

Case for a Second Energy Gap in Superconducting Niobium†

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Low-temperature tunneling studies of high-purity single crystals of niobium indicate the existence of two energy gaps Δ_s and Δ_d , one for each of the two bands lying at the Fermi level. The value of Δ_s is approximately $\Delta_d/10$. The crystallographic dependence of Δ_s indicates that Δ_s does not appear in directions where there is no s - d overlap at E_F . The behavior of Δ_s with temperature and magnetic field indicates that interband coupling is significant in niobium. The results are related to current theories of multiband superconductivity.

I. INTRODUCTION

Tunneling experiments can provide much information on the electronic properties of transition-metal superconductors. The calculations of Mattheiss on the band structure of these metals,¹ experimentally confirmed by Fawcett, *et al.*,² opened up the possibility of correlating tunneling data with realistic Fermi-surface models. Satisfactory-quality tunneling measurements on transition metals, however, are quite difficult to obtain, since both a high purity and a suitable surface must be achieved. The formation of an acceptable barrier in the fabrication of the tunnel junction is extremely difficult, and the problems have been overcome only in the past few years.^{3,4} Good tunneling data are now available for Nb, and the behavior of the gap parameter $\Delta(\mathbf{k})$ has been reported.^{3,5}

Niobium is a group-VB transition metal crystallizing with a bcc structure, and having five conduction electrons per atom. The Fermi surface is an admixture of s and d bands except in the $\langle 100 \rangle$ directions, which is d in nature.¹ It is reasonable to expect that superconducting pairs may form in both bands, leading to measurable effects on thermodynamic and transport properties. This paper reports direct evidence that both s and d pairs are formed in niobium, and that both pairs exhibit a distinct gap in their respective quasiparticle energy spectra as determined from tunneling experiments.

II. CURRENT THEORETICAL PREDICTIONS

Shortly after the formulation of the BCS theory,⁶ Suhl, Matthias, and Walker⁷ (SMW) extended it to pure superconductors with two (or more) overlapping energy bands. In this model, the BCS Hamiltonian is modified to allow s - d pairing interactions. The interband phonon interaction energy U_{sd} , as well as the intraband energies U_{ss} , U_{dd} , are assumed to be constant; no consideration is made of the Coulomb terms. The usual BCS phonon cutoff energy is employed. The model

leads to the existence of an energy gap corresponding to each band. For niobium, no phonon coupling between the bands ($U_{sd}=0$) means that two gaps Δ_s and Δ_d appear, with two distinct transition temperatures T_c^s and T_c^d . In the case of weak interband coupling, however, Δ_s and Δ_d exist simultaneously to T_c^d . The usual BCS temperature dependence holds for Δ_d ; while Δ_s is constant until $T \sim T_c^s$, where it rapidly decreases. With stronger interband coupling, Δ_s shows no particular temperature dependence up to T_c^d ; while with very strong coupling, the second gap disappears. Figure 1 shows Δ_s and Δ_d for the cases discussed.

Garland arrives at essentially similar conclusions concerning the effect of multibands on energy-gap behavior.⁸ He considers three possible contributions to superconductivity in transition metals: (a) an attractive Coulombic interaction between electrons in the s band resulting from the inability of the heavier d electrons to respond to the motion of the s electron (an "antishielding" effect); (b) a BCS-like intraband phonon coupling; (c) an attractive "effective" interaction $U_{sd}[\Delta d/\Delta s]$, arising from coupling terms in the gap equations.

