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Improper magnetic ferroelectricity of nearly pure electronic nature in helicoidal spiral $\text{CaMn}_7\text{O}_{12}$

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Abstract

Helicoidal magnetic order breaks inversion symmetry in quadruple perovskite $\text{CaMn}_7\text{O}_{12}$, generating one of the largest spin-induced ferroelectric polarizations measured to date. Here, the microscopic origin of the polarization, including exchange interactions, coupling to the spin helicity, and charge density redistribution, is explored via first-principles calculations. The B -site Mn^{4+} (Mn3) spin adopts a noncentrosymmetric configuration, stabilized by spin-orbit coupling as well as fully anisotropic Hubbard J parameter, to break inversion symmetry and generate polarization. Berry phase computed polarization ($P_{\text{elec}} = -2169 \mu\text{C}/\text{m}^2$) exhibits nearly pure electronic behavior, with negligible Mn displacements ($\approx 0.7 \text{ m}\text{\AA}$). Orbital-resolved density of states shows that p - d orbital mixing is microscopically driven by nonrelativistic exchange striction within the commensurate ionic structure. Persistent electronic polarization induced by helical spin order in nearly inversion-symmetric ionic crystal lattice suggests opportunities for ultrafast magnetoelectric response.

Multiferroics, simultaneously displaying ferroelectricity and intrinsic magnetic ordering, have gained much attention due to the complex physics underlying the magnetoelectric effect and its potential applications in spin-driven electronics^{1,2}. Based on the nature of the order parameter coupling, multiferroics are classified into type-I and type-II³. Type-I consists of $6s^2$ lone-pair proper ferroelectrics⁴⁻⁶ and improper ferroelectrics of electronic⁷ and geometric origins⁸ including hybrid improper ferroelectrics⁹, where ferroelectricity remains largely independent of magnetism. Type-II essentially refers to improper magnetic ferroelectrics, where spin ordering breaks inversion symmetry, resulting in ionic displacements and/or electronic charge redistribution that provide macroscopic polarization. Numerous examples include: (a) cycloidal spiral systems¹⁰⁻¹⁷, (b) triangular lattice systems with proper screw-type spiral¹⁸⁻²², and (c) exchange striction systems with collinear magnetism²³⁻²⁶. Despite relatively small polarization and low Curie temperature, type-II multiferroics can potentially lead to the design of robust room-temperature multiferroics with large spontaneous polarization and ultrafast switchability.

Historically, three microscopic models have been established in the literature²⁷⁻³⁰. First, the exchange striction model proposes that nonrelativistic symmetric exchange interactions in a $\uparrow\uparrow\downarrow\downarrow$ spin order cause ferromagnetically coupled ions to move toward each other and/or electronic charge density to shift, generating $\mathbf{P}_{12} \propto \mathbf{e}_{12} (\mathbf{S}_1 \cdot \mathbf{S}_2)$. Here, \mathbf{P}_{12} is the intersite vector polarization, and \mathbf{e}_{12} is a unit vector connecting the two magnetic ions. Second, the spin-current (KNB) model³¹, analytically equivalent to the inverse Dzyaloshinskii-Moriya (DM) model²⁴, is derived from spin-orbit coupling (SOC). Here, a nonmagnetic anion and/or electronic charge density shifts in response to relativistic DM interaction between the two canted spin sites, generating $\mathbf{P}_{12} \propto \mathbf{e}_{12} \times (\mathbf{S}_1 \times \mathbf{S}_2)$. Third, in the spin-dependent p - d hybridization model, SOC causes an intrasite polarization along the metal-ligand bond, $\mathbf{P}_{\text{ml}} \propto (\mathbf{S}_{\text{m}} \cdot \mathbf{e}_{\text{ml}})^2 \mathbf{e}_{\text{ml}}$ ^{20,32,33}, where \mathbf{e}_{ml} is the metal-ligand unit vector. While these three models are microscopic in nature, they depend on specific crystal lattice geometries.

