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Strain-tunable ferroelectricity and its control of Rashba effect in KTaO$_3$

L. L. Tao and J. Wang$^{a)$}

Department of Physics and The Center of Theoretical and Computational Physics, The University of Hong Kong, Hong Kong, China

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The effects of epitaxial strain on the ferroelectric, structural properties of KTaO$_3$ are studied by means of first-principles calculations. We show that the ferroelectric polarization magnitude as well as the orientation can be tuned by an in-plane strain: the $c$-phase is energetically more stable than the $aa$-phase at a large compressive strain while a phase transition from $c$- to $aa$-phase is observed at a large tensile strain, owing to the significant polarization-strain coupling. More importantly, based on relativistic first-principles calculations, we demonstrate a large Rashba spin splitting in the strained KTaO$_3$. Interestingly, the spin textures in momentum space can be controlled and switched via polarization switching. Our tight-binding analysis indicates that the combination of spin-orbit coupling and ferroelectric distortion plays a key role for the observed Rashba spin splitting. Our results present some fundamental understanding of the interplay between Rashba effect and ferroelectricity in oxides and open avenues for nonvolatile spintronic device applications.

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I. INTRODUCTION

The Rashba effect, characterized by the momentum-dependent spin splitting of energy levels, has recently aroused a great interest due to the fascinating physics it displayed as well as the potential applications in spintronic devices. Generally, the Rashba effect is found on the surface of heavy metals, e.g., Au(111) and Ir(111), the surface of oxide, e.g., SrTiO$_3$(001), and heterojunction interfaces, e.g., InGaAs/InAlAs. Recently, a sizable Rashba effect was also observed in bulk materials with inversion asymmetry, such as BiTeI, ferroelectric (FE) GeTe and ferroelectric organic perovskites. It is known that the presence of both time-reversal symmetry $\epsilon_{kI} = \epsilon_{-kI}$ (eigenvalues) and spatial inversion symmetry $\epsilon_{kI} = \epsilon_{-kI}$ leads to the spin degeneracy $\epsilon_{kI} = \epsilon_{kI}$. The Rashba-like spin splitting can thus be expected in those materials with spatial inversion symmetry broken, namely, the potential $V(\vec{r}) \neq V(-\vec{r})$. Among those materials, FE materials are promising candidates to be exploited as novel spintronic devices due to the nonvolatile property of FE polarization as well as potential all-electric control of spin. Recently, giant Rashba effect was theoretically predicted in the FE semiconductor GeTe, and the spin textures can be fully controllable and switchable via the polarization switching. The similar phenomenon was also reported in other FE materials. In this regard, the FE Rashba semiconductors or insulators as a kind of novel multifunctional materials can be used to design new types of devices, such as nonvolatile spin-field-effect transistor and ferroelectric tunnel junctions.

It would be beneficial to find FE Rashba materials with both large polarization and strong spin-orbit coupling (SOC) for realization of controlling the spin via an electric field. Here we consider an appealing perovskite oxide-KTaO$_3$ (KTO). First, it was shown in the experiment that the strained KTO films exhibit significant FE effects. Secondly, unlike the widely used lead-related PbTiO$_3$, the lead-free KTO is one of the environment-friendly FE materials. Thirdly, KTO is a polar oxide that the two-dimensional electron (hole) gas can be naturally formed in the TaO$_2$-phase at a large compressive strain while a phase transition from $c$- to $aa$-phase is identified and the corresponding polarization was calculated. A large Rashba-like spin splitting in the strained KTO was observed. We also show that spin textures can be fully controllable by the FE polarization. The microscopic physics for FE-driven Rashba effect has been analyzed from a tight-binding (TB) model calculation.

II. COMPUTATIONAL METHOD AND DETAILS

Our atomic and electronic structure calculations were performed using the plane-wave ultrasoft pseudopotential method implemented in the Quantum Espresso package.

