# Two-Band Superconductivity in Nb-Doped $SrTiO_3$

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Tunneling measurements have been performed on Nb-doped and reduced superconducting $SrTiO_3$. Beyond a certain carrier concentration, when a second conduction band gets filled, a distinctive double-gap structure is observed in Nb-doped samples. Its sharpness and anomalous temperature dependence can be related to the onset of two-band superconductivity in accordance with theoretical expectations. The observation of a single gap $\Delta \simeq 1.76\ kT_c$ in reduced $SrTiO_3$ is attributed to enhanced interband scattering.

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Two-band superconductivity (2BS) offers the promise of observing novel effects within a single homogeneous superconductor. Hitherto, some of their analogs have only been studied with separate superconductors coupled through a barrier or interface. In this Letter, we report distinctive features in the tunneling characteristics of Nb-doped $SrTiO_3$, which represent the first clear-cut experimental evidence for 2BS. This opens the door to exciting nonequilibrium experiments involving coupling between order parameters and/or quasiparticles in different bands.

The unique properties of superconducting $n$-type $SrTiO_3$ have stimulated numerous investigations.[1-3] The possibility of 2BS, however, has not so far been considered. Superconducting $SrTiO_3$ is an ideal candidate for 2BS: (i) According to Mattheiss,[4] the two lowest conduction bands of the low-temperature phase of $SrTiO_3$ occur at the center of the Brillouin zone ($\vec{k}=0$) and are only 20 meV apart. Therefore, by increasing the amount of doping, one expects to fill the first, and then the second band, within a range of carrier concentrations $n \sim 10^{19}$–$10^{20}$ cm$^{-3}$, where the material is superconducting.[1-3] (ii) The unusally large dielectric constant of the nearly ferroelectric host drastically reduces scattering by ionized donors. Interband scattering may therefore be weak enough to preclude averaging of the energy gap.

Following a description of experimental details, we present our results and interpret them within the two-band model of superconductivity. Finally, we discuss some remaining questions raised by our observations, and explain why they cannot be due to inhomogeneities.

Free carriers were produced by direct $n$ doping of Verneuil-grown crystals with Nb, or by reduction of nominally pure single crystals in a hydrogen atmosphere. Neither x-ray diffraction nor microprobe analysis revealed any foreign phases. From all samples, $1\times1\times10$ mm$^3$ bars oriented in the [100] direction were cut, and subsequently bonded to two (current and voltage) contacts. Tunneling junctions were prepared by cleaving the bars in air and rapidly touching the fresh surface with the tip of a small piece of freshly cut indium. This produced rugged contacts with a thin Schottky layer serving as the tunneling barrier and with leakage currents mostly below 1%.

The samples were cooled in a specially designed fast-loading dilution refrigerator with a sample cooldown time of ~10 min.[5] This prevented In diffusion. Measurements of the tunneling $I$-$V$ and $(dI/dV)$-$V$ characteristics were carried out using a self-balancing conductance bridge.

The Schottky tunnel barrier allowed direct determination of the *local Fermi energy* $\mu_F$ (contact area $\approx 10^{-3}$ mm$^2$) from the position of the pronounced minimum in the conductance $dI/dV$ at voltages much higher than any structure due to superconductivity.[6] The resistance of the Schottky barrier could be reversibly tuned in the range 1 Ω to 1 MΩ by application of an appropriate electric field while the junction is being cooled. All features reported below were independent of the barrier resistivity. Those attributed to superconductivity in $SrTiO_3$ vanished at the *same transition temperature* $T_c$. For the Nb-doped samples, our results are distinctly different for $\mu_F$ smaller and larger than a certain $\mu_c$.

In all reduced, as well as in the *low*-$\mu_F$ Nb-doped samples, the $dI/dV$ characteristics are close to those of an ideal asymmetric tunnel junction between two superconductors (*S*-*S*), i.e., with relatively sharp peaks at the difference and the sum of the energy gaps of In and $SrTiO_3$. Sufficiently below $T_c$ the difference peak disappears; a shift in the remaining peak is attributed to the temperature-dependent gap, $\Delta(T)$, of $SrTiO_3$, since $\Delta_{In}$ is constant in that range. The dependence $\Delta(T)$, the ratio $\Delta(0)/kT_c \simeq 1.76$, and the shape of the tunneling conductance are as expected from the BCS theory, although $dI/dV$ is somewhat broader in the reduced sample IV and in some of the Nb-doped samples (4 and 5) near $\mu_c$. Samples 4 and 5 also show an additional small, smeared-out maximum at about $\Delta_{In}+2\Delta(T)$ to which we revert later.

