Multiorbital Ferroelectric Superconductivity in doped SrTiO$_3$

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(Dated: April 26, 2019)

SrTiO$_3$ is a unique example of a system which exhibits both quantum paraelectricity and superconductivity. Thus, it is expected that the superconducting state is closely related to the intrinsic ferroelectric instability. Indeed, recent experiments suggest the existence of a coexistent phase of superconductivity and ferroelectricity in Ca-substituted SrTiO$_3$. In this paper, we propose that SrTiO$_3$ can be a platform of the ferroelectric superconductivity, which is characterized by a ferroelectric transition in the superconducting state. By analyzing a multiorbital model for $t_{2g}$ electrons, we show that the ferroelectric superconductivity is stabilized through two different mechanisms which rely on the presence of the spin-orbit coupling. First, the ferroelectric superconducting state is stabilized in the dilute carrier density regime due to a ferroelectricity-induced Lifshitz transition. Second, it is stabilized under a magnetic field independent of the carrier density. The importance of the multiorbital or multiband nature for the ferroelectric superconductivity is clarified. Then, we predict a topological Weyl superconducting state in the ferroelectric superconducting phase of SrTiO$_3$.

The origin of the superconductivity in SrTiO$_3$ (STO) has remained to be a long standing problem of the condensed matter physics for more than half a century. The superconductivity in doped STO begins to emerge at an extraordinary low carrier density on the order of $10^{17}$ cm$^{-3}$ [1, 2], where the Fermi energy $\epsilon_F$ is smaller than the characteristic phonon energy $\omega_p$. Therefore, conventional BCS or Migdal-Eliashberg theories are invalid for this superconducting state since the retardation condition ($\epsilon_F \gg \omega_p$) is not satisfied. To reveal the origin of the dilute superconducting state, various pairing glues have been proposed theoretically, e.g., plasmons [3, 4], localized longitudinal optical phonons [5], and soft transverse optical phonons [6–10]. However, there is still no consensus about the pairing mechanism in STO.

Recently, the superconductivity in STO receives extensive attention also in terms of the ferroelectric (FE) quantum criticality. STO is a quantum paraelectric (PE) [11] which exists in the vicinity of the FE quantum critical point [12]. The avoided FE ordering can be activated by some chemical or physical operations, e.g., isovalent substitution of Sr with Ca [13], isotopic substitution of $^{16}$O with $^{18}$O [14], and application of tensile strain [15] or electric field [16]. Incidentally, doped STO exhibits metallic behavior at very low carrier densities on the order of $10^{16}$ cm$^{-3}$ [1, 17, 18], thanks to the quantum paraelectricity and resulting long effective Bohr radius [19]. Thus, it is naturally considered that the dilute superconductivity and the FE quantum criticality are closely related. Indeed, enhancement of the superconducting transition temperature $T_c$ by a FE quantum fluctuation was proposed theoretically [20], and later confirmed experimentally [21, 22]. Furthermore, a phase transition structurally indistinguishable from the FE phase transition was observed in metallic Sr$_{1-x}$Ca$_x$TiO$_{3-\delta}$ [21] similarly to a FE metal LiOsO$_3$ [24]. This experimental observation suggests existence of the superconducting phase which coexists with the ferroelectricity. Therefore, STO is a candidate of a FE superconductor in which FE-like phase transition occurs in the superconducting state.

Another extensively debated issue about the superconducting STO is its multiband nature. Early tunneling measurements on doped STO observed two peaks in the local density of states (DOS) [23] which implies the multiple superconducting gaps. This result is supported by recent quantum oscillation measurements [2] and thermal conductivity data [26]. Thus, it has been suggested that STO is a multiband superconductor with multiple nodeless gaps, and the multiband effect has been theoretically discussed [27, 28]. In contrast, recent tunneling experiments [30] and optical conductivity data [31] indicate only single superconducting gap.

Although multiband nature in the superconducting STO is still under debate, it is certainly true that the superconducting state has multiorbital features. The conduction bands in STO originate from three Ti $t_{2g}$ orbitals. Three-fold degeneracy of the $t_{2g}$ orbitals is lifted due to antiferrodistortive (AFD) rotation of TiO$_6$ octahedra below 105 K [32]. Thus, STO has three distinct bands all centered at the $\Gamma$-point and constructed from multiple orbitals [Fig. 1]. Therefore, the multiorbital features may affect superconductivity even in the dilute carrier density regime with single Fermi surface. Consequently, the superconductivity in doped STO has multiorbital character regardless of the carrier density.

Considering all the unique aspects of the superconducting STO, in this paper, we show that STO can be a platform of the FE superconductivity through two different mechanisms that rely on the antisymmetric spin-orbit coupling (ASOC). First mechanism originates from the ferroelectricity-induced Lifshitz transition in dilute carrier density regimes. Another one is the magnetic-field-induced FE superconductivity caused by...
spin-momentum locking in the FE phase. It is shown that, in both mechanisms, the FE superconductivity is strongly influenced by the multiorbital or multiband nature of STO. In particular, we predict a Weyl FE superconductor state arising from the multiorbital effect. The three distinct bands in STO are reproduced by the following tight-binding Hamiltonian 33:

$$\mathcal{H}_0 = \sum_{k, l, \sigma} \xi_l(k) c_{k, l, \sigma}^\dagger c_{k, l, \sigma} + \Delta_T \sum_{k, \sigma} c_{k, xz, \sigma}^\dagger c_{k, xz, \sigma} + \lambda \sum_i L_i \cdot S_i, \quad (1)$$

where $c_{k, l, \sigma}$ is the annihilation operator for an electron with momentum $k$, orbital $l = yz, xz, xy$, and spin $\sigma = \uparrow, \downarrow$. The first term is the kinetic energy with the single electron energy $\xi_l(k)$. The second and third terms express the tetragonal crystal field for AFD transition and LS coupling of Ti ions, respectively. The model parameters are determined based on the first principles calculations 33, 34.

Then, we discuss effects of the ferroelectricity on the electronic structure. Since the electric polarization is not well defined in metallic or superconducting states, we define the ferroelectricity in conducting systems as a spontaneous nonpolar-to-polar inversion symmetry breaking. This FE transition is realized by opposite displacement of Sr/Ti cation and O anion, and thus the crystal symmetry descends to one of polar space groups. Although the origin of superconductivity in STO is unclear, thermodynamic properties such as the specific heat jump 29 are in good agreement with the BCS theory. Therefore, we investigate the superconductivity within the mean-field theory. By assuming the $s$ wave and orbital-independent intraorbital pairing interaction, the superconductivity is discussed by solving the simultaneous gap equations 33

$$\Delta_i = -\frac{V_s}{N} \sum_k \langle c_{-k, l, \uparrow} c_{k, l, \uparrow} \rangle, \quad (3)$$

where $V_s > 0$ is the interaction strength and $N$ is the number of Ti sites. $V_s$ is determined to satisfy $T_c \ll E_{\text{SO}}$, where $E_{\text{SO}}$ is a typical energy of the spin-orbit splitting. This condition is reasonable in STO since the superconducting transition temperature is extremely small, i.e., about 0.3 K. Then, the effect of the Rashba splitting in the FE phase is reflected to the superconductivity.

In addition, we introduce the Zeeman coupling

$$\mathcal{H}_Z = -\mu_B \sum_{k, l, \sigma, \sigma'} H \cdot \sigma \sigma' c_{k, l, \sigma}^\dagger c_{k, l, \sigma'}, \quad (4)$$

to discuss the magnetic response of the superconducting state. Since the orbital depairing effect can be suppressed in the dilute superconducting state with tiny $\xi_F$, we only take into account the Pauli depairing effect. Indeed, the upper critical field exceeding the Pauli limit has been observed in Sr$_{1-x}$Nd$_x$TiO$_3$ 40. We fix the magnetic field in a direction parallel to the polar [001] axis, i.e., $H = (0, 0, H_z)$. Thus, an asymmetric deformation of the Rashba split Fermi surface, which is destructive for the FE superconductivity 41, is not induced under the magnetic field.