$^{a)$Electronic mail: jianwang@hku.hk
An energy cutoff of 680 eV and local density approximation (LDA)\textsuperscript{26} for the exchange and correlation functional were used throughout. Atomic relaxation was performed using a $10 \times 10 \times 10$ $k$-point mesh until the forces on each atom were smaller than 2.6 meV/Å. A dense, $20 \times 20 \times 20$, $k$-point mesh was used for the self-consistent calculations to obtain the total energies and electronic structures. We evaluated the FE polarization $P$ by using\textsuperscript{27,28}

$$P = \frac{1}{\Omega} \sum_{m} Z_{m}^{*} \delta z_{m},$$

where $\Omega$ is the unit-cell volume, $Z_{m}^{*}$ the Born effective charge of the $m$th atom, and $\delta z_{m}$ the displacement of the $m$th atom. The Born effective charges $Z_{m}^{*}$ were calculated using density functional perturbation theory.\textsuperscript{29} $Z_{m}^{*}$ for K, Ta, O, (TaO plane) and O$_{\parallel}$ (KO plane) ions in cubic KTO phase ($a_0 = 3.94 \text{ Å}$) are, respectively, 1.15, 8.62, 1.69, and 6.41 electrons. Note that the calculated $a_0 = 3.94 \text{ Å}$ agrees well with the previous results using LDA function.\textsuperscript{20,30}

III. RESULTS AND DISCUSSION

A. Strain-tunable ferroelectricity

We first present the strain tunable structural and FE properties. The epitaxial strain provides an efficient way to design artificial structures, which reveal rich physical properties. For example, paraelectric (PE)-to-ferroelectric transition in SrTiO$_3$ films can be triggered by an epitaxial strain.\textsuperscript{31,32} Fig. 1(a) shows the total energies and $c/a$ ratios of bulk KTO under different strains. The in-plane strain is defined as $(a - a_0)/a_0$, where $a$ ($a_0$) is the in-plane lattice constant of tetragonal (cubic) KTO. Fig. 1(b) shows the values of polarization for different phases as a function of strain. To find the most stable phase at each strain, we fully relaxed the atomic positions as well as the out-of-plane lattice constants starting from three possible phases:\textsuperscript{33} (i) the paraelectric $p$ phase ($P_x = P_y = P_z = 0$), (ii) the $c$ phase ($P_x = P_y = 0, P_z \neq 0$), and (iii) the $aa$ phase ($P_x = P_y \neq 0, P_z = 0$) and identified the minimum energy phase. First, the energy differences between different phases are negligible at small strains, indicating that no phase transition occurs, and KTO is in the stable $p$ phase. The strain dependency of $c/a$ is almost linear. As the tensile strain increases (exceeds 0.5%), a phase transition from $p$ to $aa$ phase occurs, characterized by the lower total energy and sizable polarization value $P_{110}$. On the other hand, with increase of the compressive strain (exceeds 1%), the stable $c$ phase appears, and a large polarization value $P_{001}$ is observed. Note that the similar strain-tunable phase transition was also predicted in strained BaZrO$_3$ by first-principles calculations.\textsuperscript{34} At large compressive (tensile) strain, the increase (decrease) of $c/a$ is significant. The polarization becomes larger than 40 $\mu$C/cm$^2$ at the compressive (tensile) strain of $-3.5\%$ ($3\%$), which is comparable to that of the strained BaTiO$_3$.\textsuperscript{19} It can be seen that an epitaxial strain can induce rich phase transitions and provide an efficient way to tune the polarization of KTO.

B. Rashba effect

We now investigate the Rashba effect in FE KTO. Fig. 2(a) shows the crystal structure and first Brillouin zone of $c$-phase KTO induced by the compressive strain of $-3.0\%$. Fig. 2(b) shows the fully relativistic band structure. We see that KTO is an indirect-band-gap insulator that the valence-band maximum (VBM) and conduction-band minimum (CBM) are located at the $M$ and $\Gamma$ point, respectively. Clearly, the spin splittings of bands along $\Gamma - X$ and $\Gamma - M$ directions are pronounced and are suppressed along the $\Gamma - Z$ direction. As highlighted by the red box, a zoom of conduction bands around the $\Gamma$ point reveals a Rashba-like band splitting, characterized by the distinct momentum offset. For those bands with a larger spin splitting effect, we calculate the expectation values of the spin operators $s_x$ ($x = x, y, z$) on the spinor wave-functions $\psi_{k\alpha}$, namely, $s_x = \frac{h}{2} \langle \psi_{k\alpha} | \sigma_x | \psi_{k\alpha} \rangle$. The in-plane spin textures ($s_x$ and $s_y$ components) of CBM bands near the $\Gamma$ point are shown in Figs. 2(c) and 2(d), while the $s_z$ component is negligible. The two branch bands show clearly the Rashba-like features with the spin orientation perpendicular to the momentum direction and the outer and inner branch bands having opposite spin textures. Intriguingly, the spin textures are fully reversed upon switching the polarization as evident by comparing Figs. 2(c) and 2(d). As for the $aa$-phase, KTO induced by a tensile strain, the polarization axis changes from [001] to
Hamiltonian as follows:

\[ H = \frac{p_x^2 + p_y^2}{2m_x^*} + \frac{p_z^2}{2m_z^*} + \frac{\hbar}{\ell} (\mathbf{p} \times \mathbf{z}) \cdot \mathbf{\sigma}, \]

where \( \sigma_R \) is the well-known Rashba coefficient, \( \hbar \) the reduced Planck’s constant, \( \mathbf{p} = (p_x, p_y, p_z) = \hbar \mathbf{k} \) the electron momentum, \( m_x^* (m_z^*) \) the electron mass in the \( xy \) plane (along the \( z \) axis), and \( \mathbf{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \) the Pauli spin matrices. For \( c \)-phase KTO, the polarization is along the \( z \) axis along which the inversion symmetry is broken. We find that the eigenenergies \( \epsilon_k \) and eigenstates \( \psi_k \) are, respectively, given by

\[ \epsilon_k = \frac{\hbar^2}{2m_{xy}^*} (k_x^2 + k_y^2) + \frac{\hbar^2}{2m_z^*} k_z^2 + |\sigma_R| \sqrt{k_x^2 + k_y^2}, \]

\[ \psi_k = \frac{1}{\sqrt{2}} \left( \begin{pmatrix} |\sigma_R| e^{ik_z} \\ 1 \end{pmatrix} \right) e^{i\mathbf{k} \cdot \mathbf{r}}, \]

where \( \tan(\gamma_k) = \frac{k_y}{k_x} \). Taking the upper branch \( (\epsilon_k^+, \psi_k^+) \) as an example, it is straightforward to obtain the expectation value of the spin operators \( \sigma_z \)

\[ \sigma_z = \frac{|\sigma_R|}{\hbar} \cos(\gamma_k), \quad \sigma_x = -\frac{|\sigma_R|}{\hbar} \sin(\gamma_k), \quad \sigma_z = 0. \]

We see that the spin orientations are determined by the Rashba coefficient \( \sigma_R \), which is directly related to the potential gradient resulting from the FE distortion. One can thus anticipate that the change of the sign of \( \sigma_R \) induced by switching polarization will result in the reversal of spin textures in the plane perpendicular to the polarization axis.

From the symmetry point of view, the reversal of spin textures induced by the polarization switching does not depend on the specific form of Hamiltonian.\(^{11}\) This is due to the fact that \( \langle \psi_k^- (\mathbf{F}) | \sigma | \psi_k^- (\mathbf{F}) \rangle = -\langle \psi_k^+ (\mathbf{F}) | \sigma | \psi_k^+ (\mathbf{F}) \rangle \),\(^{11}\)

We now analyze the physical origin of Rashba spin splittings observed in \( c \)-phase KTO from a tight-binding Hamiltonian. Take the case of \(-3.0\%\) strain, for example, we consider the following Hamiltonian:\(^{35-38}\)

\[ H = H_0 + H_{SO} + H_{\sigma}, \]

where the first and second terms are hopping and atomic SOC Hamiltonian, respectively. The third term arises due to the inversion symmetry broken. We consider the band dispersion along \( \Gamma - X \) direction, which is in the plane

FIG. 2. (a) Crystal structure and first Brillouin zone of bulk KTO. (b) Band structure with SOC for \( c \)-phase KTO (\(-3.0\%\) compressive strain) along the high symmetry lines \( \Gamma(0 0 0) - X(0.5 0 0) - M(0.5 0.5 0) - \Gamma(0 0 0) - Z(0 0 0.5) \). Inset: zoom of the band structure in the red box. (c) and (d) In-plane spin textures (\( \sigma_x \) and \( \sigma_y \)) near the \( X \) point for the CBM outer (left) and inner (right) branches. (c) for up polarization case and (d) for down polarization case, as denoted by the red arrows.

