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Emergent cross-product-type spin-orbit coupling under ferroaxial ordering

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A ferroic alignment of a time-reversal-even axial vector, which is called the ferroaxial ordered state, is identified by the spontaneous rotational distortion of the lattice structure to break vertical mirror symmetry. We theoretically investigate what happens in the electronic structure once ferroaxial ordering occurs by analyzing a tetragonal d - p cluster model with transition metal oxide in mind. By adopting the symmetry-adapted multipole representation, we elucidate the emergent cross-product form of the spin-orbit coupling by the interplay between the atomic spin-orbit coupling and the d - p hybridization according to vertical mirror symmetry breaking, which corresponds to the electronic order parameter of ferroaxial ordering.

Introduction. In condensed matter physics, various types of spontaneous symmetry breaking owing to electron correlation have been extensively explored. In particular, the cooperation between the lattice and electron degrees of freedom gives rise to unconventional quantum states of matter, such as orbital ordering by the Jahn-Teller effect [1–3] and noncollinear magnetic ordering by spin-lattice coupling [4–6].

Among them, ferroaxial ordering has drawn growing interest in recent years since its direct observation in $\text{RbFe}(\text{MoO}_4)_2$ [7, 8] and NiTiO_3 [8–11]. These ferroaxial ordered phases are driven by the rotational structural distortion of the ligand sites surrounding the transition metal (TM) sites so as to break the mirror symmetry parallel to the principal axis, whose emergence requires the breaking of neither spatial inversion ($\mathcal{P}$) symmetry nor time-reversal ($\mathcal{T}$) symmetry. The different $\mathcal{P}$ and $\mathcal{T}$ parities of ferroaxial ordering from those of ferromagnetic and ferroelectric orderings indicate the appearance of further intriguing physical properties [12, 13]. For example, the ferroaxial ordering exhibits a rotational response of the conjugate physical quantities with the same $\mathcal{P}$ and $\mathcal{T}$ symmetries; an input field along the x (y) direction induces the conjugate physical quantities as an output along the y ($-x$) direction [14]. Furthermore, ferroaxial ordering shows an unconventional optical response such as electric gyration, which is the optical rotation induced by an external electric field parallel to the principal axis [8, 9].

From a symmetry viewpoint, the ferroaxial ordered phase is microscopically described as the ferroic alignment of a $\mathcal{T}$ -even axial vector. Since such an axial vector belongs to the identity irreducible representation in 13 out of 32 point groups [15], there are various candidate ferroaxial materials, such as $\text{Cu}_3\text{Nb}_2\text{O}_8$ [16], $\text{CaMn}_7\text{O}_{12}$ [17], BaCoSiO_4 [18], $\text{Ca}_5\text{Ir}_3\text{O}_{12}$ [19–22], $\text{K}_2\text{Zr}(\text{PO}_4)_2$ [23], $\text{Na}_2\text{Hf}(\text{BO}_3)_2$ [24], Na-superionic conductors [25], MnTiO_3 [26], and $1T\text{-TaS}_2$ [27, 28]. Nevertheless, the effect of rotational distortion on electronic structures has been less studied [14, 29], and the fundamental issue of how the lattice and electronic degrees of freedom are coupled has not been elucidated so far.

The symmetry-adapted multipole representation reveals that the ferroaxial order parameter is an electric

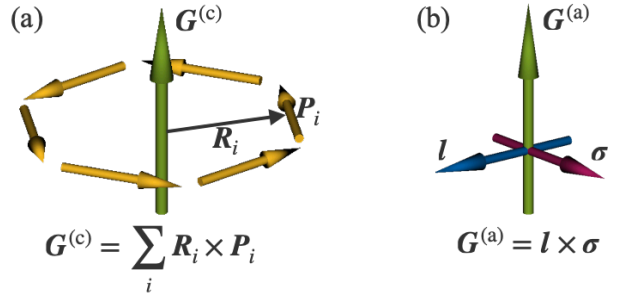


FIG. 1. Schematic pictures of (a) the cluster ETD $\mathbf{G}^{(c)}$ (green arrow) and (b) the atomic ETD $\mathbf{G}^{(a)}$ (green arrow). The cluster ETD is represented as a vortex of electric polarization (yellow arrows), while the atomic ETD is represented as an outer product of orbital angular momentum $\mathbf{l}$ (blue arrow) and spin angular momentum $\boldsymbol{\sigma}$ (purple arrow).

toroidal dipole (ETD) [30], which is often defined as a vortex consisting of multiple electric dipoles [31–33];

$$\mathbf{G}^{(c)} = \sum_i \mathbf{R}_i \times \mathbf{P}_i, \quad (1)$$

where $\mathbf{R}_i$ and $\mathbf{P}_i$ are the position and electric polarization of site i , respectively, as shown in Fig. 1(a).