Using $\Delta_i$ obtained by solving Eqs. (3), we calculate the electronic free energy $\mathcal{F}_{\text{ele}}(\Delta = (\Delta_{yz}, \Delta_{xz}, \Delta_{xy}), P)$.
In addition, we include the free energy arising from the polar lattice distortion

\[
F_{\text{lat}}[P] = \frac{1}{2} \kappa_2 P^2 + \frac{1}{4} \kappa_4 P^4 + \frac{1}{6} \kappa_6 P^6.
\]  

(5)

Here, \(\kappa_2, \kappa_4,\) and \(\kappa_6\) are lattice parameters which describe the elasticity of the lattice. The thermodynamically stable state is determined by minimizing the total free energy \(F[\Delta, P] = F_{\text{ele}}[\Delta, P] + F_{\text{lat}}[P]\) with respect to \(\Delta\) and \(P\). The FE superconducting state is realized when both \(\Delta\) and \(P\) have finite values. Here, we adopt a value of \(\kappa_2\) to realize a PE normal state near a FE transition point. This condition expresses quantum PEs. The lattice parameters \(\kappa_4\) and \(\kappa_6\) are introduced to cutoff the FE order parameter \(\gamma \propto P\) in realistic regime. The cutoff value of \(\gamma\) is estimated based on the first principles calculation \[38, 39\]. Then, we elucidate the feasibility of a FE transition caused by the superconductivity.

Figure 2 shows the magnetic field versus temperature phase diagrams in three different carrier density regimes which are distinguished by the number of Fermi surfaces [see Fig. 3(a)]. In the single-band regime where the Fermi surface is composed of only the lower band, the FE superconducting state is stabilized at zero magnetic field [Fig. 2(a)]. This is a consequence of a Lifshitz transition induced by the ferroelectricity. Upon decreasing the carrier density in the FE phase, the Fermi energy becomes lower than the crossing point of the spin-orbit split bands at the \(\Gamma\)-point [see Fig. 1], and thus the topology of Fermi surfaces is changed in stages. These Lifshitz transitions enhance the DOS due to an effective reduction of dimensionality \[42\]. Therefore, the Lifshitz transition stabilizes the FE superconducting state \[41\]. However, the effect of the Lifshitz transitions of the middle or upper band does not realize the zero field FE superconductivity. This is because the lower band with the largest Fermi surface mainly stabilizes the superconductivity even in the two- or three-band regime, and thus the contribution of the middle or upper band is negligible. This is a consequence of the multiband nature of STO. The zero field FE superconductivity is possible only in the dilute region where the Lifshitz transition of the lower band can be induced by the ferroelectricity.

Irrespective of the carrier density, the FE superconducting state is stabilized under the magnetic field, despite an absence of the zero field FE superconducting phase in the two- or three-band regime [Figs. 2(b) and 2(c)]. This magnetic-field-induced FE superconductivity originates from the anomalous Pauli depairing effect in noncentrosymmetric superconductors \[43–47\]. In Rashba superconductors, the Pauli depairing effect is suppressed under a magnetic field parallel to the polar axis. This is because the BCS-type depairing effect is possible even under the magnetic field thanks to the Rashba-type spin-momentum locking. To avoid the Pauli depairing effect superconductivity induces the FE order giving rise to the Rashba ASOC, and then the upper critical field is enhanced compared to the PE state.

In particular, the enhancement of the upper critical field is remarkable in the single-band regime [Fig. 2(a)]; \(\mu_B H/T_c \sim 5.5\) far exceeds the Pauli limit \(\sim 1.25\). This is owing to the Lifshitz transition and the multiorbital effect. In this carrier density, the free energy is minimized at a large value of \(\gamma\) so that the Lifshitz transition of the lower band occurs. Consequently, the first-order FE transition occurs at the same time as the superconducting transition. In addition, the spin-orbit splitting of the lower band particularly becomes large around the \(\Gamma\)-point thanks to the multiorbital effect [see Fig. 3(b)] and derivation of the Rashba ASOC in Supplemental Material \[33\]. This is in contrast to conventional single-orbital Rashba model which shows small spin-orbit splitting near the \(\Gamma\)-point. Therefore, the Rashba spin-orbit splitting
with energy
where the wave function of a Bogoliubov quasiparticle rounds the above Weyl nodes with opposite Weyl charges. In a two-dimensional Rashba superconductor, a gapped topological superconducting state in class D can be realized under a perpendicular magnetic field \[ H_z \] in the single-, two-, and three-band regime, overwritten on the magnitude of spin-orbit splitting. Color of Fermi surfaces corresponds to the colored lines in (a).

As a consequence of the drastically enhanced upper critical field, the dilute superconducting state in STO may realize a topological Weyl superconductor. In a two-dimensional Rashba superconductor, a gapped topological superconducting state in class D can be realized under a perpendicular magnetic field \[ H_z \]. In our three dimensional case, a Weyl superconducting state, which is characterized by topologically-protected Weyl nodes, is realized in the FE phase for a wide range of the magnetic field along the polar axis. We identify Weyl nodes by calculating \( k_z \)-dependent Chern number,

\[
\nu(k_z) = \frac{1}{2\pi} \int dk_x dk_y F_z(k),
\]
on a two-dimensional \( k_x-k_y \) plane. The Berry flux \( F_a(k) \) is defined as

\[
F_a(k) = -i\epsilon^{abc} \sum_{E_m(k)<0} \partial_{k_b} \langle u_m(k)|\partial_{k_a} u_m(k) \rangle,
\]
where the wave function of a Bogoliubov quasiparticle with energy \( E_m(k) \) is denoted as \( |u_m(k)\rangle \). Since a jump in \( \nu(k_z) \) is equivalent to the sum of Weyl charges at \( k_z \), we can detect Weyl charges by counting point nodes and comparing it with the jump. As shown in Fig. (1b), the Chern number jumps by +1 and −4. Thus, we identify five pairs of Weyl nodes [Fig. 4(b)]. One of them is located at poles of the Fermi surface. The rest of Weyl nodes, which are protected by \( C_4 \) symmetry, surrounds the above Weyl nodes with opposite Weyl charges. These four pairs of Weyl nodes arise as a consequence of the anisotropic Fermi surfaces due to the multiorbital effect. Therefore, a Weyl superconducting state with Chern number \( \nu(k_z) = (+1) \times 1 + (-1) \times 4 = -3 \) is obtained. Thus, multiorbital nature of STO leads to topological property distinct from the single-orbital topological Rashba superconductor with Chern number \( \nu = \pm 1 \) \[48, 49\]. It gives rise to three Majorana arcs in the surface state, and the zero-field thermal conductivity \( \kappa_{xy} \sim T \int dk_z \nu(k_z) \) \[52\] in STO should be larger than that in the single-orbital Rashba model.

