures, the dominant relaxation mechanism is a one-phonon process. Therefore, if a static magnetic field (2–5 kOe for these experiments) is used to tune the doublet's splitting to the frequency of the phonons present, the phonons will be resonantly absorbed. Resonant absorption of the phonons perturbs the population levels of the Tm^{++} ground state. The difference in population of the levels is monitored using an optical technique which exploits the strong paramagnetic circular dichroism exhibited by the Tm^{++}-SrF_2 system. The Gd crystal-detector system is placed at the bottom center of a TE_{101} cavity with the appropriate detector shielding, and the whole assembly is immersed in a liquid helium bath. In the experiment, the angle between the rf and static magnetic fields applied in the c plane was varied from 0 to $\pi/2$. Phonons propagating along the c axis at the rf angular frequency, ω, were