Definable s and d regions of the Fermi surface are required for the existence of two gaps. If these regions are not distinct, the s and d characters of the electrons are indistinguishable owing to mixing of the wave functions, and only one gap value, Δ_d , will be observed. Garland concludes, then, that in impure transition metals no second energy gap should appear. However, no quantitative measure has been established for categorizing a superconductor as pure or impure, except for the definition by Anderson.⁹ Anderson shows that when the mean free path of the superconductor, l , is on the order of, or greater than, 1.6 times the coherence length ξ_0 , wave function mixing due to scattering is minimal. In this cleanliness region, anisotropy of the superconducting gap should be evident. MacVicar and Rose³ have found that such anisotropy was observable in single crystals of niobium with resistivity ratios of

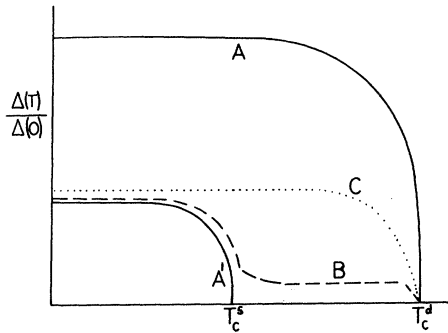


FIG. 1. Behavior of the energy gap in a two-band superconductor (after SMW). Curve *A* represents the BCS behavior of Δ_d , while curves *A'*, *B*, *C* represent the behavior of Δ_s for the following cases: (a) in the intraband limit ($U_{sd}=0$), Δ_s follows the BCS curve *A'*; (b) for weak intraband coupling, Δ_s follows curve *B*; (c) when the interband coupling is moderately strong, Δ_s exhibits the same qualitative behavior as Δ_d (curve *C*); (d) for very strong coupling ($U_{sd} \geq U_d$) only Δ_d exists.

approximately 175 and greater. According to Garland, ranges of ρ_r that are Anderson clean might still not be clean enough to allow Δ_s to be seen. However, Chow,¹⁰ using a modified SMW approach to the case of an impure superconductor, shows that the stringent clean conditions of Garland do not apply in the presence of nonmagnetic impurities, and that the existence and behavior of Δ_s and T_c^s follow that for interband coupling much as SMW concluded. Thus, observations of Δ_s in moderately clean superconductors should be possible.

When Δ_d is much larger than Δ_s , Chow finds that T_c^s is enhanced and, if interband scattering is negligible, the upper critical field H_{c2} is enhanced.¹¹ In considering the ratio of Ginzberg-Landau parameters $K_1(0)/K_1(T_c)$,¹² as determined from experimental measurements of the upper critical field, Wong and Sung¹³ found positive deviation from the expected theoretical value near T_c . The assumption of the existence of a small energy gap, $\Delta_s \sim \frac{1}{10}\Delta_d$, is enough to account for this behavior. The small density of states of the *s* band compared to that of the *d* band means H_{c2} near T_c is dominated by *s* electrons, consistent with H_{c2} being an electromagnetic property characterized by the lighter *s* quasiparticles, and H_c being a thermodynamic property determined only by the heavier *d* quasiparticles.

III. EVIDENCE FOR A SECOND GAP

Low-temperature heat-capacity measurements in 1965 by Shen, Senozan, and Phillips¹⁴ showed that the behavior of niobium deviates from that expected for a single-gap superconductor. At very low temperatures, for both single-crystal ($\rho_r=110$) and polycrystalline ($\rho_r=24$) samples, the slopes of the curves of heat capacity versus inverse temperature deviated from values corresponding to the usual gap magnitude to values implying the existence of a second energy gap

approximately a factor of 10 smaller. The point of deviation of these slopes showed inverse-temperature dependence on ρ_r , consistent with reasonable expectations from "dirty superconductor"¹⁹ theory. Similar deviatory heat-capacity behavior was also observed in vanadium and tantalum. Sung and Shen,¹⁵ fitting the above temperature-dependent behavior of niobium to the model of Suhl, Matthias, and Walker,⁷ obtained a "best fit" with $\Delta_s=0.16kT_c$. No fit was made to tantalum or vanadium data. Radebaugh and Keesom¹⁶ determined experimentally in 1966 that the upper limit of Δ_s is $0.030\Delta_d$ for vanadium.

