Evidence for multi-band superconductivity above the Pauli limit in \( \text{Nd}_x\text{Sr}_{1-x}\text{TiO}_3 \)

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Superconductivity in doped \( \text{SrTiO}_3 \) (STO) was discovered over 50 years ago, yet STO has remained one of the most intriguing known superconductors. Here we report superconductivity in STO doped with a novel dopant, Nd, which is expected to carry a net spin. A major open question for STO relates to the possibility that multiple bands could be involved in establishing the superconducting state. Here we offer evidence of two-band superconductivity in \( \text{Nd}_x\text{Sr}_{1-x}\text{TiO}_3 \) thin films based on the temperature dependence of the upper critical field, an approach that has not been previously used to investigate multi-band effects in doped STO. Specifically, we observe a pronounced positive curvature of the temperature-dependence of the out-of-plane upper critical field, which extends substantially below the critical temperature and changes to negative curvature at the lowest temperatures. Moreover, we find that the out-of-plane upper critical field can exceed the Pauli paramagnetic limit by a factor of nearly two. We show that these unusual observations are consistent with enhancement of the critical field by multi-band superconductivity effects, in conjunction with weakening of paramagnetic pair-breaking by strong spin-orbit coupling. Currently, there exist no models for describing the temperature dependence of the critical field for a multi-band superconductor that take into account the combined orbital, paramagnetic and spin-orbital coupling effects. We propose such a two-band model and find very good agreement with our data. Our analysis also suggests that intra-band superconducting coupling dominates over inter-band coupling.

I. INTRODUCTION

In most known superconductors, the electrons that form the Cooper pairs originate from a single band. An interesting scenario, which occurs in a relatively small subset of superconductors, involves electrons from multiple bands, leading to multiple, interacting superconducting condensates. The coherent interactions between the condensates in multi-band superconductors are predicted to give rise to unique effects, such as vortices with fractional flux [1], time-reversal breaking solitons [2], and enhanced upper critical fields \( (H_c^2) \) [3]. Experimental evidence for multi-band superconductivity has been reported in
several materials, including MgB$_2$ [4], iron-based superconductors [5], the heavy-fermion superconductor PrOs$_4$Sb$_{12}$ [6], and NbSe$_2$ [7]. The majority of these are bulk, three-dimensional superconductors. Here we report evidence of multi-band two-dimensional superconductivity in thin films of Nd-doped SrTiO$_3$ (Nd$_x$Sr$_{1-x}$TiO$_3$).

Undoped SrTiO$_3$ (STO) is a band insulator and is the first insulating system to show superconductivity when doped. Superconductivity in STO has remained a rich and widely-studied problem since its initial discovery, over half a century ago [8]. To date, STO has been shown to superconduct when doped with one of three main dopants: O vacancies [8], Nb [9] and La [10], with critical temperatures in the range of few hundred mK. In addition, superconductivity has been reported in ionic-liquid-gated STO [11], with a similar range of critical temperatures as chemically-doped doped STO. Here we observe superconductivity using a previously-unexplored dopant, Nd$^{3+}$ ([Xe]$4f^36s^0$), which substitutes for Sr$^{2+}$ and therefore n-dopes the STO, as confirmed by Hall measurements. Unlike all previous STO dopants, Nd$^{3+}$ has a net spin, suggesting that Nd could act as a magnetic dopant.

The band structure of STO is particularly interesting because up to three bands can contribute to conduction, depending on doping levels. Specifically, the conduction band of STO is composed of three $t_{2g}$ orbitals originating from titanium $d$ bands. The degeneracies of the three $t_{2g}$ orbitals are lifted by spin-orbital coupling and by the crystal field, in the low temperature tetragonal phase [12]. As a result, a natural question is whether superconductivity in STO can also involve multiple bands. The question of whether STO is a multi-band superconductor has not been fully settled experimentally, with the literature remaining inconclusive, partly because the presence of disorder can reduce the visibility of multi-band effects. The earliest report of possible two-band superconductivity in STO comes from a double-peak feature observed in tunneling spectroscopy on Nb-doped STO above a certain carrier concentration [13], which could indicate two superconducting gaps. Other work has shown that the transition temperature ($T_c$) peaks near Lifshitz transitions between STO bands [14], which could indicate that multiple bands are involved in STO superconductivity. On the other hand, more recent tunneling spectroscopy studies on thin films of Nb-doped STO have reported only a single coherence peak as a function of tunneling bias for a wide range of carrier concentrations, consistent with single-band superconductivity [15]. In addition, microwave radiation experiments on bulk Nb-doped STO have been found to be consistent with single-gap superconductivity [16]. Similarly, in superconducting LaAlO$_3$/SrTiO$_3$ interfaces, weakening of superfluid stiffness near $T_c$ at large charge densities has been attributed to the onset of multi-band superconductivity [17], yet SQUID measurements of the superfluid density vs. temperature have also
observed results consistent with only a single-band, BCS picture [18]. As also emphasized in Ref. [16], null results could be due to washing out of the multi-gap feature by disorder in certain samples.