*Beyond a certain concentration,* i.e., $\mu_F > \mu_c$, the concomitant appearance of *sharp double peaks above* $\Delta_{In}$ in $dI/dV$ of the $SrTiO_3$:Nb samples is quite dramatic (see Fig. 1). These structures are consistent with *S*-*S* tunneling from a superconductor with two different well-defined energy gaps $\Delta_1$ and $\Delta_2$. The smaller gap $\Delta_2(T)$ vanishes at $T_c$ together with $\Delta_1(T)$, and exhibits a remarkable temperature dependence never observed before (see inset in Fig. 2).

The dependence of $T_c$ and of $\Delta$ or $\Delta_1$ and $\Delta_2$ for $T \sim 0.2\ T_c$ on $\mu_F$ (or $n$) is summarized in Fig. 2 for all our samples. In the Nb-doped ones with $\mu_F > \mu_c$, $\Delta_1$ appears to continue smoothly the $\Delta(\mu_F)$ dependence observed for $\mu_F < \mu_c$, whereas $\Delta_2$ rises steeply from zero beyond $\mu_c \approx 32$ meV. For samples 7 and 8, the measurements indicate a stronger variation of $T_c$ than of $\Delta_1$, thus making the ratio $\Delta_1(0)/kT_c$ anomalously small.

The marked $\mu_F$ dependence suggests an unusual-

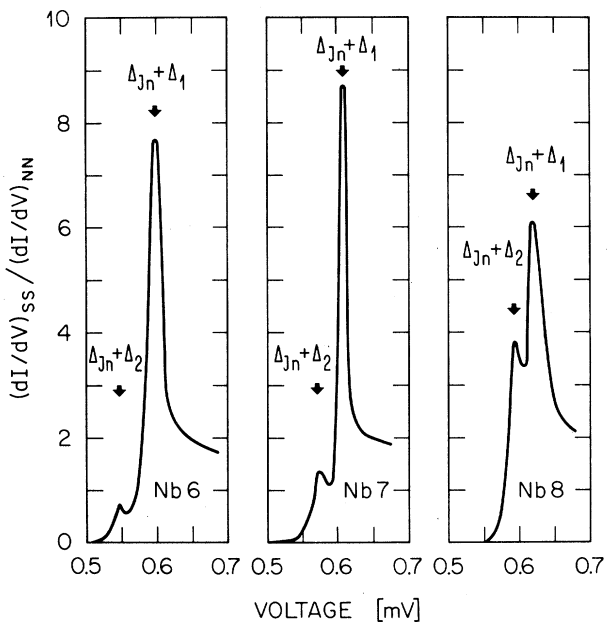


FIG. 1. Normalized tunneling conductance of Nb-doped $SrTiO_3$-In junctions in the range of two-band superconductivity ($\mu_F > \mu_c \simeq 32\ \mu$eV) measured at $T = 100$ mK. Only the portion of the voltage scale near the sum of the gaps of $SrTiO_3$ and In is shown. The latter could be determined within $\pm 2\ \mu$eV for a given sample and had a mean value $\Delta_{In} = 535\ \mu$eV.