Although the quantity in Eq. (1) provides an intuitive understanding of the emergence of ferroaxial ordering in rotationally distorted systems, the choice of the cluster origin is ambiguous in a periodic crystal structure. In addition, the description based on Eq. (1) is sometimes ill-defined, since the electric polarization is not directly related to the rotational distortion of the ligand sites.

Alternatively, the atomic description independent of the cluster origin is introduced as [34]

$$\mathbf{G}^{(a)} = \mathbf{l} \times \boldsymbol{\sigma}, \quad (2)$$

where $\mathbf{l}$ and $\boldsymbol{\sigma} = 2\mathbf{s}$ are the orbital and spin angular momenta as shown in Fig. 1(b), respectively. This corresponds to emergent cross-product-type spin-orbit coupling (SOC), which is qualitatively different from the conventional relativistic SOC defined by the inner product as $\mathbf{l} \cdot \boldsymbol{\sigma}$. In other words, further intriguing spin-orbital-lattice entangled physics is expected under ferroaxial ordering.

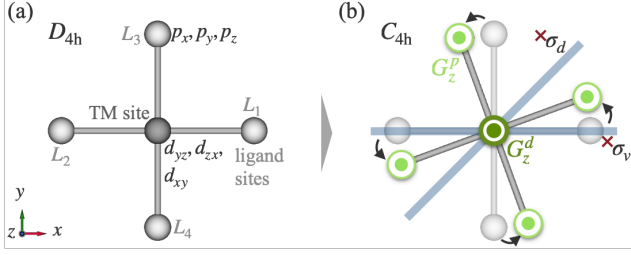


FIG. 2. Schematic structure of the five-site tetragonal cluster model under the point group (a) D_{4h} and (b) C_{4h} . The TM sites consist of d_{yz}, d_{zx}, d_{xy} orbitals and the ligand sites (L_1-L_4) consist of p_x, p_y, p_z orbitals. The z -component of the atomic ETD on the TM site (G_z^d) and ligand sites (G_z^p), which are represented by dark green and light green circles, respectively, are activated according to vertical mirror symmetry (σ_v and σ_d) breaking.

However, the microscopic origin of such an atomic ETD has not been clarified. In the present Letter, we show the microscopic origin of the atomic ETD by analyzing a fundamental d - p cluster model. We find that the interplay between the relativistic atomic SOC and the d - p hybridization caused by the rotational distortion of the ligand sites is a source of unconventional cross-product-type SOC.

Model. With the TM oxide consisting of a TM surrounded by four ligand oxygens in mind, we consider a fundamental d - p model under tetragonal D_{4h} symmetry; there are three d orbitals (d_{yz}, d_{zx}, d_{xy}) at the TM site and three p orbitals (p_x, p_y, p_z) at the ligand sites L_1-L_4 as shown in Fig. 2(a). The model Hamiltonian is given as

$$\mathcal{H} = \mathcal{H}_{\text{CEF}} + \mathcal{H}_{\text{SOC}} + \mathcal{H}_{dp}. \quad (3)$$

The first term $\mathcal{H}_{\text{CEF}}$ represents the CEF Hamiltonian, where the atomic-energy levels for the (d_{yz}, d_{zx}, d_{xy}) orbitals under the D_{4h} site symmetry are (1.7, 1.7, 1.4) at the TM site and those for the (p_x, p_y, p_z) orbitals under the C_{2v} site symmetry are (0.4, 0.2, 0) at the L_1 site; the p_z level is taken for the energy origin. The second term $\mathcal{H}_{\text{SOC}}$ represents the atomic SOC for the d orbitals at the TM site and for the p orbitals at the ligand sites, which are represented by

$$\mathcal{H}_{\text{SOC}} = \lambda_p \sum_k \mathbf{l}_k^p \cdot \mathbf{s}_k^p + \lambda_d \mathbf{l}^d \cdot \mathbf{s}^d, \quad (4)$$

where $\mathbf{l}^d$ and $\mathbf{s}^d$ ($\mathbf{l}_k^p$ and $\mathbf{s}_k^p$ for $k = L_1-L_4$) are the orbital and spin angular momentum operators at the TM (ligand) site, respectively. The third term represents the d - p hybridization between the TM and ligand sites, which is given by

$$\mathcal{H}_{dp} = \sum_{k=L_1}^{L_4} \sum_{\alpha\beta\sigma} t_{\alpha\beta}^{A_{1g}} c_{\alpha\sigma}^\dagger c_{\beta\sigma} + (\text{h.c.}), \quad (5)$$