In summary, we have studied an interplay of FE order and superconductivity in STO. In particular, we have proposed that the FE superconductivity is realized in STO near a FE transition point. The superconductivity triggers the coexisting FE order. A key ingredient is the Rashba ASOC in the FE phase. By analyzing the realistic three-orbital model, we showed that the zero field FE superconductivity is stabilized only in the dilute regime where the Lifshitz transition of the lower band can be induced by the ferroelectricity. This result is consistent with the experimental observation in Sr\(_{1-x}\)Ca\(_x\)TiO\(_3\)-δ \[21\], which indicates the FE superconducting phase only in a dilute carrier density regime. Furthermore, we revealed that the FE superconducting state is stabilized under a magnetic field independent of the number of Fermi surfaces. This magnetic-field-induced phase appears because of the suppression of the Pauli depairing effect thanks to the Rashba-type spin-momentum locking. Consequently, the upper critical field is enhanced by the FE transition. The upper critical field is particularly large in the dilute carrier density regime, because the multiorbital effect leads to a large spin-orbit splitting distinct from the conventional Rashba model. Furthermore, the high magnetic field region of dilute superconducting STO is identified as a Weyl superconducting state. This topological phase transition is realized as a result of the multiorbital effect and Lifshitz transition, in sharp contrast to the two-dimensional single-orbital model where the FE topological superconductivity is unstable \[41\].

The results of this paper suggest a tunable crystal...
symmetry through superconductivity, in the presence of a coupling between spin, orbital, and lattice degrees of freedom. Most of the novel interplay of ferroelectricity and superconductivity was uncovered in the dilute carrier density region. The dilute superconductivity in STO provides a platform for the FE superconductivity.

ACKNOWLEDGMENTS

This work was supported by Grant-in Aid for Scientific Research on Innovative Areas J-Physics (JP15H05884)

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and Topological Materials Science (JP18H04225) from JSPS of Japan, and by JSPS KAKENHI Grants No. JP15H05745, JP15K05164, No. JP18H01178, and No. JP18H05227.
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Multiorbital Ferroelectric Superconductivity in doped SrTiO$_3$

S1. THREE-ORBITAL MODEL FOR STRONTIUM TITANATE

Here, we introduce a three-orbital tight-binding model describing the electronic structure of bulk SrTiO$_3$ (STO). Although STO is a cubic crystal at high temperatures, the low temperature phase is tetragonal owing to the antiferrodistortive (AFD) transition. The three-fold degeneracy of the $t_{2g}$ orbitals at the $\Gamma$-point is lifted by the spin-orbit coupling and the tetragonal crystal field for the AFD transition. Therefore, the three distinct band structure is formed in tetragonal STO, and it is reproduced by the following model:

\[ H_0 = H_{\text{kin}} + H_{\text{AFD}} + H_{\text{LS}}, \]  
\[ H_{\text{kin}} = \sum_k \sum_{l=yz, xz, xy} \sum_{\sigma=\uparrow, \downarrow} (\varepsilon_l(k) - \mu) c_{k,l\sigma}^\dagger c_{k,l\sigma}, \]  
\[ H_{\text{AFD}} = \Delta_T \sum_k \sum_{\sigma} c_{k,xy\sigma}^\dagger c_{k,xy\sigma}, \]  
\[ H_{\text{LS}} = \lambda \sum_i L_i \cdot S_i, \]

where $c_{k,l\sigma}$ is the annihilation operator for an electron with momentum $k$, orbital $l = yz, xz, xy$, and spin $\sigma = \uparrow, \downarrow$. The first term $H_{\text{kin}}$ is the kinetic-energy term of $t_{2g}$ orbitals including the chemical potential $\mu$. The single electron kinetic energy $\varepsilon_l(k)$ are described as

\[ \varepsilon_{yz}(k) = -2t_1 \cos k_y - 2t_1 \cos k_z - 2t_2 \cos k_x - 4t_3 \cos k_y \cos k_z, \]  
\[ \varepsilon_{xz}(k) = -2t_1 \cos k_x - 2t_1 \cos k_z - 2t_2 \cos k_y - 4t_3 \cos k_x \cos k_z, \]  
\[ \varepsilon_{xy}(k) = -2t_1 \cos k_x - 2t_1 \cos k_z - 2t_2 \cos k_y - 4t_3 \cos k_x \cos k_y. \]

The second term $H_{\text{AFD}}$ expresses the tetragonal crystal field for the AFD transition, which lifts the energy of the $d_{xy}$ orbital. The third term $H_{\text{LS}}$ represents the LS coupling of Ti ions. Although the intersite hybridization term has been generally considered for perovskite oxides \cite{S1} in addition to the above three terms, first-principles band calculations have shown that it is negligible in the bulk STO \cite{S2, S3, S4}. The band structure of tetragonal STO is reproduced by $H_{\text{kin}}, H_{\text{AFD}},$ and $H_{\text{LS}}$ with the parameter set listed in Table S1. In addition, we introduce the odd-parity hybridization term

\[ H_{\text{pol}} = \sum_k \sum_{\sigma} \sum_{l=yz,zx} \zeta_l(k) c_{k,l\sigma}^\dagger c_{k,xy\sigma} + \text{H.c.}, \]

(S8)

to describe the effect of the polar inversion symmetry breaking due to ferroelectricity along the [001] axis. Here, $\zeta_{yz,zx}(k) = 2i\gamma \sin k_{xy}$. To study the superconductivity in STO, we consider an attractive interaction as follows:

\[ H_{\text{pair}} = \frac{1}{2N} \sum_{k, k', q, l', \sigma, \sigma'} V_{l', l}^{\sigma\sigma'}(k, k') c_{k, l\sigma}^\dagger c_{k, l'\sigma'}^\dagger c_{-k-q, l'\sigma'}^\dagger c_{k-q, l\sigma}, \]

(S9)

where $N$ is the number of Ti sites, and $q$ is the center-of-mass momentum of Cooper pairs. Since the $s$-wave superconductivity in STO has been confirmed \cite{S2}, we assume momentum-independent intraorbital pairing interaction $V_{ll'}^{\sigma\sigma'}(k, k') = -V_s \delta_{ll'} \delta_{\sigma\sigma'}$. Here, we neglect the interorbital pairing because the interorbital interaction is generally weak. Furthermore, we ignore the parity mixing of Cooper pairs in the ferroelectric (FE) phase, since the stability of FE superconductivity is hardly affected by an induced $p$-wave component.

The impact of the applied magnetic field is included as the Zeeman coupling term,

\[ H_Z = -\mu_B \sum_k \sum_{l} \sum_{\sigma, \sigma'} H \cdot \sigma_{\sigma\sigma'} c_{k, l\sigma}^\dagger c_{k, l\sigma'}, \]

(S10)

where $\sigma$ is the Pauli matrix and $\mu_B$ is the Bohr magneton. In the superconducting STO, the superfluid density $n_s$ is small \cite{S6}, and hence the penetration depth $\lambda_L \propto n_s^{-1/2}$ is large. Thus, STO is a superconductor near type-II limit.
TABLE S1. Model parameters for bulk SrTiO$_3$. We choose the unit of energy as $t_1 = 1$. The values of $\Delta_T$ and $\lambda$ are set to be larger than the literature values [S2, S3, S4] for simplicity of the numerical calculations. The value of $\gamma$ at the SrTiO$_3$/LaAlO$_3$ interface [S4] is also shown for reference.

|                | $t_1$ | $t_2$ | $t_3$ | $\Delta_T$ | $\lambda$ | $\gamma$ |
|----------------|-------|-------|-------|------------|-----------|----------|
| Literature values [S2, S3, S4] | 277 meV | 31 meV | 76 meV | 3.2 meV | 12 meV | 20 meV (SrTiO$_3$/LaAlO$_3$) |
| This paper     | 1     | 0.11  | 0.27  | 0.03       | 0.12      | $\lesssim 0.20$ |

with $\kappa \gg 1$, where $\kappa$ is the Ginzburg-Landau parameter. Therefore, it is justified to assume a uniform magnetic field in the bulk superconducting STO. It would be desirable to include the gauge interaction with the vector potential in addition to the Zeeman coupling term $H_Z$. The importance of the orbital depairing effect is determined by the Maki parameter $\alpha_M \propto \Delta/\epsilon_F$, where $\Delta$ is the superconducting gap and $\epsilon_F$ is the Fermi energy. When $\alpha_M > 1$, the orbital depairing effect is suppressed and the superconducting state is destroyed mainly due to the Pauli depairing effect. In the superconducting STO, $\epsilon_F$ is extremely small and hence $\alpha_M$ can be large. Thus, we assume that the orbital depairing effect is not qualitatively important in the dilute superconducting STO. Indeed, the upper critical field exceeding the Pauli limit in Sr$_{1-x}$Nd$_x$TiO$_3$ [S7] indicates the strong impact of the Pauli depairing effect on the superconducting STO.