Carlson and Satterthwaite¹⁷ have recently observed anomalous behavior in the thermal conductivity of niobium single crystals at low temperatures. Their curves suggest a value for an existent second energy gap equal to $0.05\Delta_d$. This value of Δ_s is much smaller than that predicted by most theories. Tang has shown that such a value arises only if interband coupling is neglected in the "best-fit" calculations.¹⁸ Such neglect is probably not valid in Carlson and Satterthwaite's samples. Instead, resolution of the Δ_s discrepancy can be improved by reexamining the data, and realizing that the $\Delta_s=0.05\Delta_d$ value reported is really a minimum, or lower bound, on the true magnitude.

The first tunneling measurements to take note of the possibility of a second energy gap in niobium were made by MacVicar¹⁹ in 1967, and reported as anomalous structure in curves of (dI/dV) versus applied voltage.²⁰ With tunneling into single-crystal niobium ($\rho_r > 300$) at temperatures down to 0.9°K, this structure was observed to exist even up to temperatures on the order of 1.5°K. A concentrated investigation was then undertaken by Hafstrom,²¹ and preliminary results indicated that indeed niobium exhibited behavior consistent with the existence of a small second gap directly measurable via tunneling.²² More recently, Shen has commented upon the occurrence of a small change in superconducting conductance when tunneling into clean polycrystalline tantalum, and tentatively ascribed the change to the possible existence of a second gap in this metal.⁴ The magnitude of $\Delta_s(\text{Ta})$ would have to be approximately 0.2 of the larger gap value to fit his data.

IV. EXPERIMENTAL PROCEDURES

A. Sample Preparation

The main features of our fabrication techniques have been described elsewhere.^{3,19} However, a brief description is necessary here as a backdrop against which to judge the data. Niobium single crystals were grown in ultrahigh vacua (10^{-9} Torr) by the molten-zone electron-beam method. Vacuum contamination was minimized by using an ion pump in combination with either cryosorption pumps or a cold-trapped roughing pump. Titanium sublimation pumping was used to

increase pumping capacity during the growth. Crystals of $\frac{1}{8}$ -in. diameter, and resistivity ratio up to 1200, were easily obtained from Fansteel starting stock, by suitable choices of growth rate, vacua pressures, and annealing times. Crystals of residual resistivity ratio $\rho_r=3000$ were grown from ultrapure electrolytically deposited niobium obtained from Linde Co. Since our crystals cooled under only surface tension constraints, their surfaces were of high perfection. Spectrographic analyses showed that the primary impurities in the Fansteel crystals were typically as follows: beryllium, 10 ppm; cadmium, 4 ppm; copper, 2 ppm; silicon, 5 ppm; tantalum, 70 ppm; iron, 40 ppm; oxygen, 60 ppm.

Tunneling barriers were fabricated on the Nb by one of several methods. In the first, the crystal was removed from ultrahigh vacuum, quickly sectioned into suitable lengths, and thermally oxidized in pure, flowing, oxygen at temperatures of about 110°C for approximately 20 min. The sections were then masked with Formvar to facilitate subsequent electrical connections. A schematic of the junction configuration is shown in Fig. 2. A second superconducting electrode was evaporated as a narrow (approximately 0.010-in.) thin film stripe to complete oriented niobium-thermal-oxide-stripe junctions. A second barrier fabrication procedure was also used: that of low-energy glow-discharge oxidation of the crystal sections at room temperature in an oxygen pressure of $150\ \mu$ of Hg. This procedure was only somewhat successful, and often yielded junctions exhibiting significant levels of nonsuperconducting tunneling currents. Thus, almost all data were taken from samples thermally oxidized. Typical junction resistances were 1–300 Ω , for areas approximately $1\ \text{mm}^2$. A few junctions were fabricated using a disordered carbon film barrier evaporated onto the niobium before taking it from ultrahigh vacuum.²³ Carbon films of approximately 20 \AA average thickness acted a satisfactory barriers in these niobium-carbon-indium junctions used as controls.

