Atomic-Scale Magnetic Toroidal Dipole under Odd-Parity Hybridization

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Magnetic toroidal dipole (MTD) is one of a fundamental constituent to induce magneto-electric effects in the absence of both spatial inversion and time-reversal symmetries. We report on a microscopic investigation of the atomic-scale MTD in solids by taking into account the orbital degree of freedom with a different parity. We construct an effective two-orbital $d$-$f$ tight-binding model on a polar tetragonal system for describing the atomic-scale MTD, which are obtained by incorporating the atomic spin-orbit coupling and odd-parity hybridization. The effective model exhibits two types of the MTDs: in-plane $x$, $y$ components activated through spontaneous ferromagnetic ordering or external magnetic field and an out-of-plane $z$ component by a spontaneous odd-parity hybridization without spin moments. We show that the intra-orbital (inter-orbital) Coulomb interaction in multi-orbital systems plays an important role in stabilizing the in-plane (out-of-plane) MTD orderings. We also examine the magneto-electric effect under each MTD ordering by calculating a linear response tensor. We show that the odd-parity hybridization enhances the magneto-electric effect for the in-plane MTDs, while it suppresses that for the out-of-plane MTD.

1. Introduction

Magneto-electric (ME) effect is an intriguing phenomenon where an external electric (magnetic) field induces magnetization (electric polarization) in the systems without both spatial inversion and time-reversal symmetries.\(^1\)\(^-\)\(^3\) There are several microscopic origins for such a coupling between electric and magnetic degrees of freedom. One of the most prominent examples is the ferroelectricity under the spin orderings which break the spatial inversion symmetry, as seen in a spiral magnetic structure.\(^4\)\(^-\)\(^9\) Another example is found in a collinear magnetic structure with concomitant charge disproportionation in the presence of magnetostriction.\(^10\) These ME couplings driven by electronic degrees of freedom might give rise to gigantic ME responses, which are expected for potential applications to next-generation spintronics devices.

A magnetic toroidal dipole (MTD) is one of fundamental objects showing the ME effect, which has been expressed as

\[
t = \sum_i r_i \times S_i, \tag{1}
\]

where $r_i$ is the position vector and $S_i$ is the localized spin.\(^11\),\(^12\) The expression in Eq. (1) indicates that the MTD is induced for nonzero vector products of $r_i$ and $S_i$, as schematically shown in Fig. 1(a). Such an MTD has been found in various magnetic insulators, such as Cr$_2$O$_3$ under a strong magnetic field,\(^13\) Ga$_2$-Fe$_x$O$_3$ by the X-ray scattering measurement,\(^14\) LiCoPO$_4$ by the second harmonic generation measurement,\(^15\),\(^16\) and LiFeS$_2$O$_6$ by the ME measurement.\(^17\)

Recently, a concept of the MTD has been extended to various situations beyond magnetic insulators. For example, the MTD ordered state has been indicated in a metallic compound UNi$_2$B\(^18\),\(^19\) by detecting the current-induced magnetization.\(^20\) Meanwhile, theoretical studies show extended expressions of the MTD by considering other electronic degrees of freedom, such as the kinetic orbital moment\(^21\) and the atomic orbital angular momentum.\(^22\)

Among them, we focus on the atomic-scale MTD, which is induced by the parity-mixing hybridization, such as $p$-$d$ and $d$-$f$ orbitals, without the time-reversal symmetry. When taking into account the parity-mixing hybridization, the MTD degree of freedom is described by a vortex-type spin cluster under each MTD ordering by calculating a linear response tensor. We show that the odd-parity hybridization enhances the magneto-electric effect for the in-plane MTDs, while it suppresses that for the out-of-plane MTD.

Fig. 1. (Color online) Schematic pictures of (a) the MTD from a vortex-type spin cluster and (b) the MTD from an odd-parity $d$-$f$ orbital hybridization breaking time-reversal symmetry. In (b), the shape represents the atomic-scale charge distribution and the color represents the direction of the $xy$-plane orbital angular momentum shown in the lower-right panel.
poles, we show that two types of the MTDs are potential order parameters. The one is the in-plane $x, y$ components of the MTDs composed of the spin and orbital degrees of freedom, while the other is the out-of-plane $z$ component composed of only the orbital degree of freedom. We show that the interplay among the spin-orbit coupling (SOC), the odd-parity hybridization, and the Coulomb interaction plays an important role in stabilizing the MTD orderings. Furthermore, we examine the ME responses for the atomic-scale MTD orderings by using the linear response theory. We find that the odd-parity hybridization enhances the ME effect for the in-plane MTD, whereas it suppresses the ME effect for the out-of-plane MTD.

The organization of this paper is as follows. In Sect. 2, we derive an effective two-orbital model including the atomic-scale MTD degree of freedom in a polar tetragonal crystal. We show that two types of the MTDs can be activated in the low-energy model. In Sect. 3, we discuss the stability of these MTDs from the energetics viewpoint. In Sect. 4, we investigate the ME effect under the two types of the MTD orderings. Section 5 is devoted to summary. In Appendix A, the definitions of the $d$ and $f$ orbital wave functions and multipole expressions are shown. In Appendix B, we discuss the antisymmetric spin-orbit interactions between the orbitals with the same and different parities, respectively.

2. Model with Parity-Mixing Orbitals

The MTD as the atomic-scale degree of freedom can be activated in multi-orbital systems with the different parities. In this section, we construct an effective model including the atomic-scale MTD degree of freedom in a $d$-$f$ orbital system. In Sect. 2.1, we introduce the atomic base in a local Hamiltonian under the crystalline electric field (CEF) and the atomic SOC. In Sect. 2.2, we describe active multipoles in the two-orbital $d$-$f$ base. In Sect. 2.3, we show the tight-binding model and introduce the atomic MTD moments.

2.1 Atomic basis functions

In order to derive a minimal model including the atomic MTD degree of freedom, we start from general five $d$ orbitals, $(\phi_u, \phi_\sigma, \phi_{ux}, \phi_{xy}, \phi_{yz})$, and seven $f$ orbitals, $(\phi_{xyz}, \phi_{x}, \phi_{y}, \phi_{z}, \phi_{x}, \phi_{y}, \phi_{z})$, where their functional forms are shown in Appendix A. We consider the atomic-energy level splittings for the $d$ and $f$ orbitals under the CEF and the atomic SOC. By assuming that $d$ and $f$ orbitals are located at the on-site position for simplicity, the local Hamiltonian $H_{\text{loc}}$ is given by

$$H_{\text{loc}} = H_{\text{CEF}} + H_{\text{LS}} + H_{\text{atomic}}.$$  (2)

The first term in Eq. (2) represents the CEF Hamiltonian. The second term in Eq. (2) represents the CEF Hamiltonian of the even-parity CEF and the odd-parity one $H_{\text{CEF}}$, which are written as

$$H_{\text{CEF}} = H_{\text{CEF}}^{(\text{even})} + H_{\text{CEF}}^{(\text{odd})},$$  (3)

$$H_{\text{CEF}}^{(\text{even})} = B_{\text{even}}O_{\text{even}}(r) + B_{\text{odd}}O_{\text{odd}}(r),$$  (4)

$$H_{\text{CEF}}^{(\text{odd})} = B_{\text{even}}O_{\text{even}}(r) + B_{\text{odd}}O_{\text{odd}}(r),$$  (5)

where $B_{\text{even}} (l = 0-6$ and $m = 0-4)$ is the CEF parameter and $O_{\text{even}}(r) = \sqrt{4\pi/(2l+1)}Y_{2l+1}(r)$, $O_{\text{odd}}(r)$ is the spherical harmonics $[l$ and $m$ are orbital-angular and magnetic quantum numbers $(l \geq 0, -l \leq m \leq l)$, respectively, and $r = r/|r|$]. In Eqs. (4) and (5), the tesseral harmonics are used.