Here we provide evidence for multi-band superconductivity in thin films of Nd-doped STO from the temperature-dependence of the upper critical field \( H_{c2} \). To our knowledge, this approach has not been previously applied to doped STO, yet it has the advantage that it is well-suited precisely for the dirty limit, where disorder may limit the sensitivity of other experimental probes [19]. We observe several distinguishing features of multi-band superconductivity. One of these key features is an unconventional (for single-band superconductors) positive curvature of \( H_{c2}^\perp(T) \), which occurs over a substantial range of temperatures \( T \) below \( T_c \) and which is accompanied by a change in curvature at lower \( T \). Such characteristic \( T \)-dependence has recently been proposed as a reliable signature of multi-band superconductivity in the dirty limit in STO [19] and has been previously used as evidence for two-band superconductivity in high-\( T_c \) Fe-based superconductors [5]. In addition, in the two-band superconductor MgB\(_2\) pronounced positive curvatures are commonly observed near \( T_c \) and are attributed to two-band superconductivity [3,20,21].

Quite unusually, we also observe that \( H_{c2}^\perp \) exceeds the Chandrasekhar-Clogston (Pauli paramagnetic) limit, \( H_p \sim 1.84T_c(T / K) \). For thin film superconductors it is frequent to observe in-plane critical fields \( (H_{c2}^\parallel) \) exceeding \( H_p \), due to the geometrical enhancement of the bulk critical field combined with the presence of spin-orbit coupling (SOC). However, the \( out-of-plane \) critical field, \( H_{c2}^\perp(0) \), is typically much less than \( H_p \) in most materials (including in past work on STO) because of orbital pair-breaking effects. Exceptions are certain bulk organic and heavy-fermion superconductors [22,23]. In the former case, this has been attributed to a field-dependent dimensionality crossover coupled with the presence of SOC, while in the latter the very large effective electron mass contributes to suppressing orbital effects. Below, we argue that our observation of \( H_{c2}^\perp(T) > H_p \) is the consequence of the enhancement of the orbital critical field by multi-band superconductivity, coupled with the presence of strong SOC. Theoretical work on multi-band superconductivity has so far not considered orbital, paramagnetic and SOC effects together [3,24]. Thus, in order to analyze our observations, we propose an extension of existing two-band superconductivity models to include all these effects. As described below, we find very good quantitative agreement of our extended model with the data. To our knowledge this is also the first investigation of the critical field of a two-dimensional two-band superconductor.
II. NORMAL-STATE TRANSPORT AND SUPERCONDUCTIVITY

Samples were grown by hybrid-molecular beam epitaxy on a commercially STO substrate [25]. A buffer layer of undoped STO is grown before growing the doped layer. The samples are annealed in an oxygen-rich environment post growth to drive out any residual oxygen vacancies. As-grown undoped STO films were insulating, suggesting no measurable conduction due to oxygen vacancies. XRD and RHEED analyses confirm a single-crystalline, epitaxial, smooth STO film on STO (001) (Fig. 1a). We studied five samples down to mK temperatures, with carrier densities spanning from $3\times10^{19}$ to $2\times10^{20}$ cm$^{-3}$.