The second electrode films, usually indium or lead, were evaporated in 10^{-5} Torr vacuum, to thicknesses of the order 1000–4000 \AA . The pressure and thickness ranges were chosen to prevent the resulting films from texturing, and from exhibiting disadvantageous superconducting energy-gap behavior such as anisotropy.²⁴

B. Testing

Current-voltage and differential conductance, versus voltage characteristics were obtained for the junctions using conventional dc and ac sampling techniques.¹⁹ A helium-3 cryostat enabled temperature dependence to be observed over the range 0.45–4.2°K. Magnetic field measurements could be made down to 1°K in a conventional helium-4 cryostat. Temperature measurement was done by helium-4 vapor pressure in the range above 1°K. Below this, calibrated carbon resistor

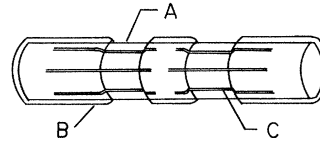


FIG. 2. Junction configuration: (a) niobium single crystal with insulating barrier; (b) Formvar insulation to facilitate electrical connections; (c) evaporated second electrode.

thermometry, or helium-3 vapor pressure, was employed.

V. RESULTS AND DISCUSSION

Junction resistances of niobium-oxide-indium were typically 100 Ω for our geometry. Junctions of lower resistance were generally not considered since observations of second gap behavior would be made more difficult by the presence of subharmonic effects often arising in very thin or “weak link” barriers. Subharmonic structure is readily identifiable by its behavior with temperature and magnetic field,^{25,26} and any junctions exhibiting subharmonic structure were discarded in our analysis.

Junctions exhibiting simply a zero-bias current in otherwise straightforward characteristics were not necessarily discarded. Such structure at zero bias can appear owing to paramagnetic impurity concentrations in the region of the metal/oxide interface. We found that relatively low applied magnetic fields (~ 800 G) erased the zero-bias structure in our junctions. Because fields in excess of several kG would be required to affect structure due to paramagnetic impurities, we ascribe our zero-bias peak seen in those few junctions included in the analysis to tiny shorts and to confirmed Josephson effects.

Some “excess” current is almost always present in niobium junctions, even under very stringent fabrication conditions.²⁵ The presence of states in the barrier can offer alternative conduction paths giving rise to this current. Our glow-discharge oxidized niobium junctions showed significantly more of this effect than did thermally oxidized samples. Only effects that cause nontunneling structure to appear in conductance curves were of any major concern in the analysis, however, so that some background current was considered tolerable.

It is also not unusual for niobium junctions to sometimes exhibit a “knee” in the I - V characteristic just above the sum gap, i.e., a small decrease in conductance just above $(\Delta_d + \Delta_{In})$.²⁰ Many investigators have seen such behavior in other junctions, including lead, tin, and tantalum. The usual explanation offered is that of surface impurity effects on the tunneling density of states. We have previously observed the “knee” to be temperature dependent, becoming increasingly marked as temperature decreases. In the present experiments on the second gap, application of even a low field

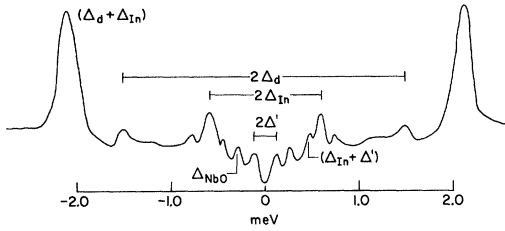


FIG. 3. Conductance (dI/dV) versus voltage characteristic at 0.45°K for a junction oriented near (110). Structures associated with a second energy gap Δ' are indicated. Structure consistent with NbO is also indicated (refer to Tables I and II).

(≈ 100 G) significantly affected the “knee,” serving to mediate its appearance without noticeable effects on other conductance structures of interest associated with energy-gap measurements.

