S-wave Superconductivity in Optimally Doped SrTi$_{1-x}$Nb$_x$O$_3$ Unveiled by Electron Irradiation

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We report on a study of electric resistivity and magnetic susceptibility measurements in electron irradiated SrTi$_{0.987}$Nb$_{0.013}$O$_3$ single crystals. Point-like defects, induced by electron irradiation, lead to an almost threefold enhancement of the residual resistivity, but barely affect the superconducting critical temperature ($T_c$). The pertinence of Anderson’s theorem provides strong evidence for a s-wave superconducting order parameter. Stronger scattering leads to a reduction of the effective coherence length ($\xi$) and lifts the upper critical field ($H_{c2}$), with a characteristic length scale five times larger than electronic mean-free-path. Combined with thermal conductivity data pointing to multiple nodeless gaps, the current results identify optimally doped SrTi$_{1-x}$Nb$_x$O$_3$ as a multi-band s-wave superconductor with unusually long-range electrodynamics.

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Scattering mixes the superconducting order parameter at separate points on the Fermi surface. As a consequence, one can probe changes in the two-particle wavefunction by tuning disorder. Its effect on the superconducting transition provides an opportunity to explore the symmetry of the superconducting gap. According to Anderson’s theorem, in a conventional s-wave superconductor the critical temperature ($T_c$) is insensitive to non-magnetic disorder [1]. On the other hand, in superconductors with non-trivial gap symmetry, e.g., cuprates [2–4], Sr$_2$RuO$_4$ [5], and heavy fermions [6], $T_c$ is extremely sensitive to potential scattering and the superconducting ground state can be completely destroyed by disorder [7–10]. In multi-band superconductors such as MgB$_2$ and iron pnictides, interband scattering rather than intraband scattering plays a key role in suppressing $T_c$ and the effect of disorder depends on the ratio of interband to intraband scattering matrix elements [11–13].

Chemical substitution can be used to introduce disorder. In cuprates, $T_c$ is drastically suppressed by Zn doping, providing strong evidence for d-wave symmetry [2]. Particle irradiation provides an alternative avenue of creating artificial defects without introducing any foreign ions. In YBa$_2$Cu$_3$O$_{7-\delta}$, scattering induced by electron irradiation suppressed $T_c$ in a manner similar to Zn substitution [4, 14, 15]. On the other hand, in the s-wave superconductor MgB$_2$, superconductivity is robust with respect to electron irradiation [16–18]. However, neutron and α-particle irradiation of MgB$_2$ led to an apparent suppression of $T_c$ [19–21]. The shape and size of defects, which influence scattering, depend on the type of irradiation. Energetic heavy ions generate columnar defects along the ion trajectories [22–24]. Protons, α-particles, and neutrons most likely produce defect clusters of nm size [11]. On the other hand, high energy electrons (1–10 MeV) generate point-like defects in the form of interstitial-vacancy pairs (Frenkel pairs) [25]. This makes electron irradiation a suitable method for introducing controlled disorder.

A band insulator with an energy gap of 3.2 eV, SrTiO$_3$ is close to a ferroelectric instability aborted due to quantum fluctuations [26]. Its huge permittivity at low temperature leads to a very long Bohr radius and a precocious metallicity. Three conducting bands, composed of Ti t$_{2g}$ orbits and centered at the Γ point can be successfully filled by n-doping [27]. A superconducting dome, with a peak $T_c \approx 450$ mK [28–32] exists between charge carrier densities of $3 \times 10^{17}$ to $3 \times 10^{20}$ cm$^{-3}$.

The symmetry of the superconducting order parameter has been barely explored in this system. In 1980, Birnig and co-authors detected two distinct superconducting gaps by planar tunneling measurements [33]. However, a recent tunneling experiment did not detect multiple gaps on the superconducting LaAlO$_3$/SrTiO$_3$ interface [34]. More recently, thermal conductivity measurements found multiple nodeless gaps in optimally doped SrTi$_{1-x}$Nb$_x$O$_3$ single crystals, paving the way for the identification of the symmetry of the superconducting order parameter [35]. A latest study reported the existence of electron pairs well beyond the superconducting ground state in quantum dots fabricated on the LaAlO$_3$/SrTiO$_3$ interface [36].

In this paper, we present a study of ac susceptibility and thermal conductivity measurements in electron irradiated SrTi$_{0.987}$Nb$_{0.013}$O$_3$ single crystals with a peak $T_c$ of 450 mK. Four samples with size of $5 \times 2.5 \times 0.5$ mm have been cut from the same
single crystal and gold was evaporated on their surface to make Ohmic contacts. Three of them were irradiated with 2.5 MeV electrons at the SIRIUS accelerator facility of the Laboratoire des Solides Irradiés. Irradiations were performed at 20 K in liquid hydrogen to obtain a uniform distribution of point defects in the material. After irradiation, the samples were stored in liquid nitrogen to avoid room temperature annealing of the irradiation-induced defects. The resistivity and Hall effect around the superconducting transition temperature were measured with a standard four probe method in a dilution refrigerator within a few days after the irradiation. The transport properties were rechecked in a Quantum Design PPMS system above 2 K a few months later. The Hall carrier density and residual resistivity have barely changed with time. Gold contacts that are large compared to the size of the samples may give rise to an uncertainty of 10% in the transport measurements. Finally, the ac susceptibility was measured in a homemade set-up, which consisted of one primary field coil and one compensating pick-up coil with two sub-coils with their turns in opposite direction. The exciting ac current was supplied and the induced voltage signal was picked up by a Lock-in amplifier. The applied ac magnetic field was as low as 10 mG, with frequencies between 2000 and 4000 Hz.