Fig. 1(b) shows the $T$-dependence of resistance ($R$) measured on Sample A (carrier density $n = 3\times10^{19}$ cm$^{-3}$, with composition Nd$_{x}$Sr$_{1-x}$TiO$_{3}$ (254 nm, $x=0.0018$)/SrTiO$_{3}$(35 nm – buffer layer)/SrTiO$_{3}$ (substrate)), which is characteristic for several of the samples we studied. For nearly square placements of contacts we observe different resistance values when we rotate our current and voltage lead configuration by 90 degrees (hereafter we refer to these two measurement configurations as channel 1 and channel 2). This variation may be due to some doping anisotropy, which could provide preferential current flow paths in the different measurement configurations, but is not expected to affect the main results presented here. The resistance is described by a quadratic law, $R = R_0 + AT^2$, across the entire temperature range, with a change in the $R_0$ and $A$ parameters near $T=180$ K. A $T^2$ dependence of the resistance at low $T$ is typically attributed to Fermi liquid behavior, including in the case of STO [26]. However, unlike in typical metals, where the Fermi temperature ($T_F$) is $\sim10^4$ K, in STO it can be as low as $\sim10$ K due to its exceptionally large dielectric constant (in excess of 20,000 at low $T$). This means that the Fermi-liquid approximation, which requires $T<<T_F$, may not generally hold for STO. Intriguingly, we find that the $T^2$ dependence extends to temperatures above $T_F$ and persists up to room temperature ($T_F\sim150$K in sample A, in the parabolic band approximation). At these elevated temperatures, the system transitions from Fermi liquid to a Boltzmann gas and hence can no longer be adequately described by Fermi liquid theory. Hence it is likely that the $T^2$ behavior, at least near and above $T_F$, has another root and may therefore not be a robust indicator of a Fermi liquid, as also recently pointed out in Ref. [27].

As our samples are cooled further, they become superconducting at temperatures ranging between 90 mK and 200 mK. These values of $T_c$ are in the same overall range as reported by previous studies on STO and STO-based interfaces [8–11,28,29]. Fig. 1(c) shows $R$ vs. $T$ curves as a function of magnetic field ($B$) in Sample A. Results from another sample (Sample B) are shown in [30]. We note that the
superconducting transition measured along channel 2 exhibits a pronounced peak just before $R$ drops to zero. Similar behavior is observed in all four superconducting samples we studied. The presence of a large peak in resistance at the superconducting transition has been observed in several other types of superconductors, but no general consensus exists on a single origin [31,32].

III. OUT-OF-PLANE CRITICAL FIELD

We now turn to the discussion of the temperature-dependence of the critical field, which underpins the key points of our paper. We focus on analyzing the behavior of sample A’s channel 1 (data for channel 2 is shown in [30]). As shown in Fig. 2, $H_{c2}^{\perp}(T)$ displays a positive curvature over a substantial range of $T$ extending from $T_c$ down to ~0.3$T_c$, below which the curvature becomes negative. This behavior is not expected from a typical single-band BCS superconductor, but is a hallmark of multi-band superconductivity, as elaborated below. For a single-band superconductor, a negative curvature would instead be expected at all $T$, as described by the WHH model [33].

A second remarkable feature of the data is that the value of $H_{c2}^{\perp}(T)$ measured at the lowest temperature (~0.25$T_c$) reaches almost twice the value of $H_p$. In the absence of strong electron correlations and in the limit of weak electron-phonon coupling, $H_{c2} > H_p$ occurs only in materials with strong SOC, where spin is not a good quantum number. This is a well-known effect, also observed in STO, but only for thin film samples under in-plane applied fields, a geometry which ensures that orbital effects are weak [34,35]. In contrast, it is highly unusual for the out-of-plane critical field to exceed $H_p$, even in the presence of strong SOC. $H_{c2}^{\perp}$ (like $H_{c2}$ for bulk samples) is generally limited by orbital depairing effects, which in practice restrict it to values $\ll H_p$ for typical single-band superconductors. In Fig. 2 we plot our data against the WHH expression in order to contrast our observations with the expectations for a single-band superconductor. It is evident that despite taking into account SOC, single-band superconductivity does not capture the striking features of the data.

In single-band superconductors the slope of $H_{c2}(T)$ near $T_c$ determines its maximum value, $H_{c2}(0)$, via the simple relation $H_{c2}(T) = -0.69T_c \left. dH_{c2}/dT \right|_{T_c}$. By contrast, a large enhancement of $H_{c2}$ beyond the single-band prediction occurs in two-band superconductors if the diffusivity of one of the bands is small. In particular, $H_{c2}(0)$ is no longer simply determined by $dH_{c2}/dT \left|_{T_c}$ . A theoretical picture of
two-band superconductivity was first developed by Suhl [36] and further extended by Gurevich to calculate critical fields [3,24]. For two-band superconductors subject to orbital effects alone, Gurevich’s model predicts that \( H_{c2}(0) \) is given by [3]:

\[
H_{c2}(0) = \frac{ck_B}{\pi \gamma eD_1} e^{-(\lambda_0 - \lambda_c)/2w}, \quad D_1 \ll D_2 e^{-\lambda_c/2w} \tag{1}
\]

Here \( D_1 \) and \( D_2 \) correspond to the diffusion constants of the two bands (we denote the lower, heavier band as band 1), \( \lambda_\perp = \lambda_{11} - \lambda_{22}, \lambda_0 = \sqrt{(\lambda_{11} - \lambda_{22})^2 + 4\lambda_{12}\lambda_{21}}, \) and \( w = \lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21} \), with \( \lambda_y \) as the intra- and inter-band coupling constants. \( \ln(\gamma) = -0.577 \) is the Euler constant, and \( c, k_B \) and \( e \) are the speed of light, Boltzmann constant and elementary charge, respectively. Importantly, \( H_{c2}(0) \) is determined by the lower of the two diffusivities. This unique feature of two-band superconductors allows much enhanced \( H_{c2}(0) \) values with respect to the single-band case.