As much as possible, only junctions of “clean” I - V characteristics were used. That is, only junctions exhibiting curves free from subharmonic structure and excessive background currents were admitted to the analysis. Most of the junctions exhibiting indications of second gap structure were also free of zero-bias and knee structures. In view of the washing out of these effects at low applied fields, such junctions were considered useful for analysis, however.

Typical differential-conductance-versus-voltage curves are shown in Figs. 3 and 4. The sum-gap structure at $(\Delta_d + \Delta_{In})$, characteristic of single-particle tunneling, is the most prominent feature of these curves.²⁷ The thermal difference peak $(\Delta_d - \Delta_{In})$ is usually not observed because of the low temperature. Conductance increases at voltages corresponding to Δ_d and Δ_{In} frequently appear in such curves and are commonly ascribed to the simultaneous tunneling of two quasiparticles through thinner regions of a non-uniform barrier.²⁸ The structure of interest is labeled Δ' , and we identify it with the existence of a second energy gap Δ_s in the niobium, corresponding to the s band. Therefore, structure should also appear at

TABLE I. Location of structure expected in a niobium-insulator-indium tunnel junction (energies in meV).

Niobium ^a	
Δ_d	1.55
Δ_s	0.15
Indium	
Δ_{In}	0.51
Single-particle events	
$\Delta_d + \Delta_{In}$	2.06
$\Delta_d - \Delta_{In}$	1.04
$\Delta_{In} + \Delta_s$	0.66
$\Delta_{In} - \Delta_s$	0.36

^a This value for Δ_d is an average value for purposes of illustration and does not indicate observed anisotropy.

$(\Delta_{In} + \Delta_s)$ and $(\Delta_{In} - \Delta_s)$. Table I lists the possible features we expect to see in our tunneling characteristics and the energies corresponding to these features. The figures are marked to show observable peak positions.

The value of Δ_s was observed to be constant over the temperature range 0.45–4.2°K, and over the applied magnetic field range 0–1.6 kG for fields perpendicular to the tunneling direction. The magnitude, $\Delta_s = 0.15 \pm 0.02$ meV, was constant for all samples as determined from the double-particle tunneling peaks in dI/dV versus V characteristics. These peaks were used for the analysis because difference peaks $(\Delta_{In} - \Delta_s)$ were infrequent in appearance. No anisotropy was observed for Δ_s , but this is not necessarily indicative of isotropy. We have noticed in earlier tunneling measurements in single-crystal niobium, and in recent measurements on single-crystal rhenium, that energy-gap values determined from double-particle peaks are isotropic, even when sum-gap energies imply certain gap anisotropy.²⁹

Figure 5 is a schematic stereographic triangle summarizing the orientations of junctions which exhibited

TABLE II. Location of possible additional structure in a niobium-oxide-indium junction arising from NbO within the barrier region (energies in meV).

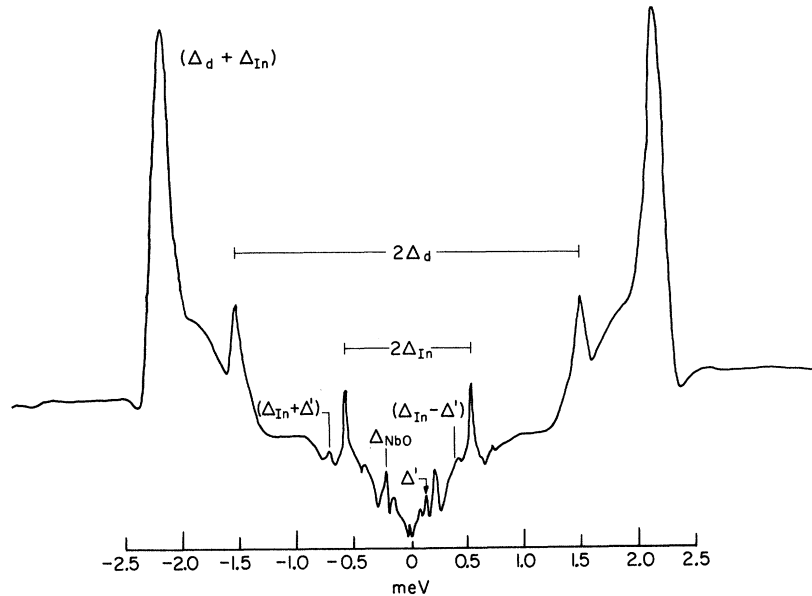
Δ_{NbO}	0.23
$\Delta_{In} + \Delta_{NbO}$	0.74
$\Delta_{In} - \Delta_{NbO}$	0.28
$\Delta_d + \Delta_{NbO}$	1.78
$\Delta_d - \Delta_{NbO}$	1.32
$\Delta_s + \Delta_{NbO}$	0.38
$\Delta_s - \Delta_{NbO}$	0.08