Fig. 1(a) shows the temperature dependence of the resistivity of the pristine sample #1 and of samples #2, #3 and #4 that were irradiated to total electron doses $Q = 300$, 460 and 1320 mC/cm$^2$ respectively. The residual resistivity $\rho_0 = \rho(2K)$ amounts to 71 $\mu$Ω cm in the pristine sample and increases with increasing irradiation dose. The increase is caused by enhanced elastic scattering due to the point-like defects induced by the electron irradiation. Fig. 1(b) plots the Hall resistivity as a function of the magnetic field at 10 K. The Hall carrier concentration $(n_H)$ plotted in Fig. 1(c) remains around 2.1 $\times$ 10$^{20}$ cm$^{-3}$ with an error of 10%, deduced from $R_H = \rho_{Hall}/B$ is the Hall coefficient. As seen in the figure, while the carrier concentration does not show any substantial change, $\rho_0$ increases linearly with the irradiation dose, indicating that the magnitude of the scattering rate is affected by the increased quantity of irradiation-induced scattering centers. $\rho_0$ amounts to 175 $\mu$Ω cm in sample #4, enhanced by 104 $\mu$Ω cm compared to #1, a magnitude comparable to what has been attained in other studies of impurity effects in superconductors such as cuprates [2] and pnictides [11]. The mean-free-path ($l$) can be extracted using $l = \hbar k_F/e$, where $\hbar$ and $e$ are the fundamental constants, $\mu$ is the Hall mobility and $k_F$ the Fermi wave factor, calculated from the carrier density assuming an isotropic single-component Fermi surface. With increasing $Q$, $l$ decreases from 50 to 19 nm.

Fig. 2 shows the superconducting transition in different samples such as observed through the real part of the susceptibility ($\chi'$) and the resistivity (normalized by its normal-state magnitude). There is a smooth transition in $\rho/\rho_n$ and the resistivity vanishes at a critical temperature ($T_{c-\rho}$) of 435 mK. On the other hand, $\chi'$ moni-

![FIG. 1: Resistivity and Hall coefficient in pristine and electron-irradiated SrTi$_{0.987}$Nb$_{0.013}$O$_3$ single crystals. a) Temperature dependence of resistivity (note the vertical log scale). The low temperature resistivity monotonically increases with irradiation dose. b) Hall resistivity ($\rho_{Hall}$) as a function of magnetic field at 10K. c) Residual resistivity ($\rho_0=\rho(2K)$) and Hall carrier concentration ($n_H$) as a function of irradiation dose ($Q$). Irradiation enhances the residual resistivity by a factor of 2.5, but leaves the carrier density virtually unchanged ($n_H \approx 2.1 \times 10^{20}$ cm$^{-3}$). The dashed line is a guide to the eyes.](image)
According to this theory, the superconducting transition evolves with irradiation. Two vertical lines mark the transition temperatures in $\chi'$ and $\rho/\rho_n$. The superconducting transition barely shifts.

Interestingly, the magnitude of $\beta$ derived using Eq. 2 is five to six times larger than the mean-free-path (see Table 1). This feature may be a peculiarity of this superconductor compared to those materials in which superconductivity emerges from a high carrier density metal. The huge electric permittivity in insulating SrTiO$_3$ leads to a long effective Bohr radius ($a_B^\text{e}$), as long as 700 nm [30], which is much larger than the mean-free-path. This may be the ultimate reason for a larger characteristic length for electrodynamic response in this low carrier density superconductor.

Let us compare our results with what has been reported in the case of other superconductors. Abrikosov and Gor'kov formulated a theory for the response of conventional superconductors to magnetic impurities [40].

$$-\ln\left(\frac{T_c}{T_{c0}}\right) = \psi\left(\frac{1}{2} + \frac{\alpha T_{c0}}{4\pi T_c}\right) - \psi\left(\frac{1}{2}\right)$$

Here, $\psi$ is the digamma function, $T_{c0}$ is the superconducting critical temperature in the clean limit, $\alpha = 2\hbar\tau/k_BT_{c0}$ is the dimensionless pair breaking parameter.
TABLE 1: Irradiation dose (Q), superconducting critical temperature from ac susceptibility (Tc−χ′) and resistivity (Tc−ρ) at zero field, residual resistivity at 2K (ρ0), superconducting effective coherence length (ξ), mean-free-path (l), and the length scale (β) for pristine and electron-irradiated SrTi0.987Nb0.013O3 single crystals.

<table>
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<th>Tc−χ′ (K)</th>
<th>Tc−ρ (K)</th>
<th>ρ0 (µΩcm)</th>
<th>ξ (nm)</th>
<th>l (nm)</th>
<th>β (nm)</th>
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</table>

Fig. 4 shows Tc/Tc,o as a function of the dimensionless pair-breaking rate α = hτimp/kBTc,o in SrTi0.987Nb0.013O3 determined from resistivity (■) and ac susceptibility (○). The data for MgB2 under electron irradiation (the horizontal dashed line) is plotted for comparison, as well as those for two unconventional superconductors, Zn-doped cuprates (●: YBa2Cu3O6.63, ◀: YBa2Cu3O6.93 ) and slightly disordered Sr2RuO4 (▲). The dotted lines are guides to the eyes. Superconductivity is robust against impurity scattering in SrTi0.987Nb0.013O3 and in MgB2, but is rapidly suppressed in the two unconventional superconductors.

and τp is the spin-flip scattering lifetime. Eq. 3 can be generalized to unconventional superconductors and their Tc evolution with non-magnetic potential scattering. This can be done by replacing α with hτp/kBTc,o, in which τp is the potential scattering lifetime [3, 7, 8]. In order to make a simple comparison between experiment and theory, we take the residual resistivity as a measure of τp, taken to be equal to the transport life time τimp, expressed by τimp = m* / ℏ.

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