$$O_{\text{even}}^{(c)}(r) = \frac{(-1)^m}{\sqrt{2l+1}}[O_{\text{even}}(r) + O_{\text{odd}}^{(c)}(r)],$$  (6)

$$O_{\text{odd}}^{(c)}(r) = \frac{(-1)^m}{\sqrt{2l+1}}[O_{\text{even}}(r) - O_{\text{odd}}^{(c)}(r)].$$  (7)

for $l \geq 1$ and $1 \leq |m| \leq l$. We use $O_{\text{even}}(r) = (-1)^mO_{\text{odd}}^{(c)}(r)$. As $O_{\text{even}}(r)$ has parity $(-1)^l$ with respect to spatial inversion, $H_{\text{CEF}}^{(\text{even})}(r) = H_{\text{CEF}}^{(\text{even})(-r)}$ and $H_{\text{CEF}}^{(\text{odd})}(r) = -H_{\text{CEF}}^{(\text{odd})(-r)}$ are satisfied. The even- and odd-parity CEFs in Eqs. (4) and (5) give rise to qualitatively different splittings: the former leads to energy splittings between orbitals with the same parity, i.e., $d$-$d$ and $f$-$f$ orbitals, while the latter leads to a mixing between orbitals with the different parity, i.e., $d$-$f$ orbitals. The second term in Eq. (2) is the atomic SOC Hamiltonian, which is given by

$$H_{\text{LS}} = \sum_{\ell = d, f} \frac{\lambda_{\ell}}{2} \mathbf{l} \cdot \mathbf{\sigma},$$  (8)

where $\lambda_{\ell}$ are the SOC constants for $d$ and $f$ orbitals. $I$ and $\sigma$ are the orbital and spin angular-momentum operators, respectively. The term in Eq. (8) mixes the orbitals with the same parity but different angular momenta. The third term in Eq. (2) represents the atomic energy difference between $d$ and $f$ orbitals where we set an appropriate value below.

In the situation where the energy scale of the even-parity CEF is larger than those of the odd-parity CEF and the SOC, the five $d$ orbitals are split into three single orbitals $\phi_0$ belonging to the irreducible representation $A_1$, $\phi_1$ to $B_1$, and $\phi_2$ to $B_2$ and a doubly-degenerate orbital $\phi_{yz}$ to $E$, while seven $f$ orbitals are into three single orbitals $\phi_{\alpha}$ to $A_1$, $\phi_{\beta}$ to $B_1$, and $\phi_{\gamma}$ to $B_2$ and two doubly-degenerate orbitals $\phi_{\alpha}$ and $\phi_{\gamma}$ to $E$. The schematic level splittings under the even-parity CEF are shown in Fig. 2. Note that the even-parity CEF in Eq. (4) corresponds to that in the centrosymmetric point group $D_{4h}$. Here and hereafter, we focus on two orbitals $\phi_{\alpha}$ and $\phi_{\gamma}$ belonging to the same irreducible representation $B_2$. The following results are straightforwardly applied to the other orbitals belonging to the different representations, such as $A_1$ and $B_1$.

Next, we consider the effect of the SOC. The spinful basis $\phi_{\alpha}$ and $\phi_{\gamma}$ ($\mathbf{\sigma} = 1, \downarrow$) belong to the double group representation $E_{3/2} \otimes E_{3/2} \rightarrow E_{3/2}$. Considering the mixing with higher energy levels in the first-order perturbation Hamiltonian with respect to $\lambda_{\ell} (\phi_{\alpha}, \phi_{\gamma})$ turns into $(\phi_{\alpha}, \phi_{\gamma})$, which are given by

$$\phi_{d, \ell} = N_{d, \ell} \left[ \phi_{\alpha, \ell} + i \Lambda^{(1)}_{\ell} \phi_{\gamma, \ell} + \Lambda^{(2)}_{\ell} \phi_{\gamma, \ell} + i \Lambda_{\ell} \phi_{\gamma, \ell} \right],$$

where the coefficients are represented by

$$\Lambda^f_{\ell} = \frac{\Lambda^{(1)}_{\ell}}{\Lambda_{\ell}^{f, \ell}} - \Lambda^{(2)}_{\ell},$$  (10)
M, MT, and ET multipoles are given by (22, 29–32) describing the atomic-scale MTD degree of freedom, as discussed in the text. The energy splitting under the odd-parity CEF in Eq. (5) due to the parity-mixing hybridization. The dashed square represents the low-energy levels considered in the present study.

$$\begin{align*}
(\hat{\Lambda}_E^{(1)}, \hat{\Lambda}_E^{(2)}) = & \left( \frac{2 \sqrt{2} \Lambda_f^l}{\Delta_{B_0}^{l} - \Delta_{E}^{(1)}, \Delta_{B_0}^{l} - \Delta_{E}^{(2)}}, 2 \sqrt{2} \Lambda_f^l \right). 
\end{align*}$$  (11)

In Eq. (9), \(N_\alpha\) and \(N_f\) are normalization factors and the subscript \(\sigma\) represents the opposite spin to \(\sigma\). \(\Lambda_E^{(i)}\) is the atomic energy level split under the even-parity CEF for \(\zeta = d, f\) and \(\Gamma = B_1, B_2, E\). \(\phi_{E}^{(\sigma)}\), with the atomic energy \(\Delta_{E}^{(i)}\) \((i = 1, 2)\) in Eq. (9) is constructed from linear combinations of \(\phi_{d,x,\sigma}, \phi_{d,y,\sigma}, \phi_{d,z,\sigma}, \phi_{f,\sigma}\). \(c_1\) and \(c_3\) in Eq. (11) are determined by the even-parity CEF parameters.

Finally, let us consider \(\mathcal{H}_{CEF}^{\text{(odd)}}\) for the basis \(\phi_{d,\sigma}, \phi_{f,\sigma}\) in Eq. (9). As \(\mathcal{H}_{CEF}^{\text{(odd)}}\) leads to the parity mixing between \(d\) and \(f\) orbitals, the off-diagonal matrix element between \(\phi_{d,\sigma}\) and \(\phi_{f,\sigma}\) becomes nonzero, which is evaluated from Eq. (5) as

$$\langle \phi_{d,\sigma} | \mathcal{H}_{CEF}^{\text{(odd)}} | \phi_{f,\sigma} \rangle = \frac{32B_{10} - 22B_{20} + 5B_{50} - 3 \sqrt{35}B_{24}}{32\sqrt{7}}.$$  (12)

Such an odd-parity hybridization plays an important role in describing the atomic-scale MTD degree of freedom, as discussed in the subsequent sections.