a second gap. No second energy gap was observed in the (100) direction, as might be expected from the calculated band structure of niobium¹ which shows no overlap of s and d bands at E_F in this direction.

No existence of Δ_s was observed for niobium crystals of resistivity ratio less than about 200. This level of cleanliness is also that seeming to correspond to the criteria for seeing Δ_d anisotropy.³ No purity dependence of Δ_s was observed in tests on higher ρ_r crystals.

In order to double check the reproducibility of Δ_s behavior, several niobium-niobium-oxide-lead junctions were tested. These exhibited structure consistent with the existence of Δ_s . Owing to the tendency of lead films to oxidize upon temperature recycling, no extensive tests using lead electrodes were done beyond checking for Δ_s structure in the conductance characteristics. To rule out the possibility of effects introduced by the oxide barrier being responsible for the Δ_s structures observed, a few niobium-amorphous-carbon-indium junctions were tested. These junctions also exhibited characteristics consistent with the existence of a second energy gap. Thus, possible objections of Dowman, MacVicar, and Waldram,³⁰ concerning

FIG. 4. Conductance versus voltage characteristic at 1°K for a junction oriented near (221). Structures associated with a second energy gap Δ' are indicated. Note the possible NbO-related structure near zero bias and above the Δ_d peak (refer to Table II). For the case $U_{sd} \sim 0$, T_c^* would be 0.8°K for Nb from theory.



selective wave-function coupling by a tunneling barrier, do not apply.

As stated above, application of a small magnetic field served to erase the effects of any zero-bias or knee structures present in the characteristics. With increasing magnetic field we observed no further changes in the peak structure of the characteristics except for those associated with the decreasing energy gap of indium. By 1.4 kG, only peak structures at Δ_s and Δ_d were left in the curves. No measurements were taken above approximately 1.6 kG.

In certain of the oxidized junctions, an additional set of peak structures appeared in the curves, as illustrated in Fig. 4. These structures were significantly affected by an applied magnetic field, in a manner consistent with the energy gap of NbO, $\Delta_{\text{NbO}} = 0.23$ meV.³¹ Table II lists the additional structures in I - V plots that this superconducting oxide could contribute. These structures disappeared by 1.2 kG. It is entirely reasonable that small regions of NbO exist at the niobium-metal-niobium-oxide interface. No such structures were seen in the junctions fabricated with amorphous carbon barriers. Increasing temperature led to the disappearance of the possible NbO

structures, then of the indium-related structures, leaving Δ_s and Δ_d peaks still intact for niobium at 4.2°K.