Recently, a phenomenological model for spin-induced ferroelectricity has been shown to be capable of reproducing the aforementioned microscopic models as its limiting subcases³⁴. The model first distinguishes between the ionic and the electronic contributions to the total polarization. Spin-induced ionic displacements have been reported to be small, usually less than 10 mÅ. Electronic contribution consists of intrasite (single-site) and intersite polarization. The intrasite term corresponds to the spin-dependent p - d hybridization term and is

considered negligible in most cases. The intersite term consists of the exchange striction term $[\propto (\mathbf{S}_1 \cdot \mathbf{S}_2)]$ and the spin-current term $[\propto (\mathbf{S}_1 \times \mathbf{S}_2)]$, where the latter was originally formulated in the generalized spin-current model³⁵. Here, \mathbf{S}_1 and \mathbf{S}_2 are the vector spins on the two neighboring sites 1 and 2. It is important to note that this model is phenomenological and does not by itself provide any microscopic information unless accompanied by first-principles analysis.

$\text{CaMn}_7\text{O}_{12}$ manifests one of the largest spin-induced polarizations measured to date ($P = 2870 \mu\text{C}/\text{m}^2$)³⁶. Exchange striction has been proposed as the main microscopic mechanism^{37–39}, with small SOC contribution from the spin-dependent p - d hybridization³⁸, as well as inverse-DM contribution in the presence of structural modulation^{39,40}. However, the exact role of ionic displacements and the origin of the polarization direction require further clarification and analysis.

Here, we report on the ferroelectric polarization of nearly pure electronic nature in $\text{CaMn}_7\text{O}_{12}$ induced by its helicoidal magnetic ground state, computed via density functional theory (DFT) calculations. For simplicity and clarity, we preserve inversion symmetry on the ionic lattice while the charge density distribution is permitted to respond to the symmetry-breaking spin pattern; these changes to orbital mixing make the dominant contribution to the polarization. We employ the Heisenberg-DM spin Hamiltonian to provide microscopic understanding of our first-principles observations.

The quadruple perovskite belongs to the $[AA'_3][B_4][\text{O}_{12}]$ family⁴¹: $[\text{CaMn}_3][\text{Mn}_4][\text{O}_{12}]$. $\text{CaMn}_7\text{O}_{12}$ undergoes structural and metal-insulator transition accompanied by charge ordering at $T = 440 \text{ K}$ with a large change in resistivity at ultrafast time scales^{42,43}. The B -site Mn ions order into Mn^{3+} and Mn^{4+} with a 3:1 ratio in a centrosymmetric rhombohedral ($R\bar{3}$) crystal structure [Fig. 1(a)], such that the formula is rewritten as $[\text{CaMn}_3^{3+}][\text{Mn}_3^{3+}\text{Mn}^{4+}][\text{O}_{12}]$. Throughout this Letter, A -site Mn^{3+} is designated as Mn1, B -site Mn^{3+} as Mn2, and B -site Mn^{4+} as Mn3.

$\text{CaMn}_7\text{O}_{12}$ exhibits complex coupling of incommensurate structural, orbital, and magnetic modulations. At $T = 250 \text{ K}$, Jahn-Teller distortions lead to structural modulation mediated by orbital ordering, with structural propagation vector $(0, 0, 2.077)$ at 150 K ^{39,40}. The material exhibits two magnetic phase transitions at Néel temperatures, $T_{\text{N}1} = 90 \text{ K}$ and $T_{\text{N}2} = 48 \text{ K}$ ³⁶. Between 90 K and 48 K , Mn3 spin modulation is coupled to the structural modulation via magneto-orbital helix, where the chiral magnetic structure with propaga-

tion vector $(0, 0, 1.037)$ is stabilized by the orbital modulation^{39,40,44}. Below 48 K, magnetic modulation with two propagation vectors $(0, 0, 0.958)$ and $(0, 0, 1.120)$ has been proposed³⁶.