FIG. 3. Spin distribution (\( \sigma_z \) component) near the \( \Gamma \) point for the CBM outer (left) and inner (right) branches. (a) for \([110]\) polarization case and (b) for \([110]\) polarization case, as denoted by the red arrows. The bulk KTO is at the \( aa \) phase induced by a tensile strain of \( 3.0\%\).
perpendicular to the polarization axis. The hopping Hamiltonian $H_0$ in the Ta-$t_{2g}$ basis set reads

$$H_0 = \frac{\epsilon_{yz}}{V_{pdz}} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \otimes \sigma_0,$$

(6)

where $t$ and $t'$ are the hopping amplitudes between Ta-$t_{2g}$ orbitals and $\sigma_0$ is the $2 \times 2$ unit matrix. $t$ is the dominant $\pi_{pd}$ hopping, namely, $t = \frac{V_{pdz}}{\Delta_{pd}}$, where $V_{pdz}$ denotes the $\pi$-bond hopping between Ta-$d$ and O-$p$ orbitals, and $\Delta_{pd}$ is the corresponding energy difference. $t'$ describes the weaker $\pi_{dd}$ hopping. The hopping processes are schematically illustrated in Figs. 4(a) and 4(b). $\Delta$ denotes the energy difference between the $d_{xy}$ orbital and the degenerate $d_{yz}/dz$ orbital. The atomic SOC Hamiltonian $H_{SO}$ is given by

$$H_{SO} = \lambda_{SO} \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & -i & 1 & 0 \\ -i & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \otimes \sigma_0,$$

(7)

in the $\{|yz\}, |zx\}, |xy\}\otimes \{1, -1\}$ basis set, where $\lambda_{SO}$ is the atomic SOC strength. $H_\gamma$ comes from the FE distortion and can be expressed as

$$H_\gamma = 2\gamma \begin{pmatrix} 0 & 0 & -i \sin k_x & 0 \\ 0 & 0 & 0 & -i \sin k_y \\ -i \sin k_x & 0 & 1 & 0 \\ 0 & -i \sin k_y & 0 & 1 \end{pmatrix} \otimes \sigma_0,$$

(8)

in the $\{|yz\}, |zx\}, |xy\}$ basis set, where $\gamma$ is the hopping integral induced by FE polarization, $\gamma = \frac{V_{pd}V_{pd}}{\Delta_{pd}}$ and the hopping process is schematically illustrated in Fig. 4(c).

Fig. 5 shows the comparison between the DFT and tight-binding band structures for $c$-phase KTO ($-3.0\%$ strain). All tight-binding parameters obtained from the best fit to the DFT results are summarized in Table I. We see that $t$ ($t'$) is relatively reduced (increased) in $c$-FE structure.
The two-fold degenerate $C_{2v}$ band gap. This is expected due to the hopping between $d_{zy}$ and $d_{zx}$ orbitals induced by FE distortion, as highlighted by the red circles and the momentum space. From the tight-binding Hamiltonian of the BaTiO$_3$/BaOsO$_3$ heterostructure, the atomic SOC yielding the Rashba spin splittings was also reported in the DFT results. The combined effect of FE distortion and SOC, which agrees well with the presence of FE polarization as expected from the increase of hopping parameter $t$. We see that the band spin splittings only occur due to the coexistence of FE distortion and SOC, which agrees well with the DFT results. Overall, the TB model reproduces those DFT results very well. Again, we see that the band spin splittings only occur due to the coexistence of FE distortion and SOC, and the Rashba spin splittings are also reported in the BaTiO$_3$/BaOsO$_3$ heterostructure.

Now we investigate the Rashba spin splitting in the momentum space. From the tight-binding Hamiltonian of Eq. (5), the spin-resolved density of states (DOS) $s_x(E, k_x, k_y)$ ($x = y, z$) can be calculated as

$$s_x(E, k_x, k_y) = -\frac{\hbar}{2\pi} \text{Tr} \{\text{Im} [\sigma_x G'(E, k_x, k_y)] \} ,$$

where $\sigma_x$ is the Pauli spin matrices, and the Tr denotes the trace over the $t_{2g}$ orbitals. The retarded Green’s function $G'(E, k_x, k_y)$ is given by