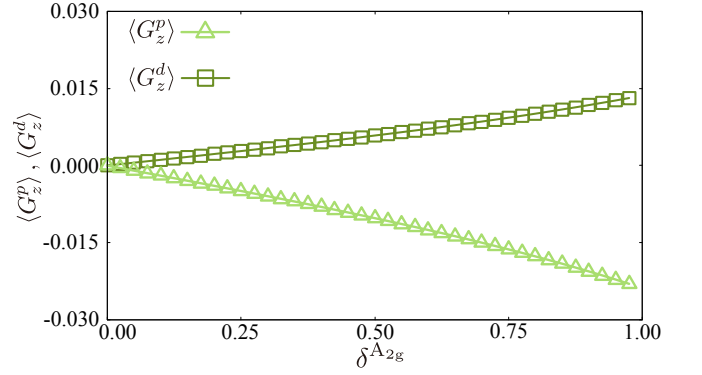


FIG. 3. Expectation values of the ETD for the p orbital ($\langle G_z^p \rangle$) and that for the d orbital ($\langle G_z^d \rangle$) against the hybridization originating from the rotational distortion, δA_{2g} , for the filling per site $n = 28/5$, $t_{x,xy}^{A_{2g}} = 0.4\delta A_{2g}$, $t_{z,yz}^{A_{2g}} = 0.2\delta A_{2g}$, $t_{y,xy}^{A_{1g}} = 0.6$, $t_{z,zx}^{A_{1g}} = 1.4$, $\lambda_p = 0.05$, and $\lambda_d = 0.07$.

where $c_{\alpha\sigma}^\dagger$ ($c_{\alpha\sigma}$) is the creation (annihilation) operator; α represents (d_{yz}, d_{zx}, d_{xy}) orbitals, β represents a set of (p_x, p_y, p_z) orbitals and ligand sites L_1-L_4 , and σ represents the up and down spins. By using the Slater-Koster parameters, there are two symmetry-allowed hybridization parameters: One is the hybridization between d_{xy} and p_y , $t_{y,xy}^{A_{1g}}$, and the other is that between d_{zx} and p_z orbitals, $t_{z,zx}^{A_{1g}}$, for the L_1 site. The hybridization parameters $t_{\alpha\beta}^{A_{1g}}$ for $k = L_2-L_4$ are obtained by the fourfold rotation around the TM site.

When the rotational structural distortion by the ligand sites to break the vertical mirror symmetry occurs as shown in Fig. 2(b), the point group symmetry reduces to C_{4h} and the A_{2g} representation under D_{4h} belongs to the identity irreducible representation A_g . Since the cross-product-type SOC in Eq. (2) also belongs to the A_{2g} representation under D_{4h} , one can expect nonzero expectation values of the atomic ETD under C_{4h} . To understand the microscopic origin of such an ETD, we focus on the modulation of the d - p hybridizations induced by the rotational distortion. Reflecting the lack of vertical mirror symmetry in Fig. 2(b), two additional hybridization parameters are symmetry-allowed in Eq. (5), which correspond to the hybridization between d_{xy} and p_x orbitals, $t_{x,xy}^{A_{2g}}$, and that between d_{yz} and p_z orbitals, $t_{z,yz}^{A_{2g}}$, in the case of the L_1 site.

Numerical results. Figure 3 represents the behavior of the atomic ETD when the hybridization parameters, $t_{x,xy}^{A_{2g}}$ and $t_{z,yz}^{A_{2g}}$, are varied. Here, we evaluate the expectation values of the ETD operators for the p and d orbitals, which are defined by $G_z^p = \sum_k (\mathbf{l}_k^p \times \boldsymbol{\sigma}_k^p)_z$ and $G_z^d = (\mathbf{l}^d \times \boldsymbol{\sigma}^d)_z$ [35]. In addition, we parametrize the modulation of the hybridization as δA_{2g} with $t_{x,xy}^{A_{2g}} = 0.4\delta A_{2g}$ and $t_{z,yz}^{A_{2g}} = 0.2\delta A_{2g}$. The other model parameters are set as $t_{y,xy}^{A_{1g}} = 0.6$, $t_{z,zx}^{A_{1g}} = 1.4$, $\lambda_p = 0.05$, and $\lambda_d = 0.07$ for the filling per site $n = 28/5$. The result shows that both $\langle G_z^p \rangle$