S2. MEAN-FIELD THEORY FOR SUPERCONDUCTIVITY

We investigate the superconductivity in STO by means of the mean-field theory. In the following discussion, we fix $q = 0$ since Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) superconductivity with finite $q$ is not stabilized in our model when the magnetic field is applied along the polar axis. The pairing interaction $H_{\text{pair}}$ is approximated as

$$H_{\text{pair}} = \frac{V_s}{N} \sum_{k,k'} \sum_l c_{k,l\uparrow}^\dagger c_{-k',l\downarrow} c_{-k',l\uparrow} c_{k,l\downarrow} + H.c.$$  \hspace{1cm} (S11)

$$\approx \sum_k \sum_l \left( \Delta_l c_{k,l\uparrow}^\dagger c_{-k,l\downarrow}^\dagger + H.c. \right) + N \sum_l \frac{|\Delta_l|^2}{V_s},$$  \hspace{1cm} (S12)

by introducing the orbital-dependent superconducting order parameters,

$$\Delta_l = -\frac{V_s}{N} \sum_k \langle c_{-k,l\downarrow}^\dagger c_{k,l\uparrow} \rangle \quad (l = yz, xz, xy).$$  \hspace{1cm} (S13)

To describe the total Hamiltonian $H = H_0 + H_{\text{pol}} + H_Z + H_{\text{pair}}$ in a matrix form, we define the vector operator as follows:

$$\hat{C}_k^\dagger = (c_{k,yz\uparrow}^\dagger, c_{k,xz\uparrow}^\dagger, c_{k,xy\uparrow}^\dagger, c_{k,yz\downarrow}^\dagger, c_{k,xz\downarrow}^\dagger, c_{k,xy\downarrow}^\dagger, c_{-k,yz\uparrow}, c_{-k,xz\uparrow}, c_{-k,xy\uparrow}, c_{-k,yz\downarrow}, c_{-k,xz\downarrow}, c_{-k,xy\downarrow}).$$  \hspace{1cm} (S14)

Then, we obtain the mean-field Hamiltonian in the matrix form

$$\hat{H} = \frac{1}{2} \sum_k \hat{C}_k^\dagger \hat{H}_{\text{BdG}}(k) \hat{C}_k + E_c,$$  \hspace{1cm} (S15)

$$E_c = N \sum_l \frac{|\Delta_l|^2}{V_s} + \sum_k \sum_l \langle \epsilon_l(k) - \mu \rangle.$$  \hspace{1cm} (S16)

The Bogoliubov-de Gennes (BdG) Hamiltonian $\hat{H}_{\text{BdG}}(k)$ is described as

$$\hat{H}_{\text{BdG}}(k) = \begin{pmatrix} \hat{H}_N(k) & \hat{\Delta} \\ \hat{\Delta}^\dagger & -\hat{H}_N(-k) \end{pmatrix},$$  \hspace{1cm} (S17)
Thus, Eq. (S13) is rewritten as

\[ \hat{H}_n(k) = \begin{pmatrix} \xi_{yz}(k) - h_z & i\lambda/2 & \xi_{yz}(k) & 0 & 0 & -\lambda/2 \\ -i\lambda/2 & \xi_{xz}(k) - h_z & \xi_{xy}(k) + \Delta_T & 0 & 0 & i\lambda/2 \\ \xi_{yz}^*(k) & \xi_{xz}^*(k) & \xi_{xy}(k) + \Delta_T - h_z & \lambda/2 & -i\lambda/2 & 0 \\ 0 & 0 & \lambda/2 & \xi_{yz}(k) + h_z & -i\lambda/2 & \xi_{yz}(k) \\ 0 & 0 & i\lambda/2 & \xi_{xy}(k) + h_z & \xi_{xz}(k) & \xi_{xz}(k) \\ -\lambda/2 & -i\lambda/2 & 0 & \xi_{yz}(k) & \xi_{xy}(k) + \Delta_T + h_z \end{pmatrix} \), \quad (S18)

and the pairing part

\[ \hat{\Delta} = \begin{pmatrix} 0 & 0 & 0 & \Delta_{yz} & 0 & 0 \\ 0 & 0 & 0 & \Delta_{xz} & 0 & 0 \\ -\Delta_{yz} & 0 & 0 & 0 & 0 & \Delta_{xy} \\ 0 & -\Delta_{xz} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\Delta_{xy} & 0 & 0 & 0 \end{pmatrix}. \quad (S19)\]

Here, we abbreviate as \( \xi_i(k) \equiv \xi_i(k) - \mu \) and \( h_z \equiv \mu_0 H_z \).

Then, we carry out the Bogoliubov transformation as follows:

\[ c_{k,\nu} = \sum_{\tau} \sum_{\sigma} \left( u_{k,\nu}^{(\nu \tau)} \alpha_{k,\nu \tau} + u_{-k,\nu}^{(\tau \nu)} \alpha_{-k,\nu \tau} \right), \quad (S20) \]
\[ c_{-k,\nu}^\dagger = \sum_{\tau} \sum_{\sigma} \left( u_{k,\nu}^{(\nu \tau)} \alpha_{k,\nu \tau}^\dagger + u_{-k,\nu}^{(\tau \nu)} \alpha_{-k,\nu \tau}^\dagger \right). \quad (S21) \]

Thus, Eq. (S13) is rewritten as

\[ \Delta_l = -\frac{V_s}{N} \sum_k \sum_\sigma \sum_\nu \sum_{\tau} \sigma \nu_{k,\nu \tau}^\dagger \nu_{k,\nu \tau} f[\sigma E_{\nu \tau}(k)] \quad (l = yz, xz, xy), \quad (S22) \]

where \( f[E] \) is the Fermi-Dirac distribution function and \( E_{\nu \tau}(k) \) is the energy of a Bogoliubov quasiparticle with momentum \( k \), pseudobond \( \nu = yz, xz, xy \), and pseudospin \( \tau = \uparrow, \downarrow \). Equations (S22) are the simultaneous gap equations to be solved numerically. In the Bogoliubov quasiparticle picture, the total Hamiltonian is described as

\[ \mathcal{H} = \sum_k \sum_\nu \sum_{\tau} E_{\nu \tau}(k) \left( \alpha_{k,\nu \tau}^\dagger \alpha_{k,\nu \tau} - \frac{1}{2} \right) + E_c. \quad (S23) \]

Therefore, the free energy per Ti site is obtained as

\[ \mathcal{F}_{\text{ele}}[\Delta] = (\Delta_{yz}, \Delta_{xz}, \Delta_{xy}), P] = -\frac{1}{N\beta} \sum_k \sum_\nu \sum_{\tau} \left[ \ln \left( 1 + e^{-\beta E_{\nu \tau}(k)} \right) + \frac{\beta E_{\nu \tau}(k)}{2} \right] + \frac{E_c}{N} + \mu n, \quad (S24) \]

where \( \beta = 1/T \) is the inverse temperature. The last term of Eq. (S24) is necessary since the carrier density of the system is fixed as \( n \). Using \( \Delta_{yz}, \Delta_{xz}, \Delta_{xy} \) obtained by solving Eqs. (S22), we calculate the electronic part of the free energy \( \mathcal{F}_{\text{ele}}[\Delta, P] \) from Eq. (S24).

