Distribution of the Energy Gap in k Space for Superconducting Nb†

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Examination of available tunneling data from junctions oriented on single-crystal niobium shows that the observed superconducting energy gap values are grouped nonrandomly in k space. These groupings are consistent with a relationship between $\Delta_{(k)}$ and Fermi-surface topology, but also suggest a significant role for phonon anisotropy.

I. INTRODUCTION

The possibility of a relation between the superconducting energy gap of a material and singularities of its Fermi surface was proposed by Zavaritskii.[1] The constant $\Delta_{(k)}$ surfaces which he was able to construct from detailed tunneling data obtained on single crystals of tin[1,2] were often similar to parts of the tin Fermi surface constructed according to the nearly free-electron model. $\Delta_{(k)}$ surfaces which differed markedly from this model could be matched with similar results from experimental studies of the tin Fermi surface. The totality of experimental data available to Zavaritskii did not contradict his hypothesis that a direct connection exists between the anisotropies of Δ and special characteristics of the Fermi surface.

We have previously reported anisotropy of Δ in pure single crystals of niobium, using fabrication procedures similar to those described below.[3] Although study of the superconducting energy gap of niobium had been undertaken by several methods including ultrasonic attenuation,[4,5] infrared absorption,[6] calorimetry,[7–9] and electron tunneling,[10–12] only the latter offered a direct way to observe $\Delta_{(k)\mathrm{Nb}}$ since the tunneling currents of junctions prepared on single crystals are particularly sensitive to crystallographic orientation. In conjunction with new data recently obtained in our laboratory,[13,14] it is fruitful now to examine the distribution in k space of niobium tunneling energy gap values, looking for large regions of constant Δ. If such regions exist, and we can relate them to features of the Fermi surface of niobium, then we have serious evidence that the behavior of Δ derives directly from consideration of the band structure of our material. A prohibitively great number of data would be necessary actually to map constant-Δ regions in detail. However, our limited data are able to show qualitative features of such regions and their boundaries.

It is not clear *a priori* that Zavaritskii's hypothesis should be valid for niobium, since niobium is a transition metal type-II superconductor, having an increased electron-phonon coupling compared to that of tin, a type-I superconductor. According to Bennett,[15] the energy gap of a non-weakly coupled superconductor may be heavily influenced in its crystallographic behavior by the superconductor's phonon spectrum. For the strongly coupled superconductors, particularly lead and mercury, in fact, Bennett believes that the most important source of energy gap anisotropy is the anisotropy in the phonon spectrum of the superconductor.

II. NIOBIUM'S FERMI SURFACE

Mattheiss has recently calculated the niobium Fermi surface using an augmented-plane-wave method.[16] The main features of this Fermi-surface model are shown in Fig. 1. This model is very similar to that calculated earlier for vanadium-group transition metals,[17] which has been found to be in good agreement with experimental results from de Haas–van Alphen[18] and galvomagnetic[19] measurements on niobium single crystals.

Niobium is bcc and has five conduction electrons which fill all of the first conduction band, most of the second (except for the closed hole sheet shown centered at Γ), and some of the third (shown as a hole ellipsoidal region centered at N, and as a multiply connected "jungle gym" hole sheet run-

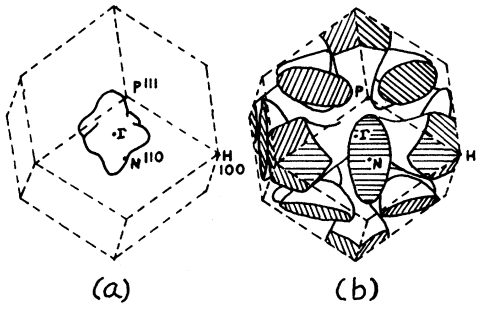

FIG. 1. Calculated Fermi surface of niobium after Mattheiss: (a) a closed hole sheet which is the second zone, centered at Γ; (b) closed hole pockets centered at N, and open hole sheets down arms toward H, making up the third zone.

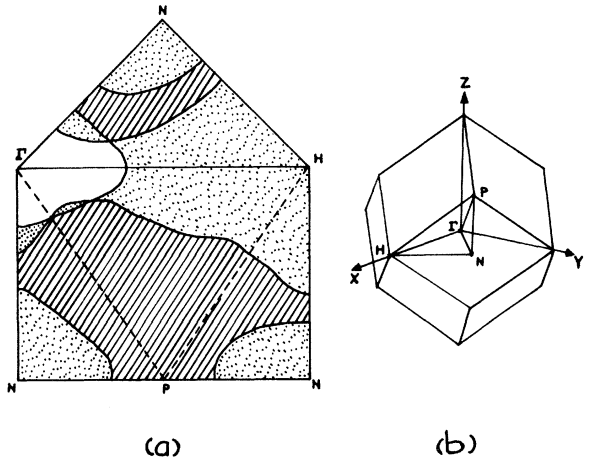

FIG. 2. (a) Central section of the calculated Fermi surface of niobium, after Mattheiss: the clear space corresponds to the second zone, the cross-hatched regions to the third zone, as in Fig. 1. (b) Conventionally labeled bcc Brillouin zone, where $\bar{\Gamma}H = \langle 100\rangle$, $\bar{\Gamma}P = \langle 111\rangle$, and $\bar{\Gamma}N = \langle 110\rangle$.

ning from Γ to H). A central cross section of the Fermi surface is shown in Fig. 2 alongside a conventionally labeled bcc Brillouin zone.