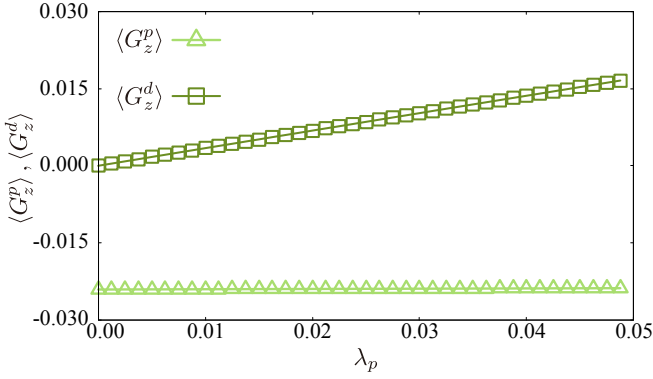


FIG. 4. λ_p dependence of $\langle G_z^p \rangle$ and $\langle G_z^d \rangle$, for the filling per site $n = 28/5$, $t_{x,xy}^{A_{2g}} = 0.4$, $t_{z,yz}^{A_{2g}} = 0.2$, $t_{y,xy}^{A_{1g}} = 0.6$, $t_{z,zx}^{A_{1g}} = 1.4$, and $\lambda_d = 0.07$.

and $\langle G_z^d \rangle$ become finite for nonzero $\delta^{A_{2g}}$, which indicates that the cross-product-type SOC emerges according to vertical mirror symmetry breaking.

Let us show the important microscopic degrees of freedom to induce the cross-product-type SOC. One is the atomic SOC. The SOC for the p orbital is necessary for nonzero $\langle G_z^d \rangle$, as demonstrated by its λ_p dependence in Fig. 4 by fixing $t_{x,xy}^{A_{2g}} = 0.4$ and $t_{z,yz}^{A_{2g}} = 0.2$ while keeping the other parameters; $\langle G_z^d \rangle$ vanishes for $\lambda_p = 0$, while $\langle G_z^p \rangle$ is less sensitive to λ_p . The opposite tendency occurs when $\lambda_d = 0$ instead of λ_p ; $\langle G_z^p \rangle$ vanishes and $\langle G_z^d \rangle$ takes nonzero values. Thus, $\langle G_z^d \rangle$ and $\langle G_z^p \rangle$ vanish in the absence of the SOC for the other orbitals. The other is the three d and p orbital degrees of freedom. Among them, p_z and d_{xy} orbitals are necessary since $\langle G_z^d \rangle$ ($\langle G_z^p \rangle$) vanishes when the p_z (d_{xy}) orbital is neglected, where the ETD operator G_z^p (G_z^d) is no longer defined in this case. In addition, the other four orbitals are also necessary to define the ETD operator in the p and d orbital space so that the orbital angular momentum $\mathbf{l}$ can be activated. Therefore, the d - p model consisting of six orbitals in Eq. (3) is a minimal model to capture the origin of the cross-product-type SOC.

Perturbation analysis. To get further deep insight into the microscopic origin of the cross-product-type SOC, we perform the perturbative analysis; we focus on the important ingredients for obtaining nonzero $\langle G_z^d \rangle$. For this purpose, we simplify the d - p model in Eq. (3) by neglecting the atomic SOC for the d orbitals and suppose the same CEF level for the three d and p orbitals as Δ and 0, respectively, since these factors are not important in the following results. The simplified Hamiltonian is given by

$$\mathcal{H}_{\text{tot}} = \mathcal{H}_0 + \mathcal{H}_{dp}, \quad (6)$$

$$\mathcal{H}_0 = \Delta \sum_{\alpha\sigma} c_{\alpha\sigma}^\dagger c_{\alpha\sigma} + \lambda_p \sum_k \mathbf{l}_k^p \cdot \mathbf{s}_k^p. \quad (7)$$

Using the perturbative wave functions within the second order of $\mathcal{H}_{dp}$, the effective hybridization paths to couple

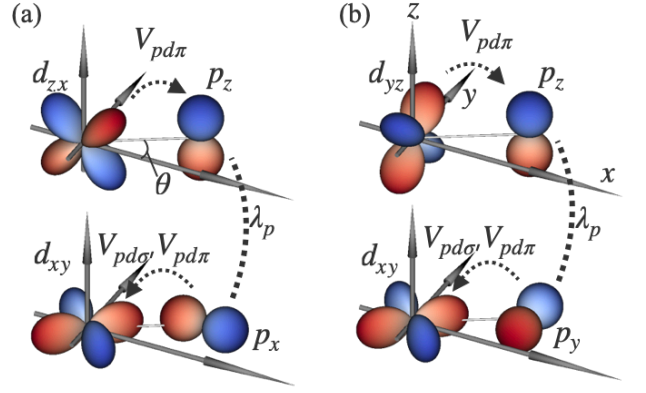


FIG. 5. Two effective hybridization paths between the TM site and the ligand L_1 site to induce the atomic ETD (cross-product-type SOC) at the TM site, which are represented by (a) $\lambda_p t_{z,zx}^{A_{1g}} t_{x,xy}^{A_{2g}}$ and (b) $\lambda_p t_{y,xy}^{A_{1g}} t_{z,yz}^{A_{2g}}$.