**S3. Lattice Polarization and Ferroelectric Instability**

In order to discuss the stability of the FE order, we take into account the free energy arising from the polar lattice distortion as follows:

\[ \mathcal{F}_{\text{lat}}[P] = \frac{1}{2} \kappa_2 P^2 + \frac{1}{4} \kappa_4 P^4 + \frac{1}{6} \kappa_6 P^6, \quad (S25) \]

where \( \kappa_2, \kappa_4, \) and \( \kappa_6 \) are the lattice parameters which describe the elasticity of the lattice.
The total free energy including the contributions of both electrons and lattice is given by

$$F[\Delta, P] = F_{\text{ele}}[\Delta, P] + F_{\text{lat}}[P].$$

(S26)

The thermodynamically stable state is determined by minimizing the free energy $F[\Delta, P]$ with respect to $\Delta$ and $P$. All the $\kappa_2$, $\kappa_4$, and $\kappa_6$ are phenomenological parameters and assumed as follows. The choice of $\kappa_4$ and $\kappa_6$ hardly alters the results of this paper. The lattice parameters $\kappa_4$ and $\kappa_6$ are introduced to cut off the value of the obtained FE order parameter $P \propto \gamma$ in a realistic regime. In this study, we set $\kappa_4$ and $\kappa_6$ to satisfy $\gamma/t_1 \lesssim 0.20$ in agreement with the first principles calculation of $\gamma$ at the SrTiO$_3$/LaAlO$_3$ interface [S4]. The value of $\kappa_2$ is determined so as to realize a paraelectric (PE) normal state near a FE phase transition point. The temperature dependence of the lattice parameters is ignored, consistent with the fact that the dielectric constant is almost temperature-independent in the quantum PE STO [S5].

### Table S2. Lattice parameters adopted for the phase diagrams in the main text [Fig. 2].

|       | $n$       | $\kappa_2$    | $\kappa_4$ | $\kappa_6$ |
|-------|-----------|---------------|------------|------------|
| Fig. 2(a) | $5.0 \times 10^{-5}$ | $6.75 \times 10^{-5}$ | 0          | 0.50       |
| Fig. 2(b) | $3.2 \times 10^{-3}$ | $1.00 \times 10^{-2}$ | 0          | 0          |
| Fig. 2(c) | $1.8 \times 10^{-2}$ | $5.30 \times 10^{-2}$ | 0          | 0          |

### S4. Multiple Lifshitz Transitions and Superconductivity

In this section, we discuss the ferroelectricity-induced Lifshitz transition and its effect on superconductivity in details. Figure S3 shows the density of states (DOS) at the Fermi energy $\rho(0)$ as a function of $\gamma$. In the single-band regime ($n = 5.0 \times 10^{-5}$), $\rho(0)$ is maximized at the Lifshitz transition point of the lowest band $\gamma = \gamma_{c1}$ [Fig. S1(a)], thanks to the effective reduction of the dimensionality [S9]. Consequently, the superconductivity is enhanced at the Lifshitz transition point $\gamma_{c1}$ as shown in Fig. S2(a). This enhanced superconductivity is the origin of the zero field FE superconductivity in the dilute region. Figure S3(b) shows the $\gamma \propto P$ dependence of the FE superconducting condensation energy $\delta F[\Delta, P] = F[\Delta, P] - F[0, 0]$ for various values of the cutoff lattice parameter $\kappa_6$. We see that the stabilization condition of the FE superconducting state, i.e., $\delta F[\Delta, P] < \delta F[\Delta, 0] < 0$, is satisfied in a wide range of lattice parameters, although the normal state is PE [see Fig. S3(a)]. This means that the FE superconductivity is stable at zero magnetic field in the dilute region. Furthermore, the large condensation energy $|\delta F[\Delta, P]|$ is one of the origins of the large upper critical field in the dilute region.

Next, we discuss the effects of Lifshitz transitions of the middle and upper bands. When the Fermi energy in the PE phase is slightly higher than the bottom of the bands, the Lifshitz transition is induced by the ferroelectricity. However, we see that these Lifshitz transitions are not significantly reflected in the total DOS $\rho(0)$ [Figs. S1(b) and

**FIG. S1.** DOS at the Fermi energy $\rho(0)$ as a function of the odd-parity hopping integral $\gamma$. The partial DOS for the Rashba split $t_{2g}$ bands are also shown. The black dashed vertical lines express the Lifshitz transition point. Different colored regions indicate different phases which are distinguished by the Lifshitz transitions. The colors correspond to the background colors in Fig. 1 of the main text. The carrier density is set to (a) $n = 5.0 \times 10^{-5}$, (b) $n = 2.0 \times 10^{-4}$, and (c) $n = 1.0 \times 10^{-2}$, respectively.
FIG. S2. (a) Orbital-dependent superconducting order parameters as a function of the odd-parity hopping integral $\gamma$. The carrier density is set to $n = 5.0 \times 10^{-5}$, i.e., a single-band regime. The temperature and magnetic field are set to $T = 1.0 \times 10^{-10}$ and $H = 0$, respectively. The vertical black dashed line shows the Lifshitz transition point. (b) and (c) The Fermi surfaces at $k_x = 0$ with (b) $\gamma = 0.050t_1 < \gamma_{c1}$ and (c) $\gamma = 0.135t_1 > \gamma_{c1}$.

FIG. S3. The free energy as a function of the odd-parity hopping integral $\gamma$ for several values of the cutoff lattice parameter $\kappa_6$. The carrier density is set to $n = 5.0 \times 10^{-5}$, i.e., a single-band regime. The temperature and magnetic field are set to $T = 1.0 \times 10^{-10}$ and $H = 0$, respectively. The black dashed vertical line shows the Lifshitz transition point. (a) $\gamma \propto P$ dependence of $\delta F[0, P] = F[0, P] - F[0, 0]$. Since $\delta F[0, P] > 0$ is satisfied in the whole range of $\kappa_6$, the PE normal state is realized. (b) $\gamma \propto P$ dependence of $\delta F[\Delta, P] = F[\Delta, P] - F[0, 0]$. The stabilization condition of the FE superconducting state, i.e., $\delta F[\Delta, P] < \delta F[\Delta, 0] < 0$, is satisfied under the red horizontal line.

Although the partial DOS for the middle or upper band is enhanced as approaching to the Lifshitz transitions, the contribution of the partial DOS is very small compared to that of the lower band. Therefore, the total DOS $\rho(0)$ is not drastically enhanced by these Lifshitz transitions, and hence the FE superconducting state is hardly stabilized at zero magnetic field in relatively high carrier density two- or three-band regimes.