All spins lie in the ab -plane, and Mn ions along the same c -chain or of the same Mn-type and c -axis height have identical spin directions. Noncollinear magnetism arises nonrelativistically via geometric frustration of the spins within the hexagonal Kagome lattice^{45–47}, where antiferromagnetic interactions among Mn1 and Mn2^{37,40} cause all spin pairs in adjacent c -chains to be 120° from each other [Fig. 1(b)]. The Mn3 spin direction is determined by the neighboring three Mn1 and three Mn2. It has been proposed that Mn3 adopts a spin direction that is $(30^\circ, 90^\circ)$ ^{36,37,48,49} or $(60^\circ, 60^\circ)$ ^{38,50} with respect to the surrounding (Mn1, Mn2) spin directions. The Mn3 spin configuration is conveniently represented by the quantity α , where $\alpha = 0^\circ$ for $(60^\circ, 60^\circ)$ and 30° for $(30^\circ, 90^\circ)$ [Fig. 1(c)]. The sign of α corresponds to the spin helicity of the B -site helicoidal spin-spiral. The local structure of the hexagonal channel consists of five equidistant ab -planes (I-V) repeating periodically along the c -axis, where the central layer consists of a single Mn3 [Fig. 1(d)]. The ferroelectric transition temperature of the material coincides with the Néel temperature, $T_C = T_{N1} = 90$ K, suggesting that the ferroelectricity is spin-driven^{36,51}. The macroscopic polarization is along the c -axis ($[111]$ in the pseudocubic coordinates), parallel to the spin helicity vector and perpendicular to the spin rotation plane (ab -plane).

We evaluate the noncollinear magnetic ground state using the PBEsol⁵² functional with Hubbard U and J (on-site Coulomb repulsion and exchange parameters) treated separately and explicitly defined within the rotationally invariant, fully anisotropic scheme^{53,54}, along with SOC as implemented in the QUANTUM ESPRESSO⁵⁵ package. It has been demonstrated that the fully anisotropic Hubbard J parameter plays a central role in correctly describing spin canting in noncollinear magnetic systems⁵⁶. All atoms are represented by norm-conserving, optimized⁵⁷, designed nonlocal⁵⁸ pseudopotentials generated with the OPIUM package⁵⁹, including spin-orbit interaction⁶⁰ as well as nonlinear core-valence interaction in the Mn pseudopotential via the partial-core correction scheme^{61–63}. The plane-wave cut-off energy is set at 70 Ry (952 eV), and the total energy is converged to 10^{-6} Ry (1.4×10^{-5} eV). The Brillouin zone is sampled using a $2 \times 2 \times 4$ Monkhorst-Pack⁶⁴ k -point mesh.

The energetics and spin direction of collinear and noncollinear magnetic configurations are used to justify the values $U = 2$ eV and $J = 1.4$ eV used in our DFT calculations⁶⁵. These values are in line with those used in previous studies^{37–39,48,49}. We use the commensu-