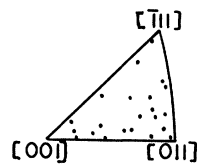
VI. CONCLUSIONS

The existence of a second small energy gap, $\Delta_s \sim \frac{1}{10} \Delta_d$, has been identified from tunneling events observed in clean single crystals of niobium. Other events appearing in junction characteristics can be isolated and do not account for the structure of interest and its behavior. The observed temperature independence of Δ_s up to 4.2°K implies that no distinct transition temperature given by a BCS relation, $2\Delta_s = 3.52kT_c^s$, is present. A second gap transition temperature other than the bulk T_c above 4.2°K could conceivably exist for Δ_s , but no current theory leads to this result. It is more probable that Δ_s falls to zero at T_c^d , as indicated in Fig. 1 for the case of fairly strong interband coupling. Tunneling experiments at temperatures approaching $T_c^d = 9.2$ °K are not easily performed on niobium, since with lower T_c second electrodes, thermal smearing of the sampling density-of-states edge affects resolution; while metallurgical difficulties accrue to using refractory metal second electrodes of high T_c . Such an investigation is underway, however.

Magnetic field measurements showed that Δ_s existed unchanged in magnitude well above 1 kG, for crystals having typical H_{c2} ($T = 2$ °K) values of 2.5 kG. At applied fields of over 1.5 kG, it became difficult to analyze Δ_s energies out of the background. Therefore, we can set only a lower limit of s -gap critical field, 1.6 kG. However, we expect that Δ_s should go continuously to zero at the bulk upper-critical field, H_{c2} , similarly to the behavior of Δ_d .

No anisotropic behavior was observed in the magni-

FIG. 5. Orientations of junctions exhibiting a second energy gap Δ_s .



tude of Δ_s ; although no indications for its existence were seen along $[\langle 100 \rangle]$, consistent with band-structure expectations. Since the existence of Δ_s has been shown by tunneling in crystals of resistivity ratio as low as 200, the clean requirements of Garland⁸ seem overly stringent. Further, even small accounts of impurities at the metal-barrier interface appear tolerable. This seems puzzling since any mixing of the s and d wave functions within a coherency length of the interface should negate any chance of observing Δ_s by tunneling. It is possible that a given junction could exhibit both Δ_s (clean) and impurity (dirty) contributions from different parts of its area. In the case of a uniformly dirty junction, therefore, no second gap would be seen at all. This could explain the fact that second gap structure was not always observed in favorable orientations even when the main gap was quite sharp. It is also possible that detection of the second gap is strongly sensitive to the topological quality of the surface, distinct from its composition, as suggested by Carlson and Satterthwaite.¹⁷

The value of Δ_s obtained in this work agrees with that of Shen *et al.*,¹⁴ i.e., $\Delta_s \simeq 0.16kT_c^d$. Tang, using the parameters of Shen *et al.*, finds $U_{sd}/U_d = 0.075$.¹⁸ The magnetic field and temperature dependence we observe in Δ_s suggest that the coupling between the s and d bands likely takes the form of Garland's enhanced coupling, $U_{sd}(\Delta_d/\Delta_s)$. Our results on niobium indicate that the interband coupling is $10U_{sd}$ leading to $U_{sd}/U_d =$

0.75, which is consistent with curve C of Fig. 1, the moderately strong interband coupling case of SMW.

The persistence of Δ_s to fairly high temperatures and magnetic fields suggests that superconductivity in the s band is dependent on the BCS condensation in the d band, and we expect Δ_s behavior at higher temperatures to closely parallel that of Δ_d . Anisotropy results⁹ showed that Δ_d was a minimum along $[100]$, while it was larger along $[110]$ and $[111]$ where s - and d -band overlap is greater. Farrell, Chandrasekhar, and Huang²² have found that the upper critical field, H_{c2} of very clean niobium ($\rho_r \sim 1500$) exhibits anisotropy of a similar sense to that observed for Δ_d , i.e., greatest along $[111]$, and least along $[100]$. The observed enhancement of Δ_d and H_{c2} in directions of s - and d -band overlap agrees with the predictions of Chow,^{10,11} and Sung and Wong.¹³ These enhancements suggest a cooperative effect between energy bands in superconducting niobium.

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