2.2 Active multipoles

We examine active multipoles including the MTD degree of freedom in \(\phi_{d,\sigma}, \phi_{f,\sigma}\) in Eq. (9). In order to describe electronic degrees of freedom in the parity-mixing orbitals, we introduce four types of multipoles: electric (E) \(\hat{Q}_{im}\), magnetic (M) \(\hat{M}_{im}\), magnetic toroidal (MT) \(\hat{T}_{im}\), and electric toroidal (ET) \(\hat{G}_{im}\) multipoles. (22, 27, 28) The operator expressions of E, M, MT, and ET multipoles are given by (22, 29–32)

$$\hat{Q}_{im} = -e \sum_j \hat{O}_{im}(r_j),$$  (13)

$$\hat{M}_{im} = -\mu_B \sum_j \left( \frac{2 J_l + 1}{l + 1} + \sigma_j \right) \cdot \nabla \hat{O}_{im}(r_j),$$  (14)

such that

$$\hat{T}_{im} = -\mu_B \sum_j \left( 2 \sigma_j \right) \cdot \nabla \hat{O}_{im}(r_j),$$  (15)

$$\hat{G}_{im} = -e \sum_{j} \sum_{\alpha, \beta} g_{\alpha, \beta}(r_j) \nabla_{\alpha} \nabla_{\beta} \hat{O}_{im}(r_j),$$  (16)

where \(\hat{\mathcal{H}}_{CEF}^{\text{(odd)}}\) is the Hamiltonian matrix of odd-parity multipoles and \(\nabla_{\alpha}\) is the spatial gradient operator in the direction \(\alpha\).

By calculating the matrix elements of the operators \(\langle \phi \mid \hat{Q}_{im} \mid \phi' \rangle = \langle \phi \mid \hat{O}_{im} \mid \phi' \rangle \) and \(\hat{X} = \hat{Q}, \hat{M}, \hat{T}, \hat{G}\) in Eqs. (13)–(16), we identify active multipoles in the basis \(\phi_{d,\sigma}, \phi_{f,\sigma}\). For simplicity, we use the notations \(\hat{X}_{0}\) for a monopole \((l = 0)\), \(\hat{X}_{x}, \hat{X}_{y}, \hat{X}_{z}\) for \(d\) orbitals \((l = 1)\), \(\hat{X}_{x}, \hat{X}_{y}, \hat{X}_{z}\) for \(f\) orbitals \((l = 2)\), and \(\hat{X}_{x}, \hat{X}_{y}, \hat{X}_{z}\) for octupoles \((l = 3)\) instead of \(\hat{X}_{0}, \hat{X}_{1}, \hat{X}_{2}, \hat{X}_{3}\). (22, 23) See Appendix A for each detailed expression.

We describe the active sixteen multipoles spanned by \(\phi_{d,\sigma}, \phi_{f,\sigma}\) in Eq. (9) by the product of two Pauli matrices \(\tau_{\mu} \) and \(\sigma_{\nu} \), where \(\mu, \nu = 0, x, y, z\). \(\tau_{\mu}\) represents the orbital degree of freedom between \(\phi_{d,\sigma}\) and \(\phi_{f,\sigma}\) and \(\sigma_{\nu}\) represents the spin degree of freedom \((\tau_0, \tau_0) = 2 \times 2 \text{ identity matrices in each space})

Among sixteen multipoles, eight multipoles are even-parity, which are excited in the intra-orbital space: E monopole \(\hat{Q}_{0} = \sigma_0 \tau_0\), E quadrupole \(\hat{Q}_{2} = -\sigma_0 \tau_0 + \tau_2\). M dipoles \((\hat{M}_{z}, \hat{M}_{y}, \hat{M}_{x}) = \sigma_0 \tau_0, \sigma_0 \tau_1, \sigma_0 \tau_i\), M octupole \(\hat{M}_{0} = \sigma_0 \tau_0 + \tau_2\), and MT quadrupoles \((\hat{T}_{yz}, \hat{T}_{zx}) = [-\sigma_0 \tau_0 + \tau_2, \sigma_0 \tau_0 + \tau_2]\).

On the other hand, remaining eight multipoles are odd-parity multipoles: E dipoles \((\hat{Q}_x, \hat{Q}_y, \hat{Q}_z) = (-\sigma_0 \tau_0 + \sigma_0 \tau_1, \sigma_0 \tau_0 + \sigma_0 \tau_1)$, M quadrupoles \(\hat{M}_n = \sigma_0 \tau_0, \text{ MT dipoles } (\hat{T}_x, \hat{T}_y, \hat{T}_z) = (\sigma_0 \tau_0 + \sigma_0 \tau_1, -\sigma_0 \tau_0 + \sigma_0 \tau_1)$, $\hat{T}_{yz}, \hat{T}_{zx}) = [-\sigma_0 \tau_0 + \sigma_0 \tau_1, \sigma_0 \tau_0 + \sigma_0 \tau_1]$. 
Table I. Active multipoles in \( (\phi_{d,\sigma}, \phi_{f,\sigma}) \) orbitals under the point group \( C_{4z} \).

For later convenience, we introduce the atomic-scale MTD and their ME responses.

\[ \mathcal{H}_{\text{hopping}} = \sum_{k} \sum_{\sigma} \mathcal{E}_{\sigma}^{k} (\mathbf{k}) \mathcal{\zeta}_{\mathbf{k} \mu}^{\dagger} \mathcal{\zeta}_{\mathbf{k} \nu} + \text{h.c.}, \]

\[ \mathcal{H}_{\text{mixing}} = \sum_{\sigma} \sum_{\sigma'} \mathcal{V} (\mathbf{k}) \left[ \mathcal{\zeta}_{\mathbf{k} \mu}^{\dagger} \mathcal{\zeta}_{\mathbf{k} \nu} - \mathcal{\zeta}_{\mathbf{k} \nu}^{\dagger} \mathcal{\zeta}_{\mathbf{k} \mu} + \text{h.c.} \right], \]

\[ \mathcal{H}_{\text{odd}} = \mathcal{V}_{\text{intra}} \left[ \sum_{\sigma} \sum_{\mathbf{k}} \mathcal{d}_{\mathbf{k} \mu}^{\dagger} \mathcal{d}_{\mathbf{k} \nu} + \text{h.c.} \right], \]

\[ \mathcal{H}_{\text{eff}} = \mathcal{H}_{\text{hopping}} + \mathcal{H}_{\text{mixing}} + \mathcal{H}_{\text{odd}} + \mathcal{H}_{f}. \]
\[ T_y \equiv \langle \hat{T}_y \rangle = \langle d_{k_1}^\dagger f_{k_1} + f_{k_1}^\dagger d_{k_1} + f_{k_1}^\dagger f_{k_1} \rangle, \]  
\[ T_z \equiv \langle \hat{T}_z \rangle = -i \langle d_{k_1}^\dagger f_{k_1} + f_{k_1}^\dagger f_{k_1} - f_{k_1}^\dagger d_{k_1} \rangle. \]

The bracket \( \langle \cdot \rangle \) is defined as
\[ \langle \hat{X} \rangle = \frac{1}{2N} \sum_{k} \sum_{q} \langle q k | \hat{X} | q k \rangle \theta(\xi_q(k) - \xi_{q_e}), \]
where \( N_k \) is the number of \( k \), and \( |q k\rangle \) is the eigenvector for the eigenenergy \( \xi_q(k) \) for the band indices \( q \) and \( k \). \( \xi_{q_e} \) represents the Fermi energy and \( \theta(\xi) \) is the Heaviside step function. Hereafter, we use the notation \( X \equiv \langle \hat{X} \rangle \) for other multipoles.

### 3. Stability

We examine when and how the MTDs in Eqs. (23)-(25) become nonzero from the energetics point of view. In Sect. 3.1, we show that the in-plane MTDs \( T_x \) and \( T_y \) are activated by the spontaneous ferromagnetic state under the intra-orbital Coulomb interaction. In Sect. 3.2, we discuss the stability of the out-of-plane MTD \( T_z \) in the presence of the inter-orbital Coulomb interaction.