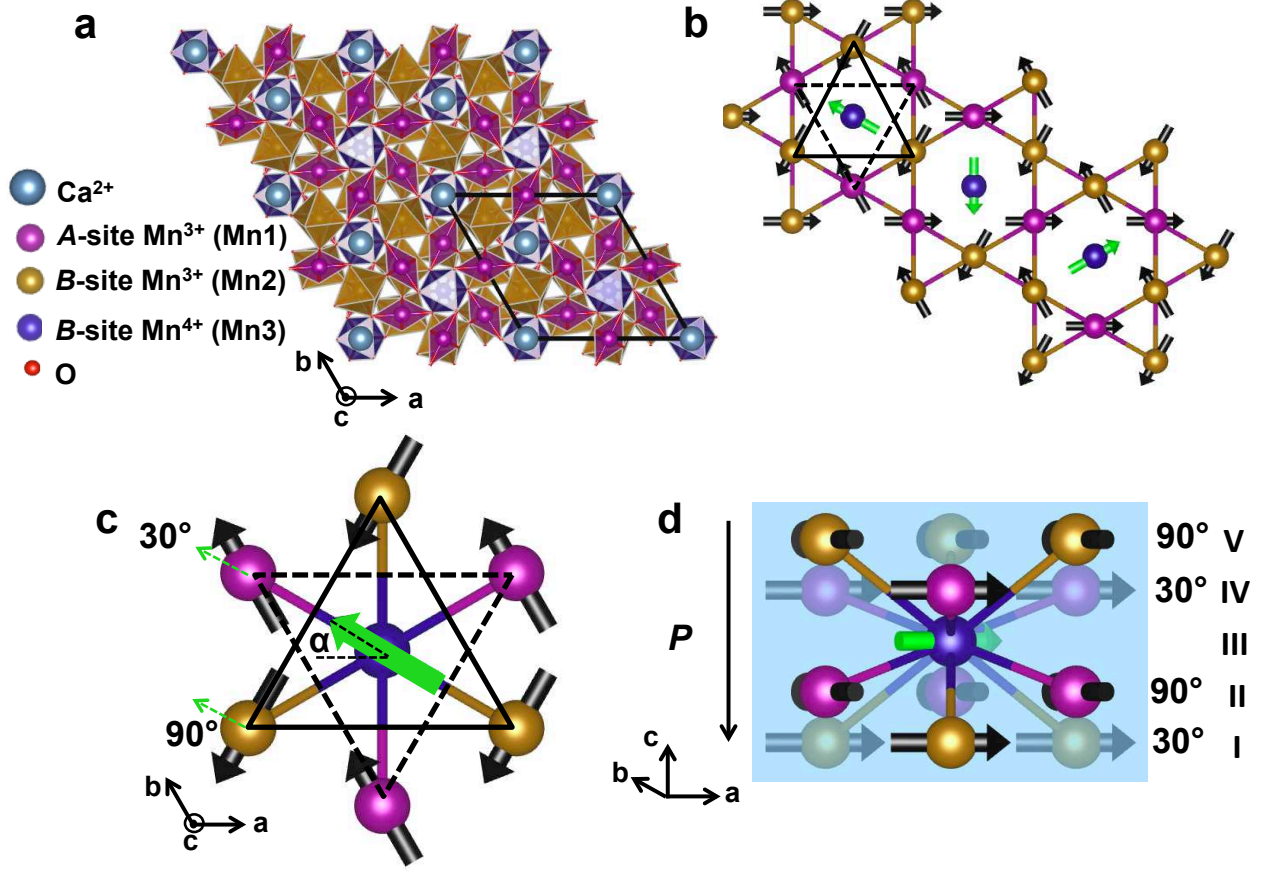


FIG. 1. (a) The crystal structure of the rhombohedral ($R\bar{3}$) phase. Mn1 (purple, square planar) and Mn2 (gold, octahedral) alternate along parallel c -chains, of which sets of three form a Kagome lattice. The hexagonal center is occupied by Ca^{2+} (light blue) and Mn3 (blue, octahedral) alternating along the c -axis. The unit cell is denoted with bold black lines. (b) Noncollinear magnetic structure with Mn1 and Mn2 spins represented as black arrows and Mn3 spins as green arrows. Black lines indicate the local hexagonal environment of Mn3 surrounded by Mn1 and Mn2, with solid lines closer to the viewer than dashed lines. (c) Zoom-in view of the local hexagonal environment in (b). Mn3 spin configuration is represented by α , where $\alpha = 30^\circ$ for $(30^\circ, 90^\circ)$ configuration with respect to the neighboring (Mn1, Mn2) spins. (d) Side view of (c) showing the local layered structure of five Mn planes (I-V), magnetically inducing net polarization along the c -axis. The blue plane is parallel to the c -axis and cuts through the central Mn3, such that the atoms farther away from the viewer are shaded by the plane.

rate, centrosymmetric ionic lattice structure⁶⁶. Starting from multiple perturbations of the commensurate noncollinear magnetic structure³⁶, our spin and electronic relaxation shows that the Mn1 and Mn2 spin directions remain $\approx 120^\circ$ apart. The converged Mn3 spin direction depends strongly on SOC and Hubbard J . With $J < 1$ eV, α remains $\approx 0^\circ$ without SOC, with deviations away from 0° upon applying SOC. Surprisingly, the experimentally observed $\alpha \approx 30^\circ$ is achieved at $J = 1.4$ eV, both with and without SOC. If Mn3 spins are started at $\alpha = 0^\circ$, they remain in that symmetry, showing that $\alpha = 0^\circ$ is higher in energy by 3 meV per formula unit.