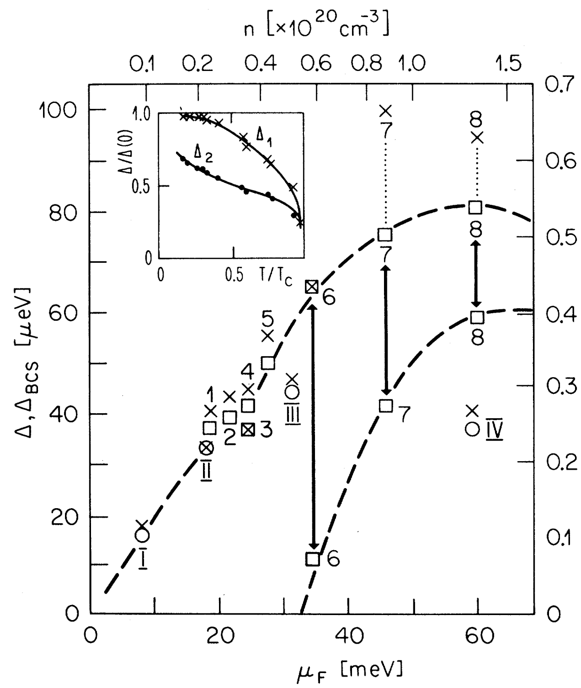


FIG. 2. Superconducting order parameters $\Delta_1$ and $\Delta_2$ (inferred from peaks in the measured tunneling conductance of *n*-type $SrTiO_3$-In junctions at $T \approx 0.2\ T_c$: open circles, reduced samples; open squares, Nb doped; curves drawn as an aid to the eye only), transition temperature $T_c$, and $\Delta_{BCS} \equiv 1.76\ kT_c$ (crosses) vs Fermi energy $\mu_F$ measured on the same junctions. The corresponding carrier concentrations estimated from Hall measurements are indicated on the top scale. The dependence $T_c(n)$ for the reduced samples is essentially that observed in previous work (see Ref. 1). The inset shows the temperature dependence of both order parameters measured on sample Nb 8.

ly strong influence of band structure on superconductivity in $SrTiO_3$:Nb. The Fermi surface of $n$-type $SrTiO_3$ calculated by Mattheiss[4] for temperatures well below the cubic-tetragonal transformation exhibits two sheets centered at $\vec{k}=0$. The lowest conduction band gives rise to an anisotropic surface similar to a "starfish" with four arms growing in ±[100] and ±[010] directions perpendicular to the tetragonal axis as the band gets filled. The second band is shifted up by ≈ 20 meV; it gives rise to a nearly isotropic, ball-shaped surface within the starfish. For sufficiently weak electron scattering by defects, these features should induce the following peculiar superconducting properties: an anisotropic energy gap, $\Delta_{\hat{k}}$, in the first band, and, for $\mu_F > 20$ meV, two order parameters $\Delta_1$ and $\Delta_2$, each corresponding to a given band.

We attribute the appearance of the double structures for $\mu_F > \mu_c$ to the development of 2BS on filling the second band. The experimentally found $\mu_c \approx 32$ meV appears reasonable, in view of the approximate nature of the band-structure calculations.[4] Furthermore, the temperature dependence of $\Delta_1$ and especially $\Delta_2$ indicates a significant coupling between these two quantities. This interpretation is in accord with existing calculations of the $T$ dependence of the order parameters[7] $\Delta_{1,2}$ and of the tunneling density of states[8] $N(E)$ for a model two-band superconductor.

This model involves five parameters: the ratio $\nu = N_2/N_1$ of the normal-state densities of states in the two bands, the total *inter*band scattering rate $\Gamma = (1+\nu)\Gamma_{21}$, the *inter*band coupling $U_{12} = \nu U_{21}$, and the hypothetical transition temperatures $T_{c1} > T_{c2}$ for $U_{21} = \Gamma_{21} = 0$. The *intra*band scattering rates $\Gamma_{11}$ and $\Gamma_{22}$ are assumed large enough to make $\Delta_1$ and $\Delta_2$ constant in the respective bands. The sharpness of the peaks shown in Fig. 1 implies that $\Gamma$ is small, viz., $\hbar\Gamma \lesssim kT_{c1}$,[8] in all Nb-doped samples with $\mu_F > \mu_c$, since the model then yields an $N(E)$ like the superposition of the density of states of two uncoupled superconductors with different gaps almost equal to $\Delta_1$ and $\Delta_2$. From the positions of the two peaks in $dI/dV$, $\Delta_1$ and $\Delta_2$ can be determined quite accurately, and the ratio of their intensities roughly reflects $\nu$. Because of the steep rise of $N_2$, $\nu$ and $T_{c2}$ should rapidly increase for $\mu_F > \mu_c$, whereas $T_{c1}$, $U_{21}$, and $\Gamma_{21}$ are expected to vary smoothly with $\mu_F$ near $\mu_c$. A strong increase of $\Delta_2$ and of the intensity of the corresponding peak in $dI/dV$ relative to that of the higher peak is therefore expected. This is exactly the behavior apparent in Figs. 1 and 2.