#### 3.1 In-plane spin-dependent MTD

We investigate how to activate the in-plane MTDs \( T_x \), \( T_y \) in Eqs. (23) and (24) in the model in Eq. (18). We focus on the fact that \( T_x \) and \( T_y \) belong to the same irreducible representation to \( M_x \) and \( M_y \), as shown in Table I, which means that \( T_x \) (\( T_y \)) is indirectly induced as a secondary order parameter once the ferromagnetic state with the \( M_x \) (\( M_y \)) component is stabilized in the presence of the odd-parity CEF \( V_{\text{intra}} \).

In order to examine the stability of the in-plane ferromagnetic ordering, we introduce the Coulomb interaction for the \( f \) orbital:
\[ \mathcal{H}_U = U \sum_i f_{i\sigma}^\dagger f_{i\sigma} f_{i\sigma}^\dagger f_{i\sigma}. \]

We apply the standard Hartree-Fock approximation as
\[ f_{i\sigma}^\dagger f_{i\sigma} f_{i\sigma}^\dagger f_{i\sigma} \rightarrow \left( \hat{Q}_{\sigma} \hat{M}^f - M^f \cdot \hat{M} \right) \text{ const.}, \]
where \( \hat{Q}_{\sigma} \) and \( \hat{M}^f \) are defined as \( \hat{Q}_{\sigma} = \sum_{\sigma'} f_{i\sigma'}^\dagger f_{i\sigma'} \) and \( \hat{M}^f = \sum_{\sigma \sigma'} f_{i\sigma}^\dagger \sigma f_{i\sigma'} \), respectively [\( \sigma_{\mu} = (1/2) \sigma_{\nu}(\tau_0 - \tau_{\mu}) \) for \( \mu = x, y, z \)].

For the mean-field calculations, we consider a single-site unit cell to examine the local magnetic anisotropy, and calculate the mean fields by taking the \( k \) summation over \( 200 \times 200 \) grid points in the first Brillouin zone. The mean fields are determined self-consistently within a precision less than \( 10^{-8} \). We set \( U = 10 \) and \( V_{\text{intra}} = 0.5 \) for the following calculations.

Figure 4(a) shows the zero-temperature phase diagram by changing \( V_{\text{intra}} \) and \( \Delta' \) at half (1/2) filling. There are two in-plane magnetic states with \( M_x \), or \( M_y \) \( M_z \) in the phase diagram. The \( M_x \) state has nonzero magnetization along the (100) direction, while the \( M_y \) \( M_z \) state has nonzero magnetization along the (110) direction. The \( M_z \) state becomes stable in the region for large negative \( \Delta' \), while the \( M_x \) \( M_z \) state appears in the region for small \( \Delta' \). Both magnetic states are metallic, while the paramagnetic state is insulating with a hybridization gap between \( d \) and \( f \) orbitals. The phase transition between two magnetic phases is of first order. On the other hand, the phase transition between the \( M_x \) \( M_z \) and paramagnetic state is of second order.

Both in-plane magnetic states are accompanied with the nonzero MTD moments: \( -T_y \) (\( T_x \)) is induced in the \( M_x \) (\( M_y \)) state, whereas \( T_x - T_y \) (\( -T_x - T_y \)) is induced in the \( M_y \) \( M_x \) (\( M_x \) \( M_y \)) state. The in-plane MTD moments are developed by increasing \( V_{\text{intra}} \) and decreasing \( \Delta' \), while in-plane dipole moments are suppressed by increasing \( V_{\text{intra}} \). This result indicates that the in-plane MTD is affected by the odd-parity CEF \( V_{\text{intra}} \) as well as the ferromagnetic moment. The amplitude of \( T_x \) \( T_y \) is roughly scaled by the products of \( \langle M_x \rangle \langle M_y \rangle \) and \( V_{\text{intra}} \), where \( V_{\text{intra}} \) becomes nonzero for nonzero \( V_{\text{intra}} \).

The preference of the in-plane magnetic states rather than the out-of-plane magnetic states is presumably understood from the effective inter-orbital Rashba-type ASOI, which consists of the odd-parity CEF \( V_{\text{intra}} \) and the spin-dependent hopping \( V_{\text{inter}} \). This tendency to stabilize the in-plane magnetic states is different from the intra-orbital Rashba-type ASOI neglected in the present study, which favors the out-of-plane magnetic anisotropy. In fact, we confirmed that the out-of-plane magnetic state is stabilized by introducing the inter-orbital Rashba-type ASOI. In other words, the inter-orbital ASOI in “multi-orbital” systems is a key ingredient to stabilize the spin-dependent in-plane MTD state.

Figure 4(b) shows the phase diagram at a different filling fraction (2/5 filling). In contrast to the case at half filling, the \( M_x \) state with the out-of-plane magnetization is stabilized in the small \( \Delta' \) region. The \( M_x \) state exhibits the \( M \) quadrupole \( M_y \), because they belong to the same irreducible representation \( A_2 \) in Table I. In the large negative \( \Delta' \) region, the \( M_x \) state is replaced by the \( M_x \) \( M_x \) state with the in-plane MTD. The phase transition between the \( M_x \) \( M_x \) and \( M_z \) phases is of first order, whereas that between the \( M_x \) and paramagnetic state is of second order. For the case in Fig. 4(b), the in-plane magnetic state is also destabilized by introducing the inter-orbital Rashba-type ASOI.

#### 3.2 Out-of-plane spin-independent MTD

Next, we discuss the stability of the out-of-plane MTD \( T_z \) in the model in Eq. (18). In contrast to \( \langle T_x, T_y \rangle \), any magnetic orders do not induce \( T_z \), as they are not coupled with each other. In order to realize the \( T_z \) ordering, we introduce the inter-orbital Coulomb interaction between \( d \) and \( f \) orbitals, which is represented as
\[ \mathcal{H}_{\text{U'}} = U' \sum_{\sigma \sigma'} f_{i\sigma}^\dagger f_{i\sigma} d_{i\sigma'}^\dagger d_{i\sigma'}. \]

The mean-field decoupling for the Fock terms leads to an effective interaction to induce \( T_z \), which is represented by
\[ \sum_{\sigma \sigma'} \left[ f_{i\sigma}^\dagger f_{i\sigma} d_{i\sigma'}^\dagger d_{i\sigma'} \right]_{\text{Fock}} \rightarrow -\frac{1}{2} \left( \langle T \cdot T \rangle + \hat{Q} \cdot \hat{Q} + G_{\mu \nu} G_{\mu \nu} \right) + \text{const.}, \]
where each multipole operator is constructed by using \( \tau_{\rho}^\sigma \) (\( \mu, \nu = 0, x, y, z \)) in Table I. When the Fock term in Eq. (30) is a dominant interaction, one of eight multipoles \( \langle T_x, T_y, T_z, Q_x, Q_y, Q_z, G_{\mu \nu} M_{\mu \nu} \rangle \) in the inter-orbital space is activated. Note that energies for eight multipole states are degenerate under the Fock term.

The energy degeneracy for eight multipoles is lifted by considering \( V_{\text{intra}} \) and \( V_{\text{inter}} \). Figure 5 shows \( V_{\text{inter}} \) dependences of
the energies per site for eight states measured from that for the $Q_2$ state at $U' = 10$, $V_{\text{intra}} = 0.5$, and half filling. We assume the saturated mean-field values for each multipole state. At $V_{\text{inter}} = 0$, the $Q_2$ state has the lowest energy among the eight states. While increasing $V_{\text{inter}}$, the energy difference between the $Q_2$ state and the $T_z$ state is smaller, and the $T_z$ state becomes the lowest energy state for $V_{\text{inter}} \geq 0.85$. While further increasing $V_{\text{inter}}$, the energy for the $M_x$ state is close to that for the $T_z$ state, and they are almost degenerate for $V_{\text{inter}} \geq 3.0$. The energy difference between the $T_z$ and $M_x$ states is determined by $V_{\text{intra}}$.