These observations suggest that nonzero α is stabilized by SOC, in agreement with previous studies^{37,39,48,49}, as well as by fully anisotropic Hubbard J . In contrast to DFT+ U_{eff} , where J is subsumed under $U_{\text{eff}} = U - J$ ⁶⁷, Hubbard U and J are defined distinctly in DFT+ $U + J$ ⁵³, where the J parameter acts directly on the nondiagonal elements of the density matrix that determine spin canting⁵⁶. This treatment results in an extra Hubbard energy correction term involving J that discourages interactions between electrons of antialigned spins on the same site, thereby encouraging magnetic ordering⁵⁴:

$$E_{\text{Hub}} = \sum_{I,\sigma} \frac{U^I - J^I}{2} \text{Tr}[\mathbf{n}^{I\sigma}(\mathbf{1} - \mathbf{n}^{I\sigma})] + \sum_{I,\sigma} \frac{J^I}{2} (\text{Tr}[\mathbf{n}^{I\sigma} \mathbf{n}^{I-\sigma}] - 2\delta_{\sigma\sigma_{\text{min}}} \text{Tr}[\mathbf{n}^{I\sigma}]). \quad (1)$$

Here, I is the atomic site index, σ is the spin index, and \mathbf{n} is the occupation matrix. By taking into account Hund's coupling, i.e. intra-orbital exchange, Hubbard J provides anisotropy and full orbital dependence across the occupations and energies of the Mn d states^{68–70}. We believe that this anisotropy is responsible for stabilizing $\alpha = 30^\circ$ even in the absence of SOC.

We use the Berry phase method⁷¹ to compute the polarization \mathbf{P} with and without SOC at different α values⁷². The most relevant scenarios with $\alpha \approx 0^\circ$ and $\approx 30^\circ$ are shown in Table I. The polarization is along the c -axis. Simultaneous ionic relaxation⁷³ gives Mn3 displacement of 0.7 mÅ with total $P = -2900 \mu\text{C}/\text{m}^2$, in good agreement with the experimental value of $2870 \mu\text{C}/\text{m}^2$ ²³⁶. The ionic displacement is negligible relative to the thermal motion at $T_C = 90$ K, and it contributes 30% of the total polarization. At $\alpha \approx 0^\circ$, the polarization vanishes; upon inverting the spin helicity by changing the sign of α , the direction of the polarization reverses with the same magnitude, in agreement with the phenomenological

TABLE I. Berry phase computed P and converged Mn3 spin direction α with DFT+ U + J with and without SOC.

	α	P ($\mu\text{C}/\text{m}^2$)
NSOC	-0.02°	-1.1
NSOC	29.0°	-2119
SOC	28.3°	-2169

ferroaxial coupling proposed by Johnson *et al.*^{36,74}, as well as the sinusoidal dependence on α derived with the exchange striction model by Lu *et al.*³⁷.

Previous study by Cao *et al.*³⁹ reported contributions from nonrelativistic (exchange striction) as well as relativistic (inverse-DM) effects to the polarization upon employing local approximation of the incommensurate structural modulation. However, our results within the commensurate ionic structure indicate negligible contribution of SOC to the polarization ($< 5\%$), suggesting that the bulk value arises from nonrelativistic effects. This observation is in alignment with Lu *et al.*³⁷, who proposed exchange striction as the main underlying mechanism.

The nonzero polarization at $\alpha \approx 30^\circ$ indicates that inversion symmetry is broken, even though the ionic lattice is fixed to be centrosymmetric. Upon inversion operation along the B -site helicoidal spiral chains in each of the Cartesian directions ($[100]$, $[010]$, and $[001]$), only $\alpha = 0^\circ$ configuration is shown to preserve inversion symmetry⁷⁵.