III. EXPERIMENT AND PROCEDURE

A. Junction Fabrication and Testing

The junctions were fabricated on clean[20] single crystals of niobium grown in ultrahigh vacua. Tunneling barriers were introduced on the cylindrical crystals by thermal oxidation, glow discharge oxidation, and amorphous carbon techniques. The crystals were then suitably masked with Formvar to aid subsequent electrical connections, and a second electrode evaporated as a narrow amorphous stripe down the crystal to form Nb-I-In junctions. A detailed account of the fabrication procedure is given elsewhere.[3,13,21,22]

Current-voltage characteristics and (dI/dV)-voltage curves were taken on the junctions using conventional dc and ac techniques in conjunction with an x-y recorder. Cryostat temperatures were usually 0.9 K, measured by a carbon resistor.

B. Data and Analysing

Determination of niobium energy gap values proceeded from analysis of the conductance sum peaks $[\Delta_{(k)\mathrm{Nb}} + \Delta^*]$, where Δ^* was the energy gap of the second electrode empirically determined from bias voltages of multiple-particle tunneling events.[23]

Sometimes nonuniform peaking was observed in the conductance peak. Such "wings" on $[\Delta_{(k)\mathrm{Nb}} + \Delta^*]$, or multiple maxima, were taken as evidence that more than one value of $\Delta_{(k)}$ contributes to tunneling current. Relative heights of the maxima are, thus, a measure of the significance of each contribution.[1] Analysis used only the absolute maximum in the peak as a reference bias.

IV. RESULTS AND DISCUSSION

A. Distribution of $\Delta_{(k)}$

The orientations of all junctions used in this study are plotted in the standard stereographic triangle shown in Fig. 3(a).

Let us consider junction orientations where $\Delta_{(k)}$ falls into certain ranges of magnitude, as shown in Figs. 3(b)–3(g). We wish to compare these distributions to Mattheiss's Fermi-surface model. The mean value of $\Delta_{(k)}$ is 3.10 meV, which is also

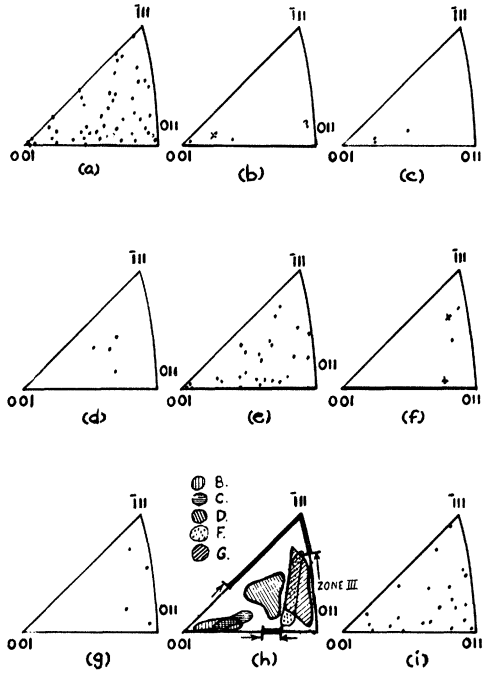

FIG. 3. (a) Stereographic plot of the total number of junction orientations in this study; (b) orientations of junctions with gap values: plus denotes 2.82±0.02; dot denotes 2.98±0.02; question mark denotes 2.94±0.02 meV; (c) orientations with gap values 3.02±0.02 meV; (d) orientations with gap values 3.06±0.02 meV; (e) orientations with gap values 3.10±0.02 meV; (f) orientations with gap values: dot denotes 3.14±0.02; plus denotes 3.18±0.02 meV; (g) orientations with gap values 3.22±0.02 meV; (h) schematic of constant gap value regions superimposed on approximated regions of Mattheiss's central section of niobium Fermi surface; (i) orientation of junctions exhibiting "second gap" structure.

that value of gap most commonly observed. (Gap values are known to ±0.02 meV.)

The extent of $\Delta_{(k)}$ greater than 3.10+0.02 meV shows a tendency to run parallel to the ⟨111⟩-⟨011⟩ side of the stereographic triangle. Gap values less than 3.06−0.02 meV are prevalent across the ⟨001⟩-⟨011⟩ side, toward ⟨100⟩, while a clustering of $\Delta_{(k)}$ values equal to 3.06±0.02 meV occurs in the middle of the triangle. A smattering of Δ = 3.10±0.02 meV occurs across all regions.