The result indicates that the out-of-plane $T_z$ state is realized in the system for the intermediate region of the intersite hybridization $V_{\text{intra}}$ and nonzero $V_{\text{intra}}$, although the self-consistent calculations are required to settle this point. The excitonic insulators, which have been often characterized by the off-diagonal orbital orderings, might be potential candidates to exhibit the $T_z$ state.\(^{35}\)

4. Magneto-Electric Effect

Let us investigate the ME effect under the MTD orderings. Before discussing the results, we briefly review the ME effect from the symmetrical point of view.\(^{23,37}\)

$$M = \hat{\alpha}E,$$  \hspace{1cm} (31)

where $\hat{\alpha}$ is the ME tensor. $\hat{\alpha}$ is calculated by the linear response theory:\(^{38}\)

$$\alpha_{\mu \nu} = \frac{e g_{\mu \nu} \hbar}{2V_i} \sum_k \sum_{p-q} \frac{f(\xi_{\mu}(k)) - f(\xi_{\nu}(k))}{\xi_{\mu}(k) - \xi_{\nu}(k)} \frac{\sigma_{\mu q}^{pq} \sigma_{\nu p}^{qp}}{\xi_{\mu}(k) - \xi_{\nu}(k) + i\hbar\delta},$$  \hspace{1cm} (32)

where $V$ is the system volume, $\hbar = h/2\pi$ is the Plank constant, and $\delta$ is the broadening factor. $f(\xi_{\mu}(k))$ represents the Fermi distribution function and $\xi_{\mu}(k)$ is the eigenenergy. As $\sigma_{\mu q}^{pq} = \langle p\hat{k}|\hat{\sigma}_{\mu q}|q\hat{k}\rangle$ and $v_{\mu k}^{(33)} = \langle p\hat{k}|v_{\mu k}|q\hat{k}\rangle$ ($\mu, \nu = x, y, z$) are matrix elements of spin moment and velocity $v_{\mu k} = \hbar\partial F/\partial \hbar k_{\mu}$ at $k$, $\alpha_{\mu \nu}$ represents the correlation of the magnetic moment and electric current.\(^{38}\) We take $e g_{\mu \nu} \hbar/2 = 1$.

The ME tensor $\alpha_{\mu \nu}$ can be divided into two parts: the dissipative part (current-driven) $\alpha_{\mu \nu}^{(J)}$ and the non-dissipative part (electric-field driven) $\alpha_{\mu \nu}^{(E)}$. The expressions are shown as

$$\alpha_{\mu \nu}^{(J)} = -\frac{\hbar\delta}{V} \sum_k \sum_{p-q} \frac{f(\xi_{\mu}(k)) - f(\xi_{\nu}(k))}{\xi_{\mu}(k) - \xi_{\nu}(k)} \Pi_{\mu q}^{pq}(k),$$  \hspace{1cm} (33)

$$\alpha_{\mu \nu}^{(E)} = \frac{1}{V_i} \sum_k \sum_{p-q} \frac{f(\xi_{\mu}(k)) - f(\xi_{\nu}(k))}{\xi_{\mu}(k) - \xi_{\nu}(k)} \Pi_{\mu q}^{pq}(k),$$  \hspace{1cm} (34)

where $\Pi_{\mu q}^{pq} = \sigma_{\mu q}^{pq} v_{\mu k}^{(33)}/[\xi_{\mu}(k) - \xi_{\nu}(k)]^2 + (\hbar\delta)^2$. The dissipative part $\alpha_{\mu \nu}^{(J)}$ represents the intra-band contribution, whereas the non-dissipative part $\alpha_{\mu \nu}^{(E)}$ represents the inter-band contribution. We set $\hbar = 1$.

Each component of the ME tensors, $\alpha_{x \mu}^{(J)}$ and $\alpha_{x \mu}^{(E)}$, is related
with the odd-parity multipoles, which is represented by \( \alpha \) function of nonzero when the corresponding multipoles are activated.

The magnetic field along the \( (x, y) \) plane under the magnetic field \( H \). For \( \alpha \) \( \beta \) = 0, \( \alpha \) \( \beta \) becomes nonzero due to the odd-parity CEF, resulting in the E dipole \( Q \). The other components become nonzero when the corresponding multipoles are activated.

It is noted that the ME tensors \( \alpha^{(E)} \) and \( \alpha^{(E)} \) are also active for different multipoles ordered states according to the crystallographic point-group symmetry. In the present model under the point group \( \alpha \) \( \beta \) and \( \alpha \) \( \beta \) become nonzero when the M dipole \( (M_\alpha, M_\beta) \) and/or the MT quadrupole \( (T_\alpha, T_\beta) \) are activated, since they belong to the same irreducible representation \( E^- \) as the MT dipole \( (T_\alpha, T_\beta) \) shown in Table I. In a similar way, \( \alpha^{(E)} \) \( \alpha^{(E)} \) in (Eq. 36) also becomes nonzero in the presence of \( M \) in Table I.

In the following, we focus on the ME tensor \( \alpha^{(E)} \) induced by the two types of MTDs. The results for the in-plane MTDs \( T_x, T_y \) are shown in Sect. 4.1, and those for the out-of-plane MTD \( T_z \) are shown in Sect. 4.2.

4.1 In-plane spin-dependent MTD

We investigate the ME effect induced by the in-plane spin-dependent MTDs, \( T_x, T_y \). As discussed in Sect. 3.1, since \( (T_x, T_y) \) is induced under the \( (M_\alpha, M_\beta) \) state, we introduce an in-plane magnetic field to the model in Eq. (18). We consider the magnetic field along the \( x \) direction, which is given by

\[ \mathcal{H}_x = -H \sum_{\mathbf{k}} M_{\mathbf{k}} x, \]

where \( \hat{\mathbf{M}}_x = \sum_{\mathbf{k}} \sum_{\sigma} c_{\mathbf{k}\sigma}^+ \hat{c}_{\mathbf{k}\sigma} \hat{\mathbf{M}}_{\mathbf{k}} \mathbf{x}/0^{\mathbf{k}} \mathbf{0} \mathbf{0}^{\mathbf{k}} \mathbf{0}^{\mathbf{k}} \) for \( \mathbf{z} = d, f \) and \( \sigma = \uparrow, \downarrow \). The \( g \) factors for \( d \) and \( f \) are taken as the same for simplicity.

Figure 6(a) shows the M dipole moment \( M_x \), the MT dipole moment \( T_y \), and the ME tensor \( \alpha^{(E)} \) for \( H_z = 0.2, 0.4, 0.6 \) as a function of \( V_{\text{intra}} \). The parameters are taken at \( \Delta' = -1, \) \( V_{\text{inter}} = 0.5, T = 0.1, \) and \( \delta = 0.01 \), and 1/5 filling. As shown in the top panel of Fig. 6(a), \( M_x \) is larger with an increase of the magnetic field \( H_x \) whereas it is almost independent of \( V_{\text{intra}} \). On the other hand, \( T_y \) becomes larger while increasing either \( H_z \) or \( V_{\text{intra}} \), as shown in the middle panel of Fig. 6(a). Note that \( T_y \neq 0 \) for \( V_{\text{intra}} = 0 \). The ME tensor \( \alpha^{(E)} \) as shown in the bottom panel of Fig. 6(a), exhibits a more complicated behavior. For \( H_z = 0.4 \), it becomes larger with an increase of \( V_{\text{intra}} \) for small \( V_{\text{intra}} \). While further increasing \( V_{\text{intra}} \), it shows a kink at \( V_{\text{intra}} \sim 0.45 \), and takes a constant value for \( V_{\text{intra}} \sim 1.8 \). Such a behavior of \( \alpha^{(E)} \) is qualitatively common to other magnetic fields, \( H_z = 0.2 \) and 0.6.