We next proceed to analyzing the \( T \)-dependence of \( H_{c2}^\perp \) using the prediction of Gurevich’s two-band model, noting that for a thin film \( H_{c2}^\perp \) is effectively \( H_{c2} \) of the bulk material. Gurevich’s model has been previously used to fit \( H_{c2}(T) \) data on two-band band superconductors such as MgB\(_2\) and Fe-pnictides with good quantitative agreement [5,37]:

\[
a_0 \left( \ln t + U(h) \right) \left( \ln t + U(\eta h) \right) + a_1 \left( \ln t + U(h) \right) + a_2 \left( \ln t + U(\eta h) \right) = 0 \tag{2}
\]

Here, \( U(x) = \psi(1/2 + x) - \psi(1/2) \), where \( \psi \) is the di-gamma function. \( a_{0,1,2} \) are determined by the band coupling constants \( \lambda_y \) as described in Ref. [3], \( h=D_2eH/2\pi c k_B T \) (we use cgs units), \( t=T/T_c \), and \( \eta=D_1/D_2 \). Note that in the limit of \( \eta = 1 \) eqn. (2) reduces to the de Gennes-Maki equation, \( \ln t + U(h) = 0 \). To determine \( a_{0,1,2} \) we use the coupling constants obtained in [38], \( \lambda_{11} = \lambda_{22} = 0.14 \) and \( \lambda_{12} = \lambda_{21} = 0.02 \), indicative of a dominant intra-band coupling. Importantly, our data is not consistent with the other published set of estimates for \( \lambda_y \) [39], which places constraints on the values of these constants [30]. Furthermore, we show that our data is inconsistent with dominant inter-band coupling, \( \lambda_{12}\lambda_{21} \gg \lambda_{11}\lambda_{22} \), or \( \lambda_{12}\lambda_{21} \approx \lambda_{11}\lambda_{22} \), suggesting that intra-band coupling is dominant [30].
Having thus fixed the $\lambda_{ij}$ using the values from Ref. [38], we are left with only two adjustable parameters, $D_1$ and $D_2$. Although the Gurevich model does not account for paramagnetic and SOC effects, we find a good agreement with our $H_{c2}^{\perp}(T)$ data (Fig. 2) by using $D_2 \sim 3$ cm$^2$/s and $D_1 \sim 0.06$ cm$^2$/s. The ratio $\eta = D_1/D_2 \sim 0.02$ indicates a large difference between the diffusivities of the two bands. Importantly, the model clearly displays the positive (upwards) curvature that characterizes the $T$-dependence of our $H_{c2}^{\perp}$ data near $T_c$, and also captures the change in curvature observed at low $T$. For completeness, we note that positive curvature has also been attributed to melting of the vortex lattice in high-$T_c$ cuprates or theoretically associated to the presence of paramagnetic impurities [40,41]. However, since STO is a low-$T_c$ superconductor, vortex fluctuations are negligible and so we can rule out the melting of a vortex lattice in our case. The Nd$^{3+}$ dopants could potentially act as paramagnetic impurities, however this, unlike two-band superconductivity, cannot account for the observed $H_{c2}^{\perp} > H_p$. In addition the per unit cell concentration of Nd, $x=0.0018$, is likely too small to lead to any spin-spin correlations.

IV. IN-PLANE CRITICAL FIELD AND OUR EXTENDED MODEL

Above, we have shown that our $H_{c2}^{\perp}(T)$ data reveals the presence of two-band superconductivity in thin-film doped STO. We now turn to a discussion of $H_{c2}^{\parallel}(T)$. As shown in Fig. 3(a), the temperature-dependence of $H_{c2}^{\parallel}(T)$ near $T_c$ is well approximated by $(1-T/T_c)^{1/2}$, as typical for 2D superconductors. The 2D nature of superconductivity is confirmed by the observed cusp in the angular-dependence of $H_{c2}^{\perp}$ (Fig. 3(b)), a standard feature of 2D superconductors, which is absent from layered (anisotropic) 3D superconducting materials, such as cuprates, MgB$_2$ and Fe-pnictides [42].