$$G'(E, k_x, k_y) = [E + i\eta - H(k_x, k_y)]^{-1} ,$$

where $\eta$ is an infinitesimal energy. Fig. 6 shows the in-plane spin DOS $s_x = (s_x, s_y)$ distributions corresponding to different energy cuts. For an energy cut ($E_1$) near the CBM as shown in Fig. 6(a), the spin splitting is nearly isotropic in momentum space, and the spin is locked to the momentum revealing the nature of Rashba spin splitting, as evident from the circular shapes and green arrows. As we shall see later, the analytic effective Hamiltonian near the CBM is a Rashba form and the Rashba parameter is isotropic. For a higher energy cut ($E_2$) in Fig. 6(b), the spin splitting is anisotropic with a large splitting along the $\Gamma - X$ direction while the splitting is reduced along the $\Gamma - M$ direction. As expected, the anisotropic splitting reflects the four-fold rotational symmetry of tetragonal KTO whose point group is $C_{4v}$ (the electric axis is along the [001] direction). For an energy cut $E_3$ in Fig. 6(c), the anisotropic splitting is also observed, and the splitting is enhanced along the $\Gamma - M$ direction compared with that along the $\Gamma - X$ direction.

As stated above, the Rashba spin splitting is nearly isotropic near the CBM. In the following, we derive an effective Hamiltonian for the energy around the CBM. The effective Hamiltonian can be obtained by using L $\delta$ $\uparrow$ $\downarrow$ $\uparrow$ $\downarrow$ downfolding technique. Namely we can rewrite the Hamiltonian of Eq. (5) in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_S + \mathcal{H}_J = \begin{pmatrix} h_0 & \beta^T \hbar \end{pmatrix},$$

where

$$h_0 = \begin{pmatrix} \epsilon_{xy} & 0 \\ 0 & \epsilon_{xy} \end{pmatrix},$$

$$h_1 = \begin{pmatrix} \epsilon_{xz} & i\lambda_{SO} & 0 \\ 0 & \epsilon_{yz} & -i\lambda_{SO} \\ -i\lambda_{SO} & 0 & \epsilon_{xz} \end{pmatrix},$$

$$\beta = \begin{pmatrix} -i\gamma_1 \sin k_x & -\lambda_{SO} \\ \lambda_{SO} & -i\gamma_1 \sin k_y \\ i\lambda_{SO} & -i\gamma_1 \sin k_y \end{pmatrix}.$$
The effective Hamiltonian $H_{\text{eff}}$ in the $h_0$ subspace can be expressed as
\begin{equation}
H_{\text{eff}} = h_0 + \beta (E - h_1)^{-1} \beta. \tag{13}
\end{equation}
For small $k$, retaining the terms up to linear $k$, we get
\begin{equation}
H_{\text{eff}} = \Delta - 4t + \frac{2 \gamma_{\text{SO}}^2}{\Delta - 2(t - r)} + \frac{4 \gamma_{\text{SO}}}{\Delta - 2(t - r)} (k_x \sigma_y - k_y \sigma_x). \tag{14}
\end{equation}
The third term in $H_{\text{eff}}$ can be rewritten as the familiar Rashba form, namely, $\alpha_R (k \times \hat{z}) \cdot \vec{\sigma}$, with the Rashba coefficient $\alpha_R = \frac{4 \gamma_{\text{SO}}}{\Delta - 2(t - r)}$. We see that the Rashba coefficient is $k$ independent, that is, being isotropic in momentum space. This is in line with the numerical result in Fig. 5(a). Moreover, $\alpha_R$ is in proportion to $\gamma$ which is directly related to the FE polarization, indicating the feasibility of FE controlling Rashba effect. The fact that $\alpha_R$ in proportion to $\gamma_{\text{SO}}$ is in line with that the Rashba effect is due to the combined effect of SOC and FE distortion.

**IV. CONCLUSIONS**

In summary, we have demonstrated the coexistence of large FE polarization and Rashba effect in the strained KTO through the first-principles calculations. More intriguingly, the spin textures can be switchable via polarization switching, which can be used to design the nonvolatile spin-field-effect transistor.9 The analysis from a tight-binding model indicates that the FE polarization and SOC play crucial roles for the observed large Rashba spin splitting. Both the isotropic and anisotropic Rashba spin splittings in momentum space were observed from a tight-binding calculation. Our results provide an insight into the nature of FE-Rashba coupling in oxides and suggest an appealing FE Rashba material that can be exploited as novel all-electric spintronic devices.

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