In order to examine \( \alpha^{(E)} \), we discuss the relationship with the band structure. We decompose the ME tensor \( \alpha^{(E)} \) into each wave number defined as \( \alpha^{(E)}(k) = \sum_{\sigma} \alpha^{\sigma}(k) = f(E_\sigma(k)) \Pi_{\sigma}(k)/\Pi(k) \). Figures 7(a) and (b) represent \( \alpha^{(E)}(k) \) at \( V_{\text{intra}} = 0 \) [Fig. 7(a)] and at \( V_{\text{intra}} = 0.1 \) [Fig. 7(b)] for fixed \( H_z = 0.4 \). The corresponding band dispersions are also shown in the lower panels of Fig. 7. At \( V_{\text{intra}} = 0 \), the energy band shows a symmetric structure with respect to the wave number \( (k_x, k_y) \leftrightarrow (-k_x, -k_y) \) because \( Q \), resulting from the odd-parity CEF is not activated. Meanwhile, \( \alpha^{(E)}(k) \) shows a symmetric structure with respect to \( k_x \), \( \alpha^{(E)}(k_x, k_y) = \alpha^{(E)}(-k_x, k_y) \), while it shows an antisymmetric structure with respect to \( k_y \), \( \alpha^{(E)}(k_x, k_y) = -\alpha^{(E)}(k_x, -k_y) \). As shown in the upper panel of Fig. 7(a) the asymmetric structure with respect to \( k_y \) is due to the breaking of the mirror symmetry in the \( xy \) plane under the magnetic field \( H_z \). Nevertheless, no MTDs are induced at \( V_{\text{intra}} = 0 \), i.e., \( \alpha^{(E)}(k_x, k_y) = \sum_{\sigma} \alpha^{(E)}(k_x, k_y) = -\alpha^{(E)}(-k_x, k_y) \). The result is consistent with the absence of \( T_x \) at \( V_{\text{intra}} = 0 \). For an infinitesimal \( V_{\text{intra}} \), the structure \( \alpha^{(E)}(k) \) shows an asymmetric modulation along the \( k_y \) direction, as shown in Fig. 7(b). This result indicates the emergence of \( T_z \), which gives rise to nonzero \( \alpha^{(E)} \).

Figures 6(b) and (c) represent the contour plots of \( T_y \) and \( \alpha^{(E)} \) in the \( V_{\text{intra}}-H_z \) plane, respectively. \( T_y \) shows a large value with an increase of either \( V_{\text{intra}} \) or \( H_z \), which is a similar tendency in Fig. 6(a). On the other hand, the ME tensor \( \alpha^{(E)} \) becomes larger with an increase of \( V_{\text{intra}} \) for small \( V_{\text{intra}} \), while it takes constant value for large \( V_{\text{intra}} \). The position of the kink is roughly scaled as \( V_{\text{intra}} \sim H_z \), which indicates that a large ME response is expected for \( V_{\text{intra}} \sim H_z \). A further analysis by taking into account the electron correlation beyond the mean-field level might also bring a large ME tensor.
found that the ME tensor $\alpha_k$ is decomposed at each wave number in the first Brillouin zone for (a) $V_\text{intra} = 0$ and (b) $V_\text{intra} = 0.1$. The other parameters are $H_z = 0.4$, $\Delta' = -1.0$, and $V_\text{inter} = 0.5$. (Lower panel) The corresponding energy bands. The dashed lines show the Fermi levels.

### 4.2 Out-of-plane spin-independent MTD

We investigate the ME effect under the out-of-plane MTD $T_z$, ordering, which is expected to show nonzero $\alpha_{xy} = -\alpha_{zy}$. We introduce the mean filed to induce $T_z$, which is given by

$$\mathcal{H} = -H_z^{(T)} \sum_k \hat{T}_z,$$

(38)

where $\hat{T}_z = \sum_k \sum_{\sigma=\uparrow,\downarrow} \xi^\sigma_\mathbf{k}|\psi^\sigma_\mathbf{k}\rangle \langle \psi^\sigma_\mathbf{k}|$ for $\mathcal{H}$, $\xi^\sigma_\mathbf{k}$ is the wave function.

Contrary to the symmetrical argument in Eq. (36), it is found that the ME tensor $\alpha_{xy}^{(E)}$ becomes zero even under the $T_z$ ordering by calculating it. In order to investigate whether a nonzero $\alpha_{xy}^{(E)}$ can be obtained or not, we examine the behavior of $\alpha_{xy}^{(E)}$ in details. For that purpose, we decompose the ME tensor $\alpha_{xy}$ in Eq. (34) into that for $(d/f)$-orbital components, which are defined as

$$\alpha_{xy}^{(E)}(\mathbf{r}) = \frac{1}{V_\text{cell}} \sum_k \frac{\sum_{\rho=q} \langle f|\xi_\rho((\mathbf{k}) - f|\xi_\rho((\mathbf{k}))\rangle \Pi_{xy}^{(E)}((\mathbf{k}), \mathbf{r}))}{\langle \Pi_{xy}^{(E)}((\mathbf{k}), \mathbf{r}) \rangle},$$

(39)

where the total spin moment $\sigma^{(E)}_{\mathbf{k},\mathbf{r}}$ in Eq. (34) is replaced with that for the $d$-orbital spin moment $\sigma_d^{(E)} = \sigma_x(t_0 + \tau_z)/2$ for $\mathbf{r} = d$ and the $f$-orbital spin moment $\sigma_f^{(E)} = \sigma_x(t_0 - \tau_z)/2$ for $\mathbf{r} = f$. The nonzero $\alpha_{xy}^{(E)}$ for $\mathbf{r} = f$ in Eq. (39) means that the $x$ component of the magnetization for the $(d/f)$ orbital is induced for an applied electric field along the $y$ direction. As the relation $\alpha_{xy}^{(E)} = -\alpha_{xy}^{(f)}$ holds from $\alpha_{xy}^{(E)} = \alpha_{xy}^{(f)} + \alpha_{xy}^{(d)} = 0$ in the present model, we discuss $\alpha_{xy}^{(E)}$ in the following.

Figure 8(a) shows $V_\text{intra}$ dependences of $T_z$ and the ME tensor $\alpha_{xy}^{(E)}$ for $H_z^{(T)} = 0.2, 0.4, 0.6$. $T_z$ shows a similar dependence on $V_\text{intra}$ for each $H_z^{(T)}$. $T_z$ becomes larger with an increase of $H_z^{(T)}$, whereas it is suppressed while $V_\text{intra}$ increases. Meanwhile, the behavior of $\alpha_{xy}^{(E)}$ is similar to that of $T_z$ except for small $V_\text{intra}$. For small $V_\text{intra}$, $\alpha_{xy}^{(E)}$ becomes slightly larger while increasing $V_\text{intra}$, and shows a broad peak around $V_\text{intra} \sim 0.8$. While further increasing $V_\text{intra}$, $\alpha_{xy}^{(E)}$ decreases gradually and approaches to zero.