with the atomic ETD for the d orbital along the L_1 site are derived as

$$\text{Tr}[\mathcal{H}_{L_1}^{(2)} G_z^d] = \frac{4\lambda_p (t_{z,zx}^{A_{1g}} t_{x,xy}^{A_{2g}} - t_{y,xy}^{A_{1g}} t_{z,yz}^{A_{2g}})}{(\Delta - \lambda_p)(\lambda_p + 2\Delta)}, \quad (8)$$

where $\mathcal{H}_{L_1}^{(2)}$ stands for the contribution from the L_1 site in the effective Hamiltonian obtained by the second-order perturbation in terms of $\mathcal{H}_{dp}$, whose general form is given by

$$\mathcal{H}^{(2)} = \sum_{\alpha\alpha'\tilde{\beta}\tilde{\sigma}\sigma''} \frac{\langle d_{\alpha,\sigma}^{(0)} | \mathcal{H}_{dp} | p_{\tilde{\beta},\sigma''}^{(0)} \rangle \langle p_{\tilde{\beta},\sigma''}^{(0)} | \mathcal{H}_{dp} | d_{\alpha',\sigma'}^{(0)} \rangle}{E_{\alpha}^{(0)} - E_{\tilde{\beta},\sigma''}^{(0)}}. \quad (9)$$

Here, $|p_{\tilde{\beta},\sigma''}^{(0)}\rangle$ and $|d_{\alpha',\sigma'}^{(0)}\rangle$ ($E_{\tilde{\beta},\sigma''}^{(0)}$ and $E_{\alpha}^{(0)}$) represent the eigenvectors (energy levels) of $\mathcal{H}_0$ for spin $\sigma', \sigma'' = \uparrow, \downarrow$, respectively; the subscripts α, α' ($\tilde{\beta}$) stand for the index for yz, zx , and xy (x, y , and z) orbitals. $E_{\alpha}^{(2)}$ denotes the second-order energy correction and $\mathbf{1}$ denotes the 6×6 identity matrix.

By taking the limit of the large energy difference between the d and p orbitals ($\Delta \gg \lambda_p$), the expression in Eq. (8) turns into

$$\text{Tr}[\mathcal{H}_{L_1}^{(2)} G_z^d] \simeq \frac{2\lambda_p}{\Delta^2} (t_{z,zx}^{A_{1g}} t_{x,xy}^{A_{2g}} - t_{y,xy}^{A_{1g}} t_{z,yz}^{A_{2g}}) \quad (10)$$

$$\propto \lambda_p \sin 4\theta (\sqrt{3}V_{pd\sigma} - 2V_{pd\pi})V_{pd\pi}. \quad (11)$$

In the last line, we introduce the Slater-Koster parameters, $V_{pd\sigma}$ and $V_{pd\pi}$, and θ corresponding to the rotational angle measured from the x -axis as shown in Fig. 5(a).

The expression in Eq. (10) reveals the important hybridization paths as well as the atomic SOC for obtaining the atomic ETD (cross-product-type SOC); the modulations of the hybridization owing to the rotational distortion, $t_{x,xy}^{A_{2g}}$ and $t_{z,yz}^{A_{2g}}$, contribute to the atomic ETD

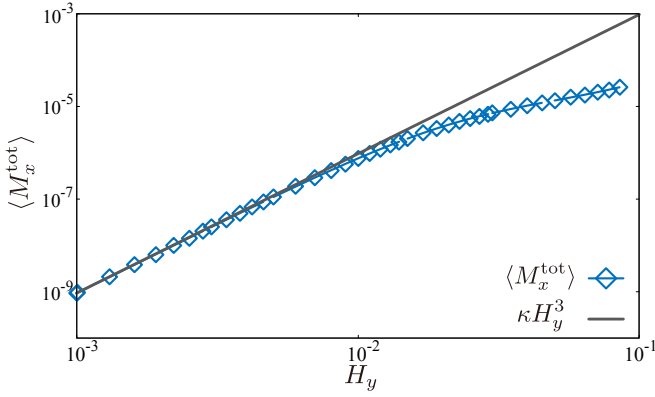


FIG. 6. H_y dependence of $\langle M_x^{\text{tot}} \rangle$ at $t_{x,xy}^{\text{A}_{2g}} = 0.4$, $t_{z,yz}^{\text{A}_{2g}} = 0.2$, $t_{y,xy}^{\text{A}_{1g}} = 0.6$, $t_{z,zx}^{\text{A}_{1g}} = 1.4$, $\lambda_p = 0.05$, $\lambda_d = 0.07$, and the filling per site $n = 28/5$. The gray line shows the fitting line by κH_y^3 with $\kappa = 0.948377$.