We compute the charge density redistribution as the magnetic structure goes from $\alpha = 0^\circ$ to 30° , i.e. $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r})_{\alpha=30^\circ} - \rho(\mathbf{r})_{\alpha=0^\circ}$ [Fig. 2]. The charge density isosurfaces reveal that the polarization is localized along the Mn3-O bonds. As discussed above, Mn3 ions do respond to the charge density redistribution but only by $0.7 \text{ m}\text{\AA}$, providing a minor contribution to the polarization. This indicates that the spin-induced ferroelectricity is nearly pure electronic in nature. Significant purely electronic contributions have also been predicted in ortho-manganites^{76–79}.

To understand the relationship between α and P , we first analyze the intersite exchange interactions using the Heisenberg-DM spin Hamiltonian:

$$\begin{aligned}
H_{12} &= H_{\text{SE}} + H_{\text{DM}} \\
&= J_{12}(\mathbf{S}_1 \cdot \mathbf{S}_2) + \mathbf{D}_{12} \cdot (\mathbf{S}_1 \times \mathbf{S}_2).
\end{aligned}
\tag{2}$$

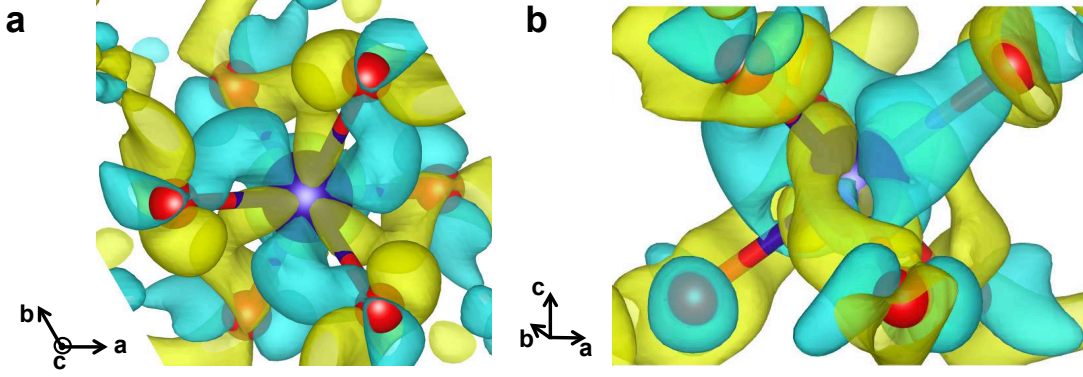


FIG. 2. Charge density redistribution along the Mn3-O bonds as the magnetic structure changes from $\alpha = 0^\circ$ to 30° . The charge density shift is purely electronic and nonionic. (a) Top- and (b) side-view of the charge density differential. The three Mn3-O bonds with $+c$ components gain electron density (cyan), whereas the three Mn3-O bonds with $-c$ components lose electron density (yellow), thereby generating a net polarization along $-c$ direction.

The first term is the nonrelativistic, isotropic Heisenberg symmetric exchange energy (H_{SE}), and the second term is the relativistic, anisotropic DM antisymmetric exchange energy (H_{DM}). J_{12} is the exchange coupling constant, and the DM vector is defined to be $\mathbf{D}_{12} \propto \mathbf{r}_1 \times \mathbf{r}_2$, where \mathbf{r}_1 and \mathbf{r}_2 are vectors connecting each metal to the intersite ligand.

We consider the local hexagonal structure from [Fig. 1(d)] and the six Mn2-O-Mn3 spin dimer interactions within the B -site helicoidal spiral chains along which the charge redistribution is found to be highly localized. Mn3 spin is designated as \mathbf{S}_{Mn3} , whereas Mn2 spins of layer I are designated as \mathbf{S}_I and Mn2 spins of layer V as \mathbf{S}_V . The total exchange energy is given by⁸⁰:

$$\begin{aligned} E_{\text{tot}} &= E_{Mn3-V} + E_{Mn3-I} \\ &= 3[J \cos(\alpha) - D^z \sin(\alpha)]. \end{aligned} \quad (3)$$

Because we use the commensurate ionic structure without orbital modulation, $J_{Mn3-V} = J_{Mn3-I} = J^{39,40}$. Furthermore, $J < 0$ ³⁷ because charge ordering along the helicoidal spiral chain promotes ferromagnetic exchange, with antiferromagnetic interactions weakened by the large deviation of Mn3-O-Mn2 bond angles from 180° ⁴⁰.