An *upper bound* for $\Gamma$ may be found from the relaxation time $1/\tau$ with use of the single-isotropic-band formula for the conductivity, $\sigma = ne^2\tau/m^*$, and a mean effective mass $m^* = 1.6\, m_e$.[4] This yields $\hbar/\tau \approx 400$ $\mu$eV for a $SrTiO_3$:Nb sample with $n \approx 7\times10^{19}$ $cm^{-3}$ whose resistance has been measured carefully.[9] Since $1/\tau$ overestimates $\Gamma$ considerably, whereas $kT_{c1} > kT_c > 0.6\Delta_1 \simeq 40$ $\mu$eV, the condition $\hbar\Gamma \lesssim kT_{c1}$ may well be satisfied in the Nb-doped samples.

Whereas $T_c \approx T_{c1}$ for small $\nu$ and $\Gamma$, $T_c$ should be significantly depressed below $T_{c1}$, and the two peaks in $N(E)$ should broaden and then merge into a single one at $E \sim \Delta_{BCS} \equiv 1.76\, kT_c$ for sufficiently large $\hbar\Gamma/kT_c$. The resistivity of *reduced* $SrTiO_3$ is about four times larger than that of Nb-doped samples with a comparable carrier concentration[9]; $\Gamma$ should also be larger. This is in line with the smaller $T_c$ and the single broader peak in $dI/dV$ observed in the reduced sample IV.

The two-band model cannot explain why $\Delta_{BCS} \equiv 1.76\, kT_c > \Delta_1$ for $\mu_F > \mu_c$ in samples 7 and 8; according to existing calculations $\Delta_{BCS}$ should lie *between* $\Delta_1$ and $\Delta_2$.[8] Moreover, interactions with different frequency cutoffs can be absorbed into renormalized ones with equal cutoffs[10]; therefore, the anomaly cannot be attributed to other mechanisms contributing to superconductivity in the second band, e.g., acoustic plasmon exchange.[11] One way out of the dilemma is that there is another $\Delta > \Delta_{BCS}$, associated, for instance, with the armtips of the starfish, and which has no noticeable effect on $N(E)$, because of strong scattering. Such a possibility is suggested by the Fig. 5 of Ref. 8 and by the additional broad structure observed in samples Nb 4 and Nb 5 (with $\mu_F \lesssim \mu_c$). This structure may be attributed to gap anisotropy in the first band, and to preferential tunneling from different zones (e.g., the central body and starfish) over which $\Delta_{\hat{k}}$ is approximately constant (minimum or maximum).[12]

Finally, we rule out more mundane explanations of the double peaks in $SrTiO_3$:Nb samples: (i) A *graded* layer with reduced $n$ and $\Delta$ might exist behind the Schottky barrier, but could not give rise to a *sharp structure* in $N(E)$ below the main gap, *a fortiori*, only in high-concentration samples. (ii) Suppose that small (< 1-$\mu$m) grains of another superconducting phase, e.g., $TiO_x$, $NbO_x$, or more complex oxides,[13] would form in such samples. They could give rise to an extra sharp peak in $N(E)$ (presumably that at $\Delta_2$ which grows with increasing Nb concentration) only if the size of the grains exceeded their coherence length on the average. Otherwise, the expected spread in sizes and separations would induce a spread in $\Delta_2$. In the former case, $\Delta_1$ and $\Delta_2$ should tend to zero at $T_{c1} \neq T_{c2}$ (for intermediate temperatures, a residual proximity effect might induce a tiny $\Delta_2$). However, the observed dependence $\Delta_2(T)$ indicates a stronger coupling which would be incompatible with two sharp peaks in $N(E)$.[14]

In summary, our tunneling measurements on superconducting $SrTiO_3$:Nb are consistent with the onset of two-band superconductivity with two coupled order parameters in the range expected from Mattheiss's band structure. The absence of a double-peak structure in $dI/dV$ and the smaller $T_c$ in reduced $SrTiO_3$ are attributed to enhanced interband scattering.

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