in collaboration with the A_{1g} -type hybridizations, $t_{z,zx}^{\text{A}_{1g}}$ and $t_{y,xy}^{\text{A}_{1g}}$, for the L_1 site, respectively. In addition, one finds that such a coupling between A_{1g} -type and A_{2g} -type hybridizations is enabled by the atomic SOC for the p orbital λ_p . In a similar manner, the conditions of inducing the atomic ETD for the p orbital is obtained by replacing λ_p with $-\lambda_d$ in Eq. (8). This perturbative result is consistent with the numerical result discussed above. Moreover, as shown in Figs. 5(a) and 5(b), two effective hybridization paths include the p_z orbital. This is why the p_z orbital is necessary for inducing the atomic ETD at the TM site.

From Eq. (11), the effective hybridization vanishes for $\theta = \pi n/4$ ($n \in \mathbb{Z}$). This is understood from the fact that the x direction is equivalent to the y direction for $\theta = \pi n/4$, which means the recovery of the vertical mirror symmetry. In other words, the point group symmetry remains D_{4h} for $\theta = \pi n/4$. This result also indicates that the lack of vertical mirror symmetry is essential for inducing the atomic ETD, which is consistent with the symmetry consideration.

Magnetic response. Once ferroaxial ordering occurs, various physical phenomena are expected to emerge,

such as electric gyration [8, 9], spin current generation [13, 14], antisymmetric thermopolarization [36], third-order transverse magnetization [37], second-order nonlinear magnetostriction [38], and magnetic instability [39]. Among them, we here evaluate the third-order transverse magnetization under ferroaxial ordering. The effect of an external magnetic field is introduced as the Zeeman coupling effect given by

$$\mathcal{H}_{\text{ex}} = -\mu_B \mathbf{M}^{\text{tot}} \cdot \mathbf{H}, \quad (12)$$

where $\mathbf{M}^{\text{tot}} = \mathbf{l}^d + 2\mathbf{s}^d + \sum_k (\mathbf{l}_k^p + 2\mathbf{s}_k^p)$ is the uniform magnetization and the Bohr magneton μ_B is set as unity. When the ferroaxial state occurs, the third-order transverse magnetization as $M_x^{\text{tot}} = \chi_{xyyy} H_y^3$ and $M_y^{\text{tot}} = -\chi_{yxxx} H_x^3$ is expected from the symmetry. The numerical evaluation indicates that the transverse magnetization $\langle M_x^{\text{tot}} \rangle$ is induced in the order of H_y^3 , as shown in Fig. 6, as expected from the symmetry analysis; model parameters are set as the filling per site $n = 28/5$, $t_{x,xy}^{\text{A}_{2g}} = 0.4$, $t_{z,yz}^{\text{A}_{2g}} = 0.2$, $t_{y,xy}^{\text{A}_{1g}} = 0.6$, $t_{z,zx}^{\text{A}_{1g}} = 1.4$, $\lambda_p = 0.05$, and $\lambda_d = 0.07$. We also confirm the relation of $M_x/H_y^3 = -M_y/H_x^3$ for the small magnetic field. Such a transverse magnetization becomes a macroscopic experimental signal of the ferroaxial ordering.

Summary. We have proposed an emergent cross-product-type SOC, which corresponds to the atomic ETD, under ferroaxial ordering with rotational structural distortion. By analyzing the d - p tetragonal cluster model, we have shown that the synergy between the atomic SOC and the d - p hybridization arising from the breaking of the vertical mirror symmetries induces an atomic ETD, which can become the origin of the intriguing responses of the conjugate physical quantities as a consequence of spin-orbital-lattice entanglement.

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[1] S. V. Streltsov and D. I. Khomskii, Orbital physics in transition metal compounds: new trends, *Phys. Usp.* **60**, 1121 (2017).
[2] B. Pandey, Y. Zhang, N. Kaushal, R. Soni, L.-F. Lin, W.-J. Hu, G. Alvarez, and E. Dagotto, Origin of the magnetic and orbital ordering in α - Sr_2CrO_4 , *Phys. Rev. B* **103**, 045115 (2021).
[3] L.-F. Lin, N. Kaushal, Y. Zhang, A. Moreo, and E. Dagotto, Orbital ordering in the layered perovskite material CsVF_4 , *Phys. Rev. Mater.* **5**, 025001 (2021).
[4] J.-H. Chung, M. Matsuda, S.-H. Lee, K. Kakurai, H. Ueda, T. J. Sato, H. Takagi, K.-P. Hong, and S. Park, Statics and Dynamics of Incommensurate Spin Order in