In contrast to the ME effect under the $T_z$ ordering in Sect. 4.1, both $T_z$ and $\alpha_{xy}^{(E)}$ become nonzero at $V_\text{intra} = 0$. Moreover, the band structure under the $T_z$ ordering is symmetric with respect to $(k_x, k_y) \leftrightarrow (-k_x, -k_y)$ because the asymmetric structure is expected to occur along the $k_z$ direction in a three-dimensional system.

Figures 8(b) and (c) show the contour plots of $T_z$ and $\alpha_{xy}^{(E)}$ in the $V_\text{intra}$-$H_z^{(T)}$ plane. $T_z$ shows a large value in the region for small $V_\text{intra}$ and large $H_z^{(T)}$, which is similar to the result in Fig. 8(a). On the other hand, the ME tensor $\alpha_{xy}^{(E)}$ shows a maximum value at $V_\text{intra} \sim 0.8$, which is almost independent of $H_z^{(T)}$, and decreases while increasing $V_\text{intra}$ or decreasing $H_z^{(T)}$.

Meanwhile, the nonzero ME tensor $\alpha_{xy}^{(E)}$ is obtained by taking into account the intra-orbital ASOI in addition to the Hamiltonian in Eq. (18), which is neglected as a higher-order contribution compared to the inter-orbital ASOI. The intra-orbital ASOI Hamiltonian is given by

$$\mathcal{H}_\text{ASOI}^{(E)} = \sum_{\mathbf{k}} \sum_{\sigma, \sigma'} \sum_{\xi, \eta} g_\xi \xi_\mathbf{r}^{(E)} \Gamma^\sigma \langle \sigma \sigma' \xi_\mathbf{r}^{(E)} (\sigma' \xi_\mathbf{r}^{(E)} \xi_\mathbf{r}^{(E)} \xi_\mathbf{r}^{(E)}) \rangle,$$

(40)

where $g_\xi$ is the magnitude of the intra-orbital ASOI for the orbital $\xi (\xi = d, f)$. The derivation of the intra-orbital ASOI in Eq. (40) is shown in Appendix B. We show the net component of the ME tensor $\alpha_{xy}$ as a function of the $d$-orbital intra-orbital ASOI $g_{d}(=2g_{f})$ in Fig. 9. The result indicates that $\alpha_{xy}^{(E)}$ becomes nonzero for an infinitesimal $g_{d}$ and increases with an increase of $g_{d}$. The behaviors of nonzero $\alpha_{xy}^{(E)}$ while changing $H_z^{(T)}$ and $V_\text{intra}$ are similar to those of $\alpha_{xy}^{(E)}$; $\alpha_{xy}^{(E)}$ is enhanced by $H_z^{(T)}$ and suppressed by $V_\text{intra}$. 

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**Fig. 7.** (Color online) (Upper panel) The ME tensor $\alpha_k$ decomposed at each wave number in the first Brillouin zone for (a) $V_\text{intra} = 0$ and (b) $V_\text{intra} = 0.1$. The other parameters are $H_z = 0.4$, $\Delta' = -1.0$, and $V_\text{inter} = 0.5$. (Lower panel) The corresponding energy bands. The dashed lines show the Fermi levels.

**Fig. 8.** (Color online) (a) $V_\text{intra}$ dependences of $T_z$ and $\alpha_{xy}^{(E)}$ for $H_z^{(T)} = 0.2, 0.4, 0.6$. (b), (c) Counter plots of (b) $T_z$ and (c) $\alpha_{xy}^{(E)}$ in the plane of $H_z^{(T)}$ and $V_\text{intra}$. The dashed lines on (b) and (c) correspond to the data presented in (a). The other parameters are $\Delta' = -1.0$, $V_\text{inter} = 0.5$, $T = 0.1$, $\delta = 0.01$ and $1/5$ filling.
Fig. 9. (Color online) The intra-orbital ASOI \( g_{dd}(=2g_f) \) dependence of \( n_{e}^{(d)} \) for \( H^{(T)} \) = 0.2, and \( V_{\text{inta}} = 1 \). The other parameters correspond to those in Fig. 8.

5. Summary

We have investigated the atomic-scale MTD originating from the parity-mixing orbital degree of freedom in the microscopic model. We derived a minimal two-orbital model to examine the nature of the MTD by taking into account the odd-parity CEF and the atomic SOC. We clarified that two types of the MTDs emerge as an atomic object. The one is the in-plane MTDs depending on both the spin and orbital degrees of freedom, and the other is the out-of-plane MTD depending on only the orbital degree of freedom. We found that the in-plane MTD is activated by the in-plane magnetic moments or external magnetic field, while the out-of-plane MTD is expected to occur when the inter-orbital Coulomb interaction becomes large. Moreover, we examined a behavior of the ME effect for each MTD. We have shown that the large (small) odd-parity hybridization is favorable for the large ME effect in the in-(out-)plane MTD.

The atomic-scale MTDs in the present study can be realized in other noncentrosymmetric crystals. For example, the atomic-scale MTD can be induced by applying an external magnetic field to materials with the polar/chiral crystal structure, such as noncentrosymmetric superconductor CePtSi\(^{60(1)} \) and CeTSi\(^{3}_{3}\)\(^{R} = \text{Rh, Ir}\).\(^{31,42(1)} \) Furthermore, such a MTD degree of freedom is emergent even in centrosymmetric crystals when there is no local inversion symmetry at lattice sites, such as CeTAsO\(^{(T} = \text{Fe, Co, Ni, Mn}\).\(^{33-46(1)} \) Our microscopic analysis will give an insight for exploring the atomic-scale MTD in these materials.

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Appendix A: Definitions of Atomic \( d \)- and \( f \)-Orbital Wave Functions and Atomic Multipoles

In this Appendix, we present the definitions of atomic \( d \)- and \( f \)-orbital wave functions. The five \( d \)-orbital wave functions (\( \phi_x, \phi_y, \phi_z, \phi_{2x^2-r^2}, \phi_{3z^2-r^2} \)) are represented by

\[
(\phi_x, \phi_y, \phi_z, \phi_{2x^2-r^2}) = \sqrt{\frac{15}{4\pi}} \left( \frac{3z^2-r^2}{r^2} \right),
\]

where \( r = \sqrt{x^2+y^2+z^2} \).