As shown in Fig. 3(a), $H_{c2}^{\parallel}(T)$ exceeds $H_p$ substantially. Similar results have been reported in previous work on STO thin films, where the data was well-described by the WHH model, consistent with single-band superconductivity and strong SOC [34]. However, as shown above, the WHH model is inconsistent with our $H_{c2}^{\perp}(T)$ data, ruling out a single-band scenario. We therefore continue our analysis with Gurevich’s two-band model for $H_{c2}^{\parallel}(T)$. We use $h=1/6D_2e^2Hd^2/\hbar c^2$, consistent with Ref. [24]. In Fig. 3(a) we show the prediction of this model using the same values of the parameters obtained for $H_{c2}^{\perp}(T)$, with only one adjustable parameter, $d$. The model describes the data well near $T_c$ (with $d \sim 17$ nm), but substantially overestimates the low-$T$ data. We argue that this overestimation is the consequence
of not taking paramagnetic effects into account. However, including them without also including the effects of SOC would limit $H_{c2}^\perp < H_p$, in contrast to our observations. Note that the reason Gurevich’s model works well for $H_{c2}^\perp(T)$, but fails for $H_{c2}^\parallel(T)$ is that the low-$T$ $H_{c2}^\parallel(T)$ data far exceeds $H_p$, and hence paramagnetic effects play a crucial role over a wider range of $T$ and $H$ than for $H_{c2}^\perp(T)$. This motivates the need for a more comprehensive two-band model, which includes orbital, paramagnetic and SOC effects, in order to account for the totality of our observations.

To our knowledge no such models have been developed. Here we propose an extension of Gurevich’s two-band model, which includes all these effects. Generalization of the single-band critical field equation to the case of two-band systems is generally straightforward. In the limit of negligible inter-band scattering, the procedure entails solving two single band equations independently and casting these into a two by two matrix equation. The diagonal matrix elements contain the intra-band coupling constants, while off-diagonal elements contain the inter-band coupling constants. This yields eqn. (2), with $U(h)$ and $U(\eta h)$ replaced with the appropriate form for the single-band model. All the existing two-band superconductor critical field equations can be understood in this fashion [3,24]. In the case of a two-band superconductor in the dirty limit with orbital, paramagnetic, and SOC effects, the relevant single-band model is the WHH model, and hence the $U(\eta h)$ and $U(h)$ in eqn. (2) are replaced with the WHH expressions, $U^*(\eta h,\alpha_1,\lambda_{so,1})$ and $U^*(h,\alpha_2,\lambda_{so,2})$, as defined below:

$$U^*(h,\alpha_1,\lambda_{so,1}) = \left( \frac{1}{2} + \frac{i\lambda_{so,1}}{4\gamma} \right) \psi \left( \frac{1}{2} + \frac{\tilde{h} + \frac{1}{2} \lambda_{so,1} + i\gamma}{2t} \right) + \left( \frac{1}{2} - \frac{i\lambda_{so,1}}{4\gamma} \right) \psi \left( \frac{1}{2} + \frac{\tilde{h} + \frac{1}{2} \lambda_{so,1} - i\gamma}{2t} \right) - \psi \left( \frac{1}{2} \right) \quad (3)$$

As in the original WHH paper, $\lambda_{so,i} = 2\hbar/3\pi k_B T_c \tau_{so,i}$, where $\tau_{so,i}$ is the spin scattering time, $\tilde{h} = D_2 eH / \pi c k_B T_c$, and $\gamma_i = \sqrt{\left(\alpha_i h \right)^2 - \left(\frac{1}{2} \lambda_{so,i} \right)^2}$, where $\alpha_i = \frac{h}{2mD_i}$. Here $\lambda_{so,i}$ represents the characteristic spin-orbital coupling energy for each band normalized by the condensation energy, and $\gamma_i$ includes the paramagnetic (Zeeman) term. Note that for small applied fields, $\frac{\mu_B H}{\pi k_B T_c} \ll \frac{1}{2} \lambda_{so,i}$, where orbital effects are dominant, we recover the orbital-only critical field model given by eqn. (2) [3], while in the absence
of SOC ($\lambda_{so,j} = 0$), this reduces to Gurevich’s model with paramagnetic effects [24], in the limit of vanishing inter-band scattering.