The minimum of the total energy in Eq. (6) depends directly on the strength of the exchange interactions. Setting $\frac{dE}{d\alpha} = 0$ leads to $\alpha_{\min} = \tan^{-1}(-\frac{D}{J})$. Previous study by Lu *et al.*³⁷ reported $|D/J| \approx 0.73$ corresponding to $|\alpha_{\min}| = 36.2^\circ$, indicating unusually strong DM

TABLE II. Energetics of the magnetic interactions for Mn3-V and Mn3-I with $\alpha = 0^\circ$ and 30° .

		E_{tot}	E_{SE}	E_{DM}
$\alpha = 0^\circ$	Mn3-V	$3J$	$\frac{3}{2}J$	$\frac{3\sqrt{3}}{2}D^z$
	Mn3-I		$\frac{3}{2}J$	$-\frac{3\sqrt{3}}{2}D^z$
$\alpha = 30^\circ$	Mn3-V	$\frac{3}{2}(\sqrt{3}J - D^z)$	0	$3D^z$
	Mn3-I		$\frac{3\sqrt{3}}{2}J$	$-\frac{3}{2}D^z$

interaction compared to other magnetic insulators where $|D/J| \lesssim 0.1$ is usually expected⁸¹. Considering $J < 0$ and $D^z > 0$, DM interaction lowers the total magnetic interaction energy by shifting α from 0° to 30° [Table II], such that $E(\alpha = 30^\circ) < E(\alpha = 0^\circ)$, consistent with our results.

SOC by itself, however, provides negligible contribution to the polarization within the commensurate ionic structure. The canting of Mn3 spin causes Mn3-V interaction (90° alignment) to be inequivalent to Mn3-I interaction (30° alignment), resulting in a weak exchange striction of nonionic character, where the electrons are slightly more localized in Mn3-V regime than in Mn3-I regime [Fig. 2]. The effect of this exchange striction on the charge density is manifested in the orbital-projected density of states (PDOS) along the $\text{O}_+ - \text{Mn3} - \text{O}_- - \text{Mn2}$ chain [Fig. 3a]. O_+ and O_- refer to the oxygens along the reduced and enhanced charge density bonds, respectively. The total $2p$ PDOS (not shown) exhibits no difference between $\alpha = 0^\circ$ and $\alpha \approx 30^\circ$. However, a significant difference arises within the p_x , p_y , and p_z orbitals [Fig. 3b-c]. At $\alpha \approx 30^\circ$, these orbital densities of O_+ and O_- become inequivalent, thereby enhancing the mixing between Mn3 $3d$ and O_- $2p$.

We also examine the densities of the spin-orbit coupled states, indexed as $J=L+S$ [Fig. 3d-e]. The splitting between Mn3 $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ is enlarged when $\alpha \approx 30^\circ$, resulting in more mixing between $3d_{\frac{5}{2}}$ and O_- $2p$. These analyses provide an orbitally resolved understanding of how the charge density is redistributed through the Mn3-O bonds.

In summary, our DFT+ U + J +SOC calculations demonstrate that $\text{CaMn}_7\text{O}_{12}$ adopts non-collinear magnetism due to the geometric frustration within the hexagonal Kagome lattice, and the Mn3 spins adopt the noncentrosymmetric (30° , 90°) configuration stabilized relativistically by DM interaction as well as by fully anisotropic Hubbard J . The resulting Berry phase polarization is nearly pure electronic in nature with negligible Mn displacements. The