S5. MULTIOBJECTAL EFFECT FOR RASHBA SPIN-ORBIT SPLITTING

Here, we investigate the multiorbital effect for the Rashba spin-orbit splitting in the FE STO. We elucidate the nature of the Rashba antisymmetric spin-orbit coupling (ASOC) by calculating the energy spectrum in the normal state $E_m(k)$ for $m < m'$. In the absence of the inversion symmetry ($\gamma = 0$), the two-fold degeneracy holds as $E_1(k) = E_2(k)$, $E_3(k) = E_4(k)$, and $E_5(k) = E_6(k)$. On the other hand, Rashba-type spin-orbit splitting is induced by the polar inversion symmetry breaking ($\gamma \neq 0$) as $E_1(k) < E_2(k)$, $E_3(k) < E_4(k)$, and $E_5(k) < E_6(k)$ except at the time-reversal invariant momentum. Figures S3(a), S3(b) and S3(c) show the magnitude of the spin-orbit splitting $\delta E_{\alpha}(k) = E_{2\alpha}(k) - E_{2\alpha-1}(k)$ ($\alpha = 1, 2, 3$) and the direction of the $g$-vector $g_{\alpha}(k) = \delta E_{\alpha}(k)S_{\alpha}(k)$ for each Rashba split bands at $k_z = 0$. Note that the lower, middle, and upper bands are denoted by $\alpha = 1$, 2, and 3, respectively.
Spin direction of each Rashba split bands is calculated by taking the average $S_\alpha(k) = \langle \sum_m \sum_{\sigma,\sigma'} \sigma_{\sigma'} c_{k,m\sigma}^\dagger c_{k,m\sigma'} \rangle_\alpha$ for the wave function of the $\alpha$-th band. We see that the $k$-dependence of the Rashba spin-orbit splitting in STO is completely different from that of the conventional Rashba ASOC with $g(k) = (\sin k_y, -\sin k_x, 0)$ [Fig. S4(d)]. The spin-orbit splitting in the lower band is large at $k$ slightly away from the $\Gamma$-M line, whereas that in the middle or upper band is large at $k$ slightly away from the $\Gamma$-X line. In particular, the spin-orbit splitting in the lower band is maximized near the $\Gamma$-point where the spin-orbit splitting of the conventional Rashba ASOC is tiny. Moreover, the $g$-vectors of the lower and middle bands are almost parallel to the [100] or [010] axis, and rapidly rotates by $\pi/2$ at the $\Gamma$-M line. In the following discussion, we clarify the origin of this unconventional Rashba ASOC by deriving the effective Hamiltonian from two approaches.

### A. Perturbation analysis for LS coupling

First, we carry out the perturbation analysis for the LS coupling $\lambda$ and the odd-parity hybridization $\gamma$. This analysis is valid when $\lambda$ is much smaller than other energy scales such as the band-width. As a result of the first-order
FIG. S5. The magnitude of the spin-orbit splitting, which is derived by the perturbation analysis for λ and γ, in the (a) lower band, (b) middle band, and (c) upper band at $k_z = 0$. The odd-parity hopping integral is set to $\gamma/t_1 = 0.105$. The arrows show the direction of the effective $g$-vector $g^\nu(k)$.

perturbation expansion for $\lambda$, we obtain a new $k$-dependent basis as follows:

$$
|k, d_{yz}, \uparrow\rangle = |d_{yz}, \uparrow\rangle + \frac{\lambda}{2} \left( \frac{|d_{xy}, \downarrow\rangle}{\delta_{xy-yz}(k) + \Delta_T} + i \frac{|d_{xz}, \uparrow\rangle}{\delta_{xz-xz}(k) + \Delta_T} \right),
$$

(S27)

$$
|k, d_{xz}, \uparrow\rangle = |d_{xz}, \uparrow\rangle + \frac{\lambda}{2} \left( \frac{i |d_{xy}, \downarrow\rangle}{\delta_{xy-yz}(k) + \Delta_T} + i \frac{|d_{yz}, \uparrow\rangle}{\delta_{xz-xz}(k) + \Delta_T} \right),
$$

(S28)

$$
|k, d_{xy}, \uparrow\rangle = |d_{xy}, \uparrow\rangle + \frac{\lambda}{2} \left( \frac{|d_{yz}, \downarrow\rangle}{\delta_{xy-yz}(k) + \Delta_T} + i \frac{|d_{xz}, \downarrow\rangle}{\delta_{xz-xz}(k) + \Delta_T} \right),
$$

(S29)

$$
|k, d_{yz}, \downarrow\rangle = |d_{yz}, \downarrow\rangle - \frac{\lambda}{2} \left( \frac{|d_{xy}, \uparrow\rangle}{\delta_{xy-yz}(k) + \Delta_T} + i \frac{|d_{xz}, \downarrow\rangle}{\delta_{xz-xz}(k) + \Delta_T} \right),
$$

(S30)

$$
|k, d_{xz}, \downarrow\rangle = |d_{xz}, \downarrow\rangle - \frac{\lambda}{2} \left( \frac{i |d_{xy}, \uparrow\rangle}{\delta_{xy-yz}(k) + \Delta_T} - i \frac{|d_{yz}, \downarrow\rangle}{\delta_{xz-xz}(k) + \Delta_T} \right),
$$

(S31)

$$
|k, d_{xy}, \downarrow\rangle = |d_{xy}, \downarrow\rangle - \frac{\lambda}{2} \left( \frac{|d_{yz}, \downarrow\rangle}{\delta_{xy-yz}(k) + \Delta_T} - i \frac{|d_{xz}, \downarrow\rangle}{\delta_{xz-xz}(k) + \Delta_T} \right),
$$

(S32)

where $|t_{2g}, \uparrow\rangle (t_{2g} = d_{yz}, d_{xz}, d_{xy}, \sigma = \uparrow, \downarrow)$ is the wave function of the local $t_{2g}$ orbitals and $\delta\varepsilon_{l-l'}(k) \equiv \varepsilon_l(k) - \varepsilon_{l'}(k)$. Then, we carry out the $k$-dependent basis transformation for $H_0 + H_{pa}$ from the local $t_{2g}$ orbital space $|t_{2g}, \sigma\rangle$ to the renormalized $t_{2g}$ orbital space $|k, t_{2g}, \sigma\rangle$. In addition, we perform a block diagonalization for up and down pseudospin sectors to derive the effective ASOC. Finally, we neglect the interorbital component since the orbital hybridizations by $\lambda$ and $\gamma$ are assumed to be small. Thus, in the case of a weak spin-orbit coupling, the effective Hamiltonian is described as

$$
\hat{H}_0^k = \sum_k \sum_{\alpha=1,2,3} \sum_{\sigma=\uparrow,\downarrow} \left( \varepsilon_{l}^\alpha(k) - \mu \right) c_{k,\alpha\sigma}^\dagger c_{k,\alpha\sigma} + \sum_k \sum_{\alpha, \alpha'} \sum_{\sigma, \sigma'} g_{l}^\nu(k) \cdot \sigma_{\sigma'} c_{k,\alpha\sigma}^\dagger c_{k,\alpha'\sigma'}. 
$$

(S33)

Here, the renormalized energy dispersion $\varepsilon_{l}^\nu(k)$ and the effective $g$-vector $g_{l}^\nu(k)$ are obtained as follows:

$$
\varepsilon_{1}^l(k) = \{\varepsilon_{yz}(k) + \varepsilon_{xz}(k) - |\varepsilon_{xz-yz}(k)|\} / 2,
$$

(S34)

$$
\varepsilon_{2}^l(k) = \{\varepsilon_{yz}(k) + \varepsilon_{xz}(k) + |\varepsilon_{xz-yz}(k)|\} / 2,
$$

(S35)

$$
\varepsilon_{3}^l(k) = \varepsilon_{xy}(k) + \Delta_T,
$$

(S36)

$$
g_{1}^l(k) = 2\lambda \gamma \left[ \sin k_y \left( 1 - \frac{\text{sgn}[\delta\varepsilon_{xz-yz}(k)]}{\delta\varepsilon_{xy-xz}(k) + \Delta_T} \right), \right. \left. - \sin k_x \left( \frac{1}{\delta\varepsilon_{xy-yz}(k) + \Delta_T}, 0 \right) \right],
$$