To assess our extended model, we fit both the $H_{c2}^\perp(T)$ and $H_{c2}^{\parallel}(T)$ data using the same literature values of the coupling constants $a_{0,1,2}$ as used above for the orbital-only model. There are five adjustable parameters: $D_1$, $D_2$, $\lambda_{so,1}$, $\lambda_{so,2}$ and $d$. However, physical insight about the role and type of SOC (detailed below) helps reduce their effective number. Moreover, the parameters must satisfy both the $H_{c2}^\perp(T)$ and the $H_{c2}^{\parallel}(T)$ data simultaneously, which places a further constraint on the model. To fit to both data sets we use an iterative approach. We begin by obtaining an initial best fit to the $H_{c2}^\perp(T)$ data, which we find to be relatively insensitive to the SOC strength, so that the fit is essentially based on only $D_1$ and $D_2$. Using these initial values for $D_1$ and $D_2$, we then fit to the $H_{c2}^{\parallel}(T)$ data by varying $\lambda_{so,1}$, $\lambda_{so,2}$ and $d$. We note that the $H_{c2}^{\parallel}(T)$ data is sensitive primarily to the value of $d$ below $H_p$, where SOC effects are weak, and most sensitive to $\lambda_{so,1}$ and $\lambda_{so,2}$ above $H_p$, where SOC and paramagnetic effects play the biggest role. The iterative process is then repeated, using the values of $\lambda_{so,1}$, $\lambda_{so,2}$ and $d$ so obtained to yield a better fit to $H_{c2}^\perp(T)$ on the next iteration. We repeat the iterations until the fits to both data sets converge and the parameters no longer change appreciably. To further constrain $\lambda_{so,1}$ and $\lambda_{so,2}$ and to shed light on the origin of the SOC, we consider two commonly occurring SOC mechanisms: Elliot-Yafet (EY) and Dyakonov-Parel (DP). For EY, the transport lifetime ($\tau_p$) is proportional to the spin lifetime, $\tau_{so} \propto \tau_p$. The opposite is true for the DP mechanism: $\tau_{so} \propto 1/\tau_p$. Using $v_F^2 = 10v_F^2$ [12,19] and $D_i = v_F^2 \tau_{p,i} / 3$ we find that $\lambda_{so,1}/\lambda_{so,2} \simeq (1/10)D_2/D_1 = 1/10\eta$ for EY SOC and $\lambda_{so,1}/\lambda_{so,2} = 10\eta$ for DP SOC. This allows the SOC to be described by only one parameter instead of two. Assuming that the DP mechanism dominates, we obtain a good fit to the data with $D_1 \sim 0.04$ cm$^2$/s, $D_2 \sim 3$ cm$^2$/s, $d \sim 14$ nm, $\lambda_{so,1} \sim 2$ and $\lambda_{so,2} \sim 20$. The value $\lambda_{so,2} \sim 20$ corresponds to a spin-orbit energy $h/k_B\tau_{so,1} \sim 120K$, which is rather large, suggesting that the DP mechanism is not the main source of SOC. On the other hand, fitting under the assumption that EY dominates, we obtain $D_1 \sim 0.05$ cm$^2$/s, $D_2 \sim 3$ cm$^2$/s, $\lambda_{so,1} \sim 5$ and $\lambda_{so,2} \sim 0.8$, with the same value of $d$. In this case, the maximum SOC energy $(h/k_B\tau_{so,2})$ corresponds to $\sim 30K$. The dominance of EY over DP is consistent with the absence of inversion symmetry breaking in STO. The
obtained SOC energies of $h/\tau_{\text{so,1}} \sim 1 \text{ meV}$ and $h/\tau_{\text{so,2}} \sim 0.2 \text{ meV}$ are significantly larger than the condensation energy of $\sim 30 \mu\text{eV}$, suggesting the possible presence of exotic triplet pairing. Nd, being a heavy element, may be the source of the large SOC we observe here. We note that in STO, a third type of SOC, intrinsic SOC, could also play a role [34], however there is currently relatively little experimental understanding of the effects of this mechanism.

Interestingly, the fit yields $d \sim 14 \text{ nm}$, close to the 17 nm value obtained from the orbital-only model, but much less than the nominal thickness of the Nd$_x$Sr$_{1-x}$TiO$_3$ layer, which is $\sim 254 \text{ nm}$. The sample is effectively a two-dimensional superconductor, as corroborated by the angular-dependence of $H_{c2}$, but the reason for this thickness discrepancy is at present an open question for future studies. We also note that out of the four superconducting samples we studied, two-band effects were observed only in those two which also showed two-dimensional superconductivity, suggestive of a possible link between these two effects. In this context, it is interesting to note that non-WHH $H_{c2}^{\perp}(T)$ behavior has been observed on superconducting LaAlO$_3$/SrTiO$_3$ interfaces, an intrinsically 2D system that may have similarities with doped STO [43].