B. Comparison to the Fermi Surface

Coming across the Fermi surface from $\vec{H}$ (⟨100⟩), to N (⟨110⟩), in Fig. 2(a), we trace a path from the "jungle gym" sheet of the third zone, to the closed, distorted ellipsoidal region which is also part of this zone. In doing so, we pass through an electron region. The sheet boundaries we cross on this path, and on paths from P to N and H to P, are shown in Fig. 3(h). The well below the mean values of Δ_{Nb} falling within a region close to ⟨100⟩ seem to have a boundary corresponding roughly to the edge of the jungle gym sheet.

Values of Δ_{Nb} in the irregularly shaped cluster central in the triangle are greater than the above values, but are still below the mean value. A boundary appears to exist between this cluster and the third zone, consistent with estimated third zone edges. The above the mean gap values running upwards from ⟨001⟩ to ⟨111⟩ seem to fall within a region of k space marked out by the closed, ellipsoidal surfaces of the third zone. We expect from Zavaritskii[1,2] that Δ values observed from orientations in regions of k space corresponding to the same zone should exhibit identical values of Δ. Thus, the appearance of below-average values near H, and that of above-average values near N are perhaps puzzling since both regions comprise the third zone. Possible anisotropy in the phonon coupling, however, might allow $\Delta_{(k)}$ to vary as observed. This would mean that a significant difference in the phonon spectrum of Nb exists between ⟨100⟩ and ⟨110⟩, stronger coupling being along ⟨110⟩.

C. Second Gap, Δ'

Figure 3(i) shows the k-space distribution of junction orientations which exhibited a low bias structure implying the existence of a secondary energy gap in niobium. This gap has been studied by Hafstrom,[13,14] and behavior indicative of its existence noted by several investigators.[7,24–27]

No anisotropy was observed in these values; their magnitudes are all ~ $\Delta_{Nb}/10$. In comparing Fig. 3(i) to Fig. 3(a), we see a higher density of points corresponding to Δ' occurring in the region near ⟨110⟩ than we might expect from a random sampling of the total distribution of orientations tested. The boundary to this density of Δ' points near ⟨110⟩ roughly corresponds to the closed, ellipsoidal sheet of the third zone centered at N.

Considerations of the band structure lead us to the expectation that Δ' should not exist at H, while conditions of band overlap are favorable for existence at N and P. The data to date are ambiguous in supporting these expectations. However, the operation of a compromising influence such as phonon anisotropy may explain the observation of $\Delta'_{(k)}$.

V. CONCLUSIONS AND COMMENT

It is clear that groupings of Δ values of niobium do exist in k space, and that these groupings are suggestive of known Fermi-surface topology. It would be meaningful to investigate the existence and extent of any anisotropy of the Nb phonon spectrum, since we expect that an anisotropy does exist. Stronger coupling seems to characterize the ⟨110⟩ directions.

The distribution of second energy gap values appears to be crudely consistent with band-structure implications, but is likely to have dependences on a phonon anisotropy consistent with the above. The wave matching arguments of Dowman *et al.*[28] which show that semicrystalline oxide barriers may affect tunneling current contributions, do not enter in our considerations, since our various barriers are felt to be amorphous; thus, all k-space correlations of Δ and Δ' are most probably real.

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Ultrasonic-Attenuation Studies in Superconducting Lead*

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Measurement of the attenuation of 10-, 30-, 50-, and 70-MHz longitudinal sound waves, propagated in the [100], [110], and [111] directions, have been conducted on the normal and superconducting states of lead. Analysis of the data has been presented allowing for the possibility of multiple energy gaps. The data have also been compared to theoretical calculations for a strong coupling model.

INTRODUCTION

Recent studies[1-3] involving the attenuation of ultrasound in superconducting lead have based their data analysis on the existence of a single energy gap. In view of other recent superconductivity studies[4,5] it seems quite possible that the superconducting state of lead might involve more than one energy gap. Our intent has been to analyze the experimental data in such a manner as to allow for the observation of multiple energy gaps. Furthermore there is the question of whether superconducting lead is associated with weak[6] or strong coupled[7] interactions. We have made a comparison of our data with Woo's calculations for a strong coupling model.

Our basic experimental study of the ultrasonic attenuation was conducted on unstrained lead for 10-, 30-, 50-, and 70-MHz longitudinal sound waves propagated in the [110] and [111] directions. The data for waves propagated in the [100] direction were taken on a strained crystal previously studied, in the unstrained state, by Deaton.[1] This crystal was strained by the application of a small impulsive shock. Comparison of these results with Deaton's results should provide some additional qualitative information regarding the strain effects on the ultrasonic attentuation.

SAMPLE PREPARATION

The samples were prepared from a single crystal obtained from Research Crystals, Inc., with a specified purity of 99.9999%. The samples were spark cut, x-ray oriented, and spark polished to the desired crystallographic direction. The prepared samples were in the form of cubes of approximately 5 mm on a side. Before application of a binder, the sample faces were alternately subjected to applications of dilute nitric acid and di-