(S37)

$$
g_{2}^l(k) = 2\lambda \gamma \left[ \sin k_y \left( 1 + \frac{\text{sgn}[\delta\varepsilon_{xz-yz}(k)]}{\delta\varepsilon_{xy-xz}(k) + \Delta_T} \right), \right. \left. - \sin k_x \left( \frac{1}{\delta\varepsilon_{xy-yz}(k) + \Delta_T}, 0 \right) \right],
$$

(S38)

$$
g_{3}^l(k) = -2\lambda \gamma \sin k_y \left( \frac{1}{\delta\varepsilon_{xy-xz}(k) + \Delta_T}, \right. \left. - \sin k_x \left( \frac{1}{\delta\varepsilon_{xy-yz}(k) + \Delta_T}, 0 \right) \right) .
$$

(S39)
The magnitude of the spin-orbit splitting, which is derived by the basis transformation to the total angular momentum space, in the (a) lower band, (b) middle band, and (c) upper band at $k_z = 0$. The odd-parity hopping integral is set to $\gamma/t_1 = 0.105$. The arrows show the direction of the effective $g$-vector $g_\eta(k)$.

Figure S5 shows the $k$-dependence of the effective $g$-vector $g_\eta(k)$ for each Rashba split bands at $k_z = 0$. We see that the unconventional Rashba spin-orbit splitting in the bulk STO [Fig. S4] is well reproduced by the above perturbation analysis.

According to Eqs. (S37), (S38), and (S39), the multiorbital effect is reflected in the ASOC through the energy difference $\delta\varepsilon_{L}(k)$ in two ways. One is the denominators, i.e., $\delta\varepsilon_{xy-yz}(k) + \Delta_T$ and $\delta\varepsilon_{xz}(k) + \Delta_T$, and the other is the numerator, i.e., $1 \pm \text{sgn}[\delta\varepsilon_{xz-yz}(k)]$. The origin of the unconventional Rashba splitting in the upper band $\delta\varepsilon_3(k)$ is explained by the former multiorbital effect in the denominator of Eq. (S39). The magnitude of $\delta\varepsilon_3(k)$ is small on the line $k \parallel [100]$ [Fig. S3(c)] since $\delta\varepsilon_{xy-yz}(k) + \Delta_T$ is large and the $y$ component of the $g$-vector $g_3(k)$ is small. On the other hand, a large $x$ component of $g_3(k)$ appears upon moving slightly away from the $\Gamma$-$X$ line because of the small value of its denominator $\delta\varepsilon_{xz}(k) + \Delta_T$. Thus, the spin-orbit splitting in the upper band is large at $k$ slightly away from the $\Gamma$-$X$ line as shown in Figs. S5(c) and S5(c).

The unconventional Rashba splitting in the lower and middle bands are explained by the combination of two multiorbital effects represented by the denominator and numerator of Eqs. (S37) and (S38). Since the denominators of Eqs. (S37) and (S38) are the same as those of Eq. (S39), the Rashba splitting different from that of the upper band originates from the numerator $1 \pm \text{sgn}[\delta\varepsilon_{xz-yz}(k)]$. The $k$-dependence of $1 \pm \text{sgn}[\delta\varepsilon_{xz-yz}(k)]$ at $k_z = 0$ is described as follows:

$$\eta_{\pm}(k_x, k_y) = 1 \pm \text{sgn}[\delta\varepsilon_{xz-yz}(k_x, k_y, k_z = 0)] = \begin{cases} 0 & (|k_x| \leq |k_y|) \\ 1 & (|k_x| = |k_y|) \\ 2 & (|k_x| \geq |k_y|) \end{cases} \quad \text{(S40)}$$

Since $\eta_-(k_x, k_y) = 0$ ($\eta_+(k_x, k_y) = 0$) in $|k_x| > |k_y|$ ($|k_x| < |k_y|$), the $x$ ($y$) component of $g_3(k)$ becomes zero. Thus, $g_3(k)$ is parallel to the $[100]$ or $[010]$ axis in the most region of Brillouin zone, and rapidly rotates by $\pi/2$ when going across the line $|k_x| = |k_y|$ as shown in Figs. S4(a) and S5(a). Figure S5(a) also shows that the spin-orbit splitting is maximized near the $\Gamma$-point, and rapidly decreases by increasing the distance from the $\Gamma$-point. From similar discussions we understand that $g_3(k)$ is perpendicular to $g_T(k)$ except for the line $|k_x| = |k_y|$. Consequently, the Rashba splitting in the middle band becomes similar to that of the upper band, except the rapid $\pi/2$-rotation of the $g$-vector at $|k_x| = |k_y|$ [Figs. S4(b) and S5(b)].

### B. Total angular momentum description

Although the above perturbation analysis for the LS coupling reproduces many features of unconventional Rashba spin-orbit splitting in STO, it is not valid in the vicinity of the $\Gamma$-point. In particular, the disappearance of the spin-orbit splitting in the lower band near the $\Gamma$-point [Fig. S4(a)] is not reproduced by the perturbation analysis [Fig. S5(a)]. This is because the wave function is appropriately labeled by the total angular momentum $J = L + S$ and the perturbation analysis breaks down. Therefore, it is desirable to derive the effective ASOC in the total angular momentum description. Generally speaking, the following analysis is valid for the strong spin-orbit coupling compared to other energy scales such as the band-width. Actually, we will see that it is valid only near the $\Gamma$-point.
In the $t_{2g}$ orbital subspace, the orbital angular momentum can be treated as $L = 1$. Thus, the total angular momentum $J = 3/2$ or $J = 1/2$ are obtained as a composition of the angular momentum $L = 1$ and $S = 1/2$. The basis wave functions in the total angular momentum space $|J, M\rangle$ are obtained as follows:

\[
|\frac{3}{2}, \frac{3}{2}\rangle = -\frac{1}{\sqrt{2}} \left( |d_{yz}, \uparrow\rangle + i |d_{xz}, \downarrow\rangle \right),
\]

\[
|\frac{3}{2}, \frac{1}{2}\rangle = \frac{1}{\sqrt{6}} \left( 2 |d_{xy}, \uparrow\rangle - |d_{yz}, \downarrow\rangle - i |d_{xz}, \downarrow\rangle \right),
\]

\[
|\frac{3}{2}, -\frac{1}{2}\rangle = \frac{1}{\sqrt{6}} \left( |d_{yz}, \uparrow\rangle - i |d_{xz}, \downarrow\rangle + 2 |d_{xy}, \downarrow\rangle \right),
\]

\[
|\frac{3}{2}, -\frac{3}{2}\rangle = \frac{1}{\sqrt{2}} \left( |d_{yz}, \downarrow\rangle - i |d_{xz}, \downarrow\rangle \right),
\]

\[
|1, 1\rangle = \frac{1}{\sqrt{3}} \left( |d_{xy}, \uparrow\rangle + |d_{yz}, \downarrow\rangle + i |d_{xz}, \downarrow\rangle \right),
\]

\[
|1, -1\rangle = \frac{1}{\sqrt{3}} \left( |d_{xy}, \uparrow\rangle - |d_{xz}, \downarrow\rangle - |d_{yz}, \downarrow\rangle \right),
\]

where $M = \pm 3/2, \pm 1/2$ is the total magnetic quantum number. Then, we carry out the $k$-independent basis transformation for $\mathcal{H}_0 + \mathcal{H}_{\text{pol}}$ from the local $t_{2g}$ orbital space $|t_{2g}, \sigma\rangle$ to the total angular momentum space $|J, M\rangle$. From the procedure similar to the previous subsection, the effective Hamiltonian is derived as

\[
\hat{\mathcal{H}}_0' = \sum_k \sum_\alpha \sum_\sigma \varepsilon_\alpha' \langle k|\sigma \rangle + \sum_k \sum_\alpha \sum_{\sigma, \sigma'} g_\alpha' \langle k|\sigma \rangle \cdot \sigma \sigma' \rho_{\sigma, \sigma'} \langle k|\sigma \rangle.
\]