V. ANGULAR DEPENDENCE OF THE CRITICAL FIELD

We conclude our analysis with a discussion of the angular dependence of $H_{c2}$, which is typically used as an additional test of the effective dimensionality of a superconductor. Fig. 3(b) shows a plot of $H_{c2}$ vs. $\theta$, the angle between the applied field and the normal to the sample at $T=0.14 \text{ K}$. To describe the angular dependence of $H_{c2}$ between the out-of-plane and in-plane limits, we use

$$ h(\theta) = \frac{D_2}{2\pi c k_B T_c} \left( 2eH \left| \cos(\theta) \right| + \frac{1}{3 \hbar c} \left[ d e H \sin(\theta) \right]^2 \right) $$

We find a good agreement of our model with data over a wide range of angles, with no fitting parameters (we use the values extracted previously from fitting $H_{c2}^{\perp}(T)$ and $H_{c2}^{\parallel}(T)$). For comparison, we also fitted the data to the single-band 2D (Tinkham) and anisotropic 3D (Ginzburg-Landau) models, with two adjustable parameters, $H_{c2}^{\perp}$ and $H_{c2}^{\parallel}$. Although neither model takes paramagnetic or SOC effects into account, the 2D Tinkham model is frequently used to fit angular dependent data for thin films, even where the in-plane critical field is significantly larger than $H_p$, often with good agreement to the data [35,44]. Here however, we find the 2D Tinkham model does not yield a satisfactory fit over the whole angular range, despite using two fitting parameters vs. none for our two-band model. As seen in the inset of Fig. 3(b), the 3D anisotropic Ginzburg-Landau
model produces a rounded peak, in clear deviation from our data, further corroborating the 2D nature of the observed superconductivity.

VI. CONCLUSIONS

In conclusion, we report on the evidence of two-band two-dimensional superconductivity in the presence of strong spin-orbit coupling in thin films of Nd$_x$Sr$_{1-x}$TiO$_3$ grown by hybrid-MBE. The significant enhancement of the orbital critical field by two-band effects, together with the strong SOC, enable the out-of-plane critical field to exceed substantially the Pauli limit, unlike what is typically observed in bulk and 2D single-band superconductors. We propose a model for the temperature-dependence of the critical field of two-band superconductors, which incorporates Pauli paramagnetism and spin-orbital coupling, along with orbital effects. The model is in very good agreement with the data. These results highlight that under favorable conditions, the temperature-dependence of the upper critical field can be a powerful and sensitive approach for identifying and investigating two-band superconductors in the dirty limit. Our results suggest dominant intra-band superconducting coupling in STO. Furthermore, this is also the first observation of superconductivity in STO doped with a spinful atom.

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Fig. 1: (a) XRD and RHEED (inset) data on Sample A, indicating an epitaxial, single-crystalline, smooth film. (b) Normal state resistance ($R$) as function of temperature ($T$), along the two measurement configuration (channels 1 and 2), plotted on $T^2$ scale, showing quadratic dependence of $R$ on $T$ from 2K to 300 K, with a cross-over in the $T^2$ prefactor around 180K. (c) $R$ vs. $T$ near $T_c$ along channel 1, at several values of the out-of-plane magnetic field, showing the onset of superconductivity. Inset: $R$ vs. $T$ near $T_c$ for channel 2, for two values of the out-of-plane magnetic field.
Fig. 2: Out-of-plane critical field, $H_{c2}^{\perp}(T)$, plotted as a function of reduced temperature ($t=T/T_c$), showing pronounced positive curvature from $t=1$ down to $t=0.3$ and a change of curvature with further decreasing $t$. The critical field is defined using the mid-point ($0.5R_n$) of the resistive transition. The three solid curves correspond to three models: extrapolated WHH curve, based on the slope of $H_{c2}^{\perp}(T)$ near $T_c$ (wine); fitted curve based on Gurevich’s orbital-only two-band critical field equation (eqn. (2)) (blue); fitted curve based on our two-band critical field equation, which also takes into account Pauli and SOC effects (cyan). The horizontal purple line marks the BCS Pauli limit, $H_p$. 
Fig. 3: (a) In-plane critical field, $H_{c2}^\parallel$, plotted as a function of reduced temperature, $t$. Solid curves correspond to fits using two-band critical field equations with (cyan) and without (blue) Pauli and SOC effects. The horizontal purple line marks the Pauli-limit, $H_p$. (b) Critical field $H_{c2}$ as a function of angle, $\theta$, measured from the normal to the sample plane. The cyan curve corresponds to the two-band critical field equation which includes orbital, Pauli and SOC effects and is computed using the fitting parameters extracted from Fig 2 and Fig. 3(a). Also shown are Tinkham’s 2D model (blue) and the 3D anisotropic Ginzburg-Landau model (wine), fitted with two free parameters. Inset: a zoom-in near in-plane alignment of the field, showing the cusp in the data, which is indicative of 2D superconductivity.
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SUPPLEMENTAL MATERIAL