We also present the expressions of multipoles for 0 \( \leq l \leq 3 \). By using the real expressions for the multipole operator \( \hat{X}_{lm} \), which are given by

\[
\hat{X}^{(c)}_{lm} = \frac{1}{\sqrt{2}} \hat{X}^{(c)}_{l-m} + (-1)^m \hat{X}^{(c)}_{l+m},
\]

(A-6)

\[
\hat{X}^{(s)}_{lm} = -\frac{1}{\sqrt{2}} \hat{X}^{(s)}_{l-m} - (-1)^m \hat{X}^{(s)}_{l+m},
\]

(A-7)

a monopole, dipoles, quadrupoles, and octupoles are expressed as

\[
\hat{X}_0 = \hat{X}^{(c)}_{00},
\]

(A-8)

\[
\left( \hat{X}_x, \hat{X}_y, \hat{X}_z \right) = \left( \hat{X}^{(c)}_{11}, \hat{X}^{(s)}_{11}, \hat{X}_{10} \right),
\]

(A-9)

\[
\left( \hat{X}_{x\overline{x}}, \hat{X}_{y\overline{y}}, \hat{X}_{z\overline{z}} \right) = \left( \hat{X}_{20}, \hat{X}^{(c)}_{21}, \hat{X}^{(s)}_{21}, \hat{X}^{(o)}_{22} \right),
\]

(A-10)

\[
\hat{X}_{32} = \hat{X}^{(o)}_{32},
\]

(A-11)

\[
\hat{X}_{30} = \frac{1}{\sqrt{2}} \left[ \sqrt{5} \hat{X}^{(c)}_{13} - \sqrt{5} \hat{X}^{(c)}_{31} \right],
\]

(A-12)

\[
\hat{X}_{32} = \frac{1}{\sqrt{2}} \left[ \sqrt{5} \hat{X}^{(o)}_{13} + \sqrt{5} \hat{X}^{(o)}_{31} \right],
\]

(A-13)

\[
\hat{X}_{30} = \hat{X}^{(o)}_{30},
\]

(A-14)

\[
\hat{X}_{33} = \frac{1}{\sqrt{2}} \left[ \sqrt{3} \hat{X}^{(c)}_{33} + \sqrt{3} \hat{X}^{(c)}_{31} \right],
\]

(A-15)

\[
\hat{X}_{32} = \frac{1}{\sqrt{2}} \left[ -\sqrt{3} \hat{X}^{(o)}_{33} + \sqrt{3} \hat{X}^{(o)}_{31} \right],
\]

(A-16)

\[
\hat{X}_{30} = \hat{X}^{(o)}_{32},
\]

(A-17)

Appendix B: The Inter- and Intra-Orbital Antisymmetric Spin-Orbit Interaction

The effective model in Eq. (18) implicitly includes the inter-orbital Rashba-type ASOI, as discussed in Sect. 2 in the main text. In this Appendix, we discuss the role of the inter-orbital ASOI by taking an appropriate unitary transformation for \( (\phi_{d,x}, \phi_{d,y}) \). As the inter-site hybridization \( H_{\text{mixing}} \) in Eq. (20) and the odd-parity CEF \( H_{\text{odd}} \) in Eq. (21) are important to derive the inter-orbital ASOI, we only consider these
where the subscript $\sigma$ represents the opposite spin component to $\sigma$. $\Delta_c^f$ is the atomic energy level split under the even-parity CEF for $\xi = d, f$ and $\Gamma = B_2$. $\Delta_{E}^{(1)}$ and $\Delta_{E}^{(2)}$ are the energy levels of two pairs of $f$ orbitals belonging to the representation $E$. $\phi_{E(\pm)}^{(s)}$ is defined in Sect. 2.1. By considering the odd-parity hybridization between $\phi_{d,\sigma}$ and $\phi'_{f,\sigma}(\phi_{f,\sigma}$ and $\phi'_{d,\sigma})$, the basis functions are modulated as
\[
\phi_{d,\sigma} \rightarrow \phi_{d,\sigma} \propto \left(\phi_{f,\sigma}^{(odd)} \frac{\phi_{d,\sigma}}{\Delta_d - \Delta_f^x}\right),
\]  
\[
\phi_{f,\sigma} \rightarrow \phi_{f,\sigma} \propto \left(\phi_{d,\sigma}^{(odd)} \frac{\phi_{f,\sigma}}{\Delta_f - \Delta_d^x}\right),
\]  
where $\phi_{f,\sigma}^{(odd)}$ hybridizes with orbitals with the second lowest energy. The order of $\phi_{f,\sigma}$ to the basis diagonalizing the odd-parity CEF, the Hamiltonian in Eq. (B-1) turns into
\[
\hat{H} = \sum_k E_k^c \hat{c}_k^c \hat{c}_k^\dagger,
\]  
\[
\hat{H}' = \left(\begin{array}{ccc}
0 & V_{\text{intra}} & 0 & h(k) \\
0 & V_{\text{intra}} & 0 & 0 \\
0 & h^\dagger(k) & 0 & 0 \\
0 & V_{\text{intra}} & 0 & 0
\end{array}\right),
\]  
where $E_k^c = (d_{k,\uparrow}, f_{k,\downarrow}, d_{k,\downarrow}, f_{k,\uparrow}) |e^c_k = (d_{k,\uparrow}, f_{k,\downarrow}, d_{k,\downarrow}, f_{k,\uparrow})$. By transforming $(\phi_{d,\sigma}, \phi_{f,\sigma})$ to the basis diagonalizing the odd-parity CEF, the Hamiltonian in Eq. (B-1) turns into
\[
\mathcal{H} = \sum_k E_k^c \frac{\hat{c}_k^c \hat{c}_k^\dagger}{2V_{\text{intra}}}
\]  
\[
\mathcal{H}' = \left(\begin{array}{ccc}
0 & V_{\text{intra}} & 0 & h(k) \\
0 & V_{\text{intra}} & 0 & 0 \\
0 & h^\dagger(k) & 0 & 0 \\
0 & V_{\text{intra}} & 0 & 0
\end{array}\right),
\]  
where $E_k^c = (d_{k,\uparrow}, f_{k,\downarrow}, d_{k,\downarrow}, f_{k,\uparrow}) |e^c_k = (d_{k,\uparrow}, b_{k,\downarrow}, a_{k,\downarrow}, b_{k,\uparrow})$. $a_{k,\uparrow}$ and $b_{k,\downarrow}$ are represented by $a_{k,\uparrow} = (d_{k,\uparrow} + f_{k,\downarrow})/\sqrt{2}$ and $b_{k,\downarrow} = (d_{k,\uparrow} + f_{k,\downarrow})/\sqrt{2}$. Then, the off-diagonal part in Eq. (B-5) represents the intra-orbital ASOC, which is shown as
\[
\mathcal{H}_{\text{ASOC}} = 2V_{\text{intra}} \sum_{k,r,s} \left(\begin{array}{cc}
sin k_z \sigma_{\gamma}^\alpha^\beta^\sigma^\nu^\alpha & -\sin k_z \sigma_{\nu}^\alpha^\beta^\sigma^\alpha
\end{array}\right) (b_{k,\sigma}^\dagger b_{k,\sigma}^\dagger c_{k,\dagger} c_{k,\dagger}^\dagger)
\]  
Note that this type of ASOC is present in a staggered way for orbitals $a$ and $b$.

Next, we discuss the intra-orbital ASOC for $(\phi_{d,\sigma}, \phi_{f,\sigma})$ ignored in the main text. The intra-orbital ASOC is obtained by considering the higher-order $d-f$ hybridization with respect to the odd-parity CEF and the atomic SOC. Assuming $(\phi_{d,\sigma}, \phi'_{f,\sigma})$ has the second lowest energy, as shown in Fig. B-1 (see also Fig. 2 in the main text), the wave functions of $(\phi_{d,\sigma}, \phi'_{f,\sigma})$ are represented by
\[
\phi_{d,\sigma} \propto \left(\begin{array}{c}
\phi_{d}\sigma \\
\phi_{f}\sigma^\dagger
\end{array}\right),
\]  
\[
\phi_{f,\sigma} \propto \left(\begin{array}{c}
\phi_{f}\sigma \\
\phi_{d}\sigma^\dagger
\end{array}\right),
\]  
where $\phi_{d,\sigma}$ and $\phi_{f,\sigma}$ are the $d$ and $f$ orbitals with the lowest energy, and $\phi_{d,\sigma}$ and $\phi_{f,\sigma}$ are the $d$ and $f$ orbitals with the second lowest energy.