a Geometrically Frustrated Antiferromagnet CdCr_2O_4 , *Phys. Rev. Lett.* **95**, 247204 (2005).
[5] F. Ye, Y. Ren, Q. Huang, J. A. Fernandez-Baca, P. Dai, J. W. Lynn, and T. Kimura, Spontaneous spin-lattice coupling in the geometrically frustrated triangular lattice antiferromagnet CuFeO_2 , *Phys. Rev. B* **73**, 220404 (2006).
[6] M. Gen, T. Nakajima, H. Saito, Y. Tokunaga, and T.-h. Arima, Spin-Lattice-Coupled Helical Magnetic Order in Breathing Pyrochlore Magnets, $\text{CuAlCr}_4\text{S}_8$ and $\text{CuGaCr}_4\text{S}_8$, *Journal of the Physical Society of Japan* **93**, 104602 (2024).
[7] W. Jin, E. Drueke, S. Li, A. Admasu, R. Owen, M. Day,

- K. Sun, S.-W. Cheong, and L. Zhao, Observation of a ferro-rotational order coupled with second-order nonlinear optical fields, *Nat. Phys.* **16**, 42 (2020).
- [8] T. Hayashida, Y. Uemura, K. Kimura, S. Matsuoka, M. Hagihala, S. Hirose, H. Morioka, T. Hasegawa, and T. Kimura, Phase transition and domain formation in ferroaxial crystals, *Phys. Rev. Materials* **5**, 124409 (2021).
- [9] T. Hayashida, Y. Uemura, K. Kimura, S. Matsuoka, D. Morikawa, S. Hirose, K. Tsuda, T. Hasegawa, and T. Kimura, Visualization of ferroaxial domains in an order-disorder type ferroaxial crystal, *Nat. Commun.* **11**, 4582 (2020).
- [10] H. Yokota, T. Hayashida, D. Kitahara, and T. Kimura, Three-dimensional imaging of ferroaxial domains using circularly polarized second harmonic generation microscopy, *npj Quantum Mater.* **7**, 106 (2022).
- [11] X. Fang, C. De, F.-T. Huang, X. Xu, K. Du, K. Wang, B. Li, and S.-W. Cheong, Ferrorotational Selectivity in Ilmenites, *J. Am. Chem. Soc.* **145**, 28022 (2023).
- [12] S.-W. Cheong, S. Lim, K. Du, and F.-T. Huang, Permutable SOS (symmetry operational similarity), *npj Quantum Mater.* **6**, 58 (2021).
- [13] A. Roy, M. H. D. Guimarães, and J. Ślawińska, Unconventional spin Hall effects in nonmagnetic solids, *Phys. Rev. Materials* **6**, 045004 (2022).
- [14] S. Hayami, R. Oiwa, and H. Kusunose, Electric Ferro-Axial Moment as Nanometric Rotator and Source of Longitudinal Spin Current, *J. Phys. Soc. Jpn* **91**, 113702 (2022).
- [15] J. Hlinka, J. Privratska, P. Ondrejčokovic, and V. Janovec, Symmetry Guide to Ferroaxial Transitions, *Phys. Rev. Lett.* **116**, 177602 (2016).
- [16] R. D. Johnson, S. Nair, L. C. Chapon, A. Bombardi, C. Vecchini, D. Prabhakaran, A. T. Boothroyd, and P. G. Radaelli, $\text{Cu}_3\text{Nb}_2\text{O}_8$: A Multiferroic with Chiral Coupling to the Crystal Structure, *Phys. Rev. Lett.* **107**, 137205 (2011).
- [17] R. D. Johnson, L. C. Chapon, D. D. Khalyavin, P. Manuel, P. G. Radaelli, and C. Martin, Giant Improper Ferroelectricity in the Ferroaxial Magnet $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. Lett.* **108**, 067201 (2012).
- [18] X. Xu, F.-T. Huang, A. S. Admasu, M. Kratochvířlová, M.-W. Chu, J.-G. Park, and S.-W. Cheong, Multiple ferroic orders and toroidal magnetoelectricity in the chiral magnet BaCoSiO_4 , *Phys. Rev. B* **105**, 184407 (2022).
- [19] T. Hasegawa, W. Yoshida, K. Nakamura, N. Ogita, and K. Matsuhira, Raman Scattering Investigation of Structural Transition in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, *J. Phys. Soc. Jpn.* **89**, 054602 (2020).
- [20] H. Hanate, T. Hasegawa, S. Hayami, S. Tsutsui, S. Kawano, and K. Matsuhira, First Observation of Superlattice Reflections in the Hidden Order at 105 K of Spin-Orbit Coupled Iridium Oxide $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, *J. Phys. Soc. Jpn.* **90**, 063702 (2021).