Multi-band two-dimensional superconductivity above the Pauli limit in Nd$_{x}$Sr$_{1-x}$TiO$_3$

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I. Results from Sample B

Sample B: composition Nd$_{x}$Sr$_{1-x}$TiO$_3$(254 nm, x=0.003)/SrTiO$_3$(35 nm – buffer layer)/SrTiO$_3$ (substrate)

Fig. S1: Out of plane critical field, $H_{c2}^\perp(T)$, for sample B ($T_c$ ~100 mK), plotted as a function of reduced temperature ($t=T/T_c$), showing pronounced positive curvature. The three solid curves correspond to three models: extrapolated WHH curve, based on the slope of $H_{c2}^\perp(T)$ near $T_c$ (wine); fitted curve based on Gurevich’s orbital-only two-band critical field equation (eqn. (2)) (blue); fitted curve based on the two-band critical field equation, which also takes into account Pauli and SOC effects (cyan).
Fig. S2: (a) In-plane critical field, $H_{c2}^{||}$, for sample B, plotted as a function of reduced temperature, $t$. Solid curves correspond to fits using two-band critical field equations with and without Pauli and SOC effects, cyan and blue respectively. The horizontal purple line marks the Pauli-limit, $H_p$. (b) Critical field $H_{c2}$ as a function of angle, $\theta$, measured from the normal to the sample plane. The cyan curve corresponds to the two-band critical field equation which includes orbital, Pauli and SOC effects and is computed using the fitting parameters extracted from Fig 2 and Fig. 3(a). Also shown are Tinkham’s 2D (blue) and the 3D anisotropic Ginzburg-Landau (wine) models, fitted with two free parameters. Inset: a zoom-in near in-plane alignment of the field, showing the cusp in the data, which is indicative of 2D superconductivity.
II. Fitting using coupling constants from Ref. 39

Fig. S3: Out of plane critical field, $H_{c2}^{\perp}(T)$, for sample A, plotted as a function of reduced temperature ($t=T/T_c$). The solid curves correspond to fits to Gurevich’s orbital only equation using estimated coupling constants from [39]: $\lambda_{11} = 0.3$, $\lambda_{22} = 0.1$ and $\lambda_{12} = \lambda_{21} = 0.015$. The figure shows clearly that these values of the coupling constants do not produce a good fit. Those of Ref. [38] do produce a good fit, as discussed in the main paper. Our data is thus able to constrain the values of these parameters.
III. Showing that the data is inconsistent with the case of dominant *inter*-band coupling

![Graph](image)

**Fig. S4:** Out of plane critical field, $H_{c2}^{\perp}(T)$, plotted as a function of reduced temperature ($t=T/T_c$). The solid curves correspond to fits to Gurevich’s orbital only equation using $\lambda_{11} = \lambda_{22} = 0.05$ and $\lambda_{12} = \lambda_{21} = 0.15$, corresponding to dominant inter-band coupling. The poor resulting fits indicate that the data is inconsistent with dominant *inter*-band coupling. In contrast, as shown in the main paper, dominant *intra*-band coupling is in good agreement with the data.
IV. Results from Sample A – channel 2

Fig. S5: Critical fields as a function of temperature for sample A, measured on channel 2, in a separate cooldown from that in which the data in the main paper was taken. In this cooldown, it was not possible to reach temperatures below ~100 mK. (a) Out-of-plane critical field, $H_{c2}(T)$, showing positive curvature, but with a smaller curvature than for channel 1. (b) Temperature dependence of the in-plane critical field, $H_{c2}^\parallel(T)$. The critical fields are determined by using the $0.5R_n$ criterion, where $R_n$ is the resistance before the onset of the peak. The presence of the resistance peak in the $R$ vs. $T$ curves measured along channel 2 (Fig. 1(c) in the main paper) prevents a direct comparison with the $T_c$ and $H_{c2}$ values measured along channel 1, which displays no such peak.