Here, the renormalized energy dispersion $\varepsilon_\alpha' \langle k|\sigma \rangle$ are obtained as follows:

\[
\varepsilon_1' \langle k|\sigma \rangle = \frac{\varepsilon_{yz}(k) + \varepsilon_{xz}(k) - \lambda}{2},
\]

\[
\varepsilon_2' \langle k|\sigma \rangle = \frac{\varepsilon_0(k) + \Delta_\sigma}{4} + \sqrt{2} \gamma \left( \sin^2 k_y + \sin^2 k_z \right) + \frac{\left( \delta\varepsilon_{xy-yz}(k) + \delta\varepsilon_{xy-xz}(k) + 2\Delta_\sigma - \lambda \right)^2}{4},
\]

\[
\varepsilon_3' \langle k|\sigma \rangle = \frac{\varepsilon_0(k) + \Delta_\sigma}{4} + \sqrt{2} \gamma \left( \sin^2 k_y + \sin^2 k_z \right) + \frac{\left( \delta\varepsilon_{xy-yz}(k) + \delta\varepsilon_{xy-xz}(k) + 2\Delta_\sigma - \lambda \right)^2}{4},
\]

where $\varepsilon_0(k) = \varepsilon_{yz}(k) + \varepsilon_{xz}(k) + \varepsilon_{xy}(k)$. The effective $g$-vector $g_\alpha' \langle k|\sigma \rangle$ are described as

\[
g_1' \langle k|\sigma \rangle = 0,
\]

\[
g_2' \langle k|\sigma \rangle = -g_3' \langle k|\sigma \rangle = -\frac{\lambda \gamma (\sin k_y, -\sin k_z, 0)}{\sqrt{2} \gamma \left( \sin^2 k_y + \sin^2 k_z \right) + \frac{\left( \delta\varepsilon_{xy-yz}(k) + \delta\varepsilon_{xy-xz}(k) + 2\Delta_\sigma - \lambda \right)^2}{4}},
\]

Interestingly, the spin-orbit splitting vanishes in the lower band, i.e., $g_1' \langle k|\sigma \rangle = 0$. The lower band is labeled by $J = 3/2$ and $M = \pm 3/2$ in the total angular momentum picture, and $|3/2, \pm 3/2\rangle$ do not contain the $d_{xy}$ orbital [see Eqs. (S41) and (S44)]. This means that the orbital parity mixing effect [S1], which is a necessary condition for the Rashba spin-orbit splitting, does not occur in the lower band. Therefore, there is no Rashba splitting in the lower band, and indeed, the Rashba splitting in the full Hamiltonian disappears near the $\Gamma$-point [Fig. S3a] where the total angular momentum description is valid. On the other hand, Eq. (S52) shows that the magnitude of Rashba splitting in the middle band is finite and same as that in the upper band, although the sign of the $g$-vector is opposite. The $k$-dependence of $g_2' \langle k|\sigma \rangle = -g_3' \langle k|\sigma \rangle$ is similar to that of the conventional Rashba ASOC with $g \langle k|\sigma \rangle = (\sin k_y, -\sin k_z, 0)$, except that the magnitude of the spin-orbit splitting is maximized around the $\Gamma$-point [Fig. S6]. These momentum dependences are different from the results of numerical diagonalization [Fig. S3]. This means that the perturbation analysis for the LS coupling is better at most $k$-points in the Brillouin zone.

**S6. ENHANCED UPPER CRITICAL FIELD IN DILUTE CARRIER DENSITY REGION**

In this section, we discuss an impact of the multiorbital electronic structure on the dilute superconductivity in STO. As shown in Sec. S3, unconventional Rashba ASOC is induced by ferroelectricity as a consequence of the multiorbital
FIG. S7. (a) The temperature dependence of the upper critical field $\mu_B H_{c2}$. The magnetic field is applied along the [001] axis. The green solid line (purple dashed line) shows the upper critical field calculated for the three-orbital model (simple Rashba model). The gray dotted line shows the upper critical field of the three-orbital model with Rashba model. The carrier density and odd-parity hopping integral are set to $n = 5.0 \times 10^{-3}$ and $\gamma/t_1 = 0.105$, respectively.

effect. Unlike the conventional Rashba effect, the Rashba splitting in the lower band is maximized near the $\Gamma$-point [Fig. S4(a)]. Thus, it is implied that the Pauli depairing effect in a dilute superconducting state with a tiny Fermi surface should be strongly suppressed compared to the case of a conventional Rashba superconductor.

To test the above expectation, we introduce a simple Hamiltonian with conventional Rashba ASOC as follows:

$$\hat{H} = \hat{H}_{\text{kin}} + \hat{H}_{\text{AFD}} + \hat{H}_{\text{ASOC}} + \hat{H}_{\text{pair}},$$

$$\hat{H}_{\text{ASOC}} = \lambda \sum_k \sum_{\sigma,\sigma'} \hat{c}_k^\dagger \sigma \sigma' \hat{c}_{k,l}\sigma \hat{c}_{k,l}\sigma',$$

where the $g$-vector is assumed as $g(k) = (\sin k_y - \sin k_x, 0)$ and diagonal in the orbital space. Based on the perturbation analysis for the LS coupling [see Eq. (S37)], we assume $\alpha = 2\lambda \gamma/t_1$ in the following discussion. Here, we compare this model with our three-orbital model for STO to illuminate the multiorbital effect which is appropriately taken into account in the latter. Figure S7(a) shows the temperature dependence of the upper critical field $\mu_B H_{c2}$ in the dilute single-band regime ($n = 5.0 \times 10^{-3}$). The magnetic field is applied along the polar [001] axis. In both models, the upper critical field of the noncentrosymmetric superconductivity with Rashba splitting (green solid line and purple dashed line) is enhanced compared to that of the centrosymmetric superconductivity without ASOC (gray dotted line). This is because the Pauli depairing effect is suppressed under the magnetic field parallel to the polar axis thanks to the Rashba-type spin-momentum locking [S10]. In addition, we see that the upper critical field of the three-orbital model for STO [Eq. (S1)] is larger than that of the simple Rashba model [Eq. (S53)]. The origin of this enhanced upper critical field can be attributed to the Fermi surface anisotropy and large spin-orbit splitting. As shown in Figs. S7(b) and S7(c), the Fermi surfaces of the lower band have $d_{x^2-y^2}$ like anisotropic $k$-dependence. On the other hand, the unconventional Rashba ASOC in the three-orbital model induces a large spin-orbit splitting in the lower band particularly along $k \parallel [100]$. Furthermore, the magnitude of the spin-orbit splitting is maximized near the $\Gamma$-point, where the Fermi surfaces in the dilute region are located [Fig. S7(b)]. Therefore, the upper critical field of the dilute superconducting state with $\gamma \neq 0$ is drastically enhanced thanks to the strong spin-momentum locking on the Fermi surface. In contrast, the conventional Rashba ASOC induces a tiny spin-orbit splitting around the $\Gamma$-point as shown in Fig. S7(c). There is no cooperative correlation between the Fermi surface anisotropy and the spin-momentum locking in the case of the simple Rashba model. Thus, the enhancement of the upper critical field by spin-orbit splitting is less pronounced than that in the three-orbital model.

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