- [21] S. Hayami, S. Tsutsui, H. Hanate, N. Nagasawa, Y. Yoda, and K. Matsuhira, Cluster Toroidal Multipoles Formed by Electric-Quadrupole and Magnetic-Octupole Trimers: A Possible Scenario for Hidden Orders in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, *J. Phys. Soc. Jpn.* **92**, 033702 (2023).
- [22] H. Hanate, S. Tsutsui, T. Yajima, H. Nakao, H. Sagayama, T. Hasegawa, and K. Matsuhira, Space-Group Determination of Superlattice Structure Due to Electric Toroidal Ordering in $\text{Ca}_5\text{Ir}_3\text{O}_{12}$, *J. Phys. Soc. Jpn.* **92**, 063601 (2023).
- [23] S. Yamagishi, T. Hayashida, R. Misawa, K. Kimura, M. Hagihala, T. Murata, S. Hirose, and T. Kimura, Ferroaxial Transitions in Glaserite-type Compounds: Database Screening, Phonon Calculations, and Experimental Verification, *Chem. Mater.* **35**, 747 (2023).
- [24] T. Nagai and T. Kimura, Chemical Switching of Ferroaxial and Nonferroaxial Structures Based on Second-Order Jahn-Teller Activity in $(\text{Na,K})_2\text{Hf}(\text{BO}_3)_2$, *Chem. Mater.* **35**, 4109 (2023).
- [25] T. Nagai, Y. Mochizuki, S. Yoshida, and T. Kimura, Chemical Aspect of Displacive-Type Ferroaxial Phase Transition from Perspective of Second-Order Jahn-Teller Effect: NASICON Systems as an Example, *J. Am. Chem. Soc.* **145**, 8090 (2023).
- [26] D. Sekine, T. Sato, Y. Tokunaga, T.-h. Arima, and M. Matsubara, Second harmonic imaging of antiferromagnetic domains and confirmation of absence of ferroaxial twins in MnTiO_3 , *Phys. Rev. Mater.* **8**, 064406 (2024).
- [27] X. Luo, D. Obeysekera, C. Won, S. H. Sung, N. Schnitzer, R. Hovden, S.-W. Cheong, J. Yang, K. Sun, and L. Zhao, Ultrafast Modulations and Detection of a Ferro-Rotational Charge Density Wave Using Time-Resolved Electric Quadrupole Second Harmonic Generation, *Phys. Rev. Lett.* **127**, 126401 (2021).
- [28] G. Liu, T. Qiu, K. He, Y. Liu, D. Lin, Z. Ma, Z. Huang, W. Tang, J. Xu, K. Watanabe, *et al.*, Electrical switching of ferro-rotational order in nanometre-thick $1T$ - TaS_2 crystals, *Nat. Nanotechnol.* **18**, 854 (2023).
- [29] S. Bhowal and N. A. Spaldin, Electric toroidal dipole order and hidden spin polarization in ferroaxial materials, *arXiv:2407.08369* (2024).
- [30] S. Hayami and H. Kusunose, Unified description of electronic orderings and cross correlations by complete multipole representation, *J. Phys. Soc. Jpn.* **93**, 072001 (2024).
- [31] V. Dubovik and A. Cheshkov, Multipole expansion in classical and quantum field theory and radiation, *Sov. J. Part. Nucl.* **5**, 318 (1975).
- [32] V. Dubovik, L. Tosunyan, and V. Tugushev, Axial toroidal moments in electrodynamics and solid-state physics, *Zh. Eksp. Teor. Fiz* **90**, 590 (1986).
- [33] V. Dubovik and V. Tugushev, Toroid moments in electrodynamics and solid-state physics, *Phys. Rep.* **187**, 145 (1990).
- [34] H. Kusunose, R. Oiwa, and S. Hayami, Complete Multipole Basis Set for Single-Centered Electron Systems, *J. Phys. Soc. Jpn.* **89**, 104704 (2020).
- [35] H. Kusunose, R. Oiwa, and S. Hayami, Symmetry-adapted modeling for molecules and crystals, *Phys. Rev. B* **107**, 195118 (2023).
- [36] J. Nasu and S. Hayami, Antisymmetric thermopolarization by electric toroidicity, *Phys. Rev. B* **105**, 245125 (2022).
- [37] A. Inda and S. Hayami, Nonlinear Transverse Magnetic Susceptibility under Electric Toroidal Dipole Ordering, *J. Phys. Soc. Jpn.* **92**, 043701 (2023).
- [38] A. Kirikoshi and S. Hayami, Rotational Response Induced by Electric Toroidal Dipole, *J. Phys. Soc. Jpn.* **92**, 123703 (2023).
- [39] A. Inda and S. Hayami, Magnetic instability under ferroaxial moment, *Phys. Rev. B* **109**, 174424 (2024).