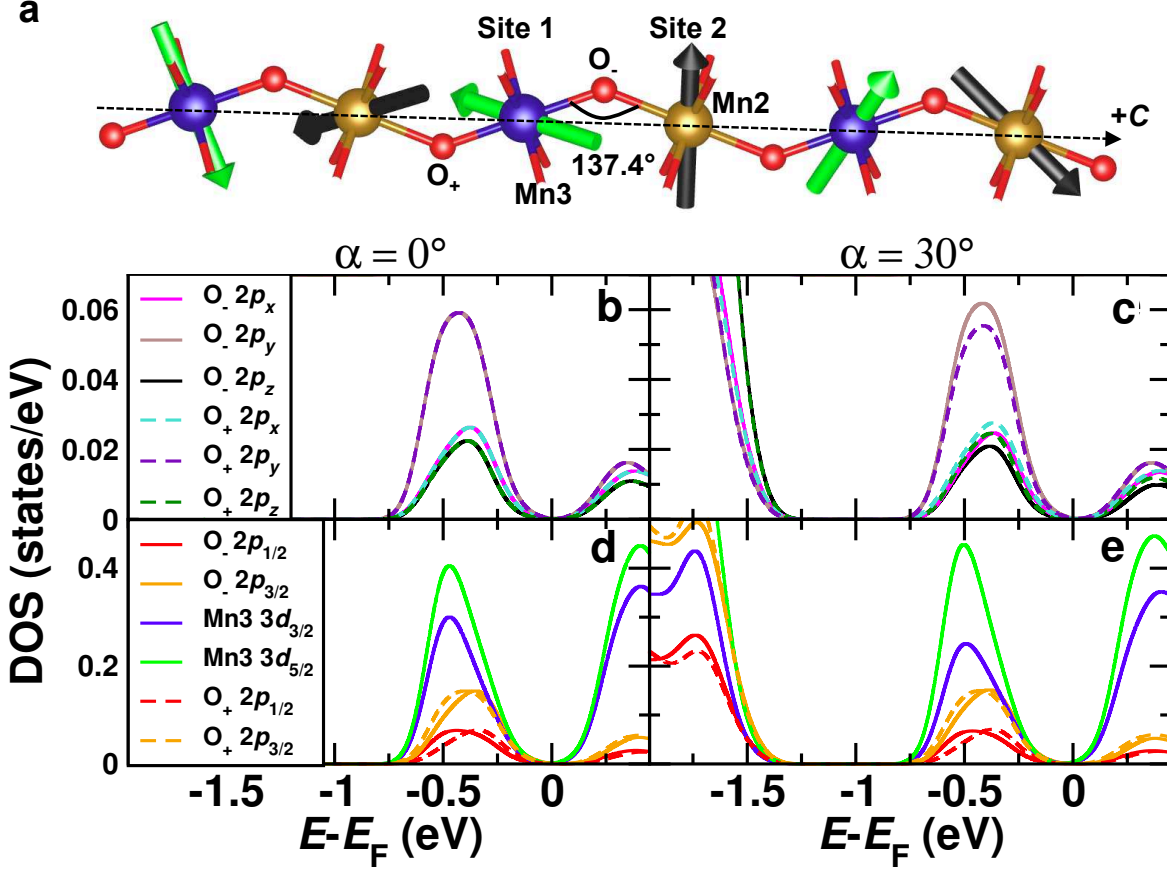


FIG. 3. (a) Mn2-O-Mn3 chain forms a zig-zag pattern with a bond angle of 137.4° . Orbital-projected density of states for all $2p$ -orbital subshells of O_+ (solid lines) and O_- (dashed lines) when (b) $\alpha = 0^\circ$ and (c) $\alpha = 30^\circ$. The spin-orbit coupled states when (d) $\alpha = 0^\circ$ and (e) $\alpha = 30^\circ$. The charge density redistribution along the Mn3-O bonds is evidenced by the changes in the orbital mixing involving O_+ vs. O_- when $\alpha = 30^\circ$.

polarization is coupled to the spin helicity, vanishing and reversing its direction at the centrosymmetric (60° , 60°) configuration. The charge density redistribution along the Mn3-O bonds, as evidenced by our orbital-projected density of states, originates nonrelativistically from weak exchange striction of nonionic character within the commensurate structure. Our findings suggest the existence of spin-induced ferroelectricity in nearly inversion-symmetric ionic lattice, opening the avenue for ultrafast magnetoelectric effect in a single ferroelectric-magnetic domain.

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