

First-principles study of KCoF_3 : Jahn-Teller effect, dynamical magnetic charges, magnetoelectric multipoles, and antimagnetoelectricity

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We study from *ab initio* density functional theory calculations the structural and magnetic properties of the crystal KCoF_3 . We found that the experimentally reported cubic to tetragonal phase transition is due to an electronic first-order Jahn-Teller effect from the R zone boundary point. We also obtain that the magnetic ground state is the G-type antiferromagnetic order, in agreement with the R -point Jahn-Teller distortion and that the magnetic moment of the Co atoms contains a strong orbital contribution ($m_L = 0.95 \mu_B$ in the cubic phase and $0.55 \mu_B$ in the tetragonal phase). Furthermore, we compute the dynamical magnetic effective charges and show that it is zero by symmetry for the Co and they can reach a value as large as $200 \cdot 10^{-2} \mu_B/\text{\AA}$ for the apical F anion. This large magnetic effective charge comes from the spin-orbit coupling (50% of the response is from the orbital moment) contrary to the rare-earth manganites and ferrites with similar order of magnitude but originating from the exchange striction mechanism. The fact that the dynamical magnetic effective charges are nonzero also proves that the tetragonal phase of KCoF_3 is antimagnetoelectric with a large magnetic sublattice magnetoelectric response of 210 ps/m per spin channel. We also discuss the generality of these magnetic effective charges.

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I. INTRODUCTION

KMnF_3 fluoride perovskite crystals (with M a 3d transition metal such as Fe, Cu, Mn, Co, Cr, Ag) have attracted significant interest from a fundamental physics and materials science perspective due to their unique properties (first-order Jahn-Teller effect, orbital ordering, Mott insulators, metal-insulator transition, electron localization, low-dimensional magnetism, magnetoelasticity, etc.) [1–12]. They provide model systems for exploring strongly localized electron physics, low dimensional magnetism, or lattice dynamics within a simple symmetric cubic framework, making them ideal for testing theoretical models [8,13–16]. Among them, the case of KCoF_3 has been less studied and those studies focused mainly on its magnetic properties, while its electronic, structural or vibrational properties were scarce. For example, a structural phase transition has been observed experimentally by the observation of cubic to tetragonal cell parameters change at the critical temperature of the antiferromagnetic (AFM) phase transition ($T_N = 115\text{K}$ [4,5,17]) but no further insight was reported regarding the space group and the atomic positions or on the exact origin of this structural transition (hypothetically reported as an elastic Jahn-Teller effect [4,17,18]).

In this article, we focus on KCoF_3 by doing density functional theory (DFT) calculations of the structural, electronic, magnetic and vibrational properties of the cubic and tetragonal phase of KCoF_3 . This allows us to clarify the first-order Jahn-Teller origin of the phase transition and that the tetragonal phase is the ground state of the system. We also scrutinized the magnetism and confirmed the G-type AFM ordering observed experimentally and found that the spin-orbit coupling

(SOC) is important, which gives a nonnegligible orbital contribution to the magnetic moment of the Co atom. Going beyond those classical studies, we originally computed the dynamical magnetic effective charges [19,20] and the atom magnetoelectric multipoles of KCoF_3 and found that they are surprisingly large for a “nonfunctional” material and that the spin and orbital contributions are on equal footing. Those later calculations allows us to conclude that KCoF_3 is antimagnetoelectric [21].

The article is organized as follows: In Sec. II we expand on the used computational framework. In Sec. III, we first report on the magnetic ground state, followed by the associated lattice distortion resulting from a Jahn-Teller instability. We then continue by calculating the dynamical magnetic charges (DMC) and compare their amplitude within the existing literature, and calculate the spin-channel-dependent antimagnetoelectric response from both spin and orbit contributions. A multipolar decomposition of the DMC is also done. We conclude in Sec. V. In Appendix A we remind of the theoretical background pertaining to (anti)magnetoelectricity and associated magnetoelectric multipoles.

II. COMPUTATIONAL DETAILS

Our DFT calculations were performed with the ABINIT code version 9.10.5 [22] in the PBEsol + U framework [23] for the exchange-correlation functional. We used the JTH projected augmented wave atomic potentials (v1.1) [24] and we included the spin-orbit coupling (SOC) treatment (unless stated otherwise). A Hubbard- U correction of 4.0 eV was

applied to the 3d Co shell, adjusted to match the total (spin + orbital) experimental magnetic moment of $3.33 \mu_B$ [25]. We have checked that the qualitative results are not affected by the U value (see Supplemental Material (SM) Table S.I [26]). The Kohn-Sham pseudo-wave functions were expanded over a plane-wave basis set with a kinetic energy cutoff of 24 Ha and with a cutoff for the PAW double grid kinetic energy cutoff of 48 Ha. We used a strict convergence threshold of 2.7×10^{-12} eV for the total energy on the self-consistent cycle, to determine the DMCs accurately. The BZ of the magnetic unit cell was sampled with a Monkhorst-Pack k -point grid of $6 \times 6 \times 4$ points in the G-AFM unit cell ($\sqrt{2} \times \sqrt{2} \times 2$ with respect to the five-atoms cubic unit cell). We also used the density functional theory perturbation (DFPT) to determine the eigenvalues and eigendisplacements of phonons as well as the Born effective charges [27], that are key ingredients to calculate the lattice contribution to the antimagetoelectric response. The orbital and spin magnetization associated with a specific atom I is computed by integrating the local magnetization density $m_\alpha(\vec{r})$ within a defined sphere Ω_I centered at the atom's position $\vec{R}_I$ [28], and the radius of the sphere is equal to the one of the PAW atom dataset [28]. This muffin-tin approximation is precise enough for the localized d-orbitals of Co for both spin and orbital magnetic moment [29] and with a very good CPU time consuming/precision with respect to a more precise implementation, e.g., Zwanziger *et al.* [30]. The magnon dispersion and the calculations of superexchange parameters were obtained through the TB2J code version 0.6.6 [31].

Finally, we determined the DMC by using a finite differences method where we displace each atom along the three Cartesian axes with the following amplitudes: $\pm 0.01 \text{ \AA}$, $\pm 0.02 \text{ \AA}$, $\pm 0.03 \text{ \AA}$ [20].

III. RESULTS

A. Cubic phase

Above 115 K, KCoF_3 is found in a nonmagnetic cubic perovskite phase described by the space group $Pm\bar{3}m$ (#221) with five atoms in the unit cell. Below this critical temperature $T_N = 115 \text{ K}$ [4,5,17], KCoF_3 is AFM with an associated cubic propagation wave vector $k = (1/2, 1/2, 1/2)$, which corresponds to the so called G-type AFM magnetic ground state (Fig. 1), i.e., each Co magnetic moment is surrounded by Co first nearest neighbors with opposite magnetic moments.

In our 0 K DFT calculations, we found that the G-AFM order is the lowest energy magnetic phase in the cubic phase as obtained through both total energy calculations (see Table I) and the magnon dispersion (see Fig. 1 where the lowest energy point in the dispersion is at the $k = (1/2, 1/2, 1/2)$ point corresponding to the G-AFM ordering). The calculated lattice parameters (Table I) are in good agreement with the experimental values of $4.069 \pm 0.001 \text{ \AA}$ [17,32]. As our calculations were done within noncollinear DFT regime and including the spin-orbit coupling, we found that all the magnetic phases break the cubic structure with a slight tetragonal distortion of the cell (see Table I) but keeping all atoms in their high symmetry positions. This broken cubic cell parameter by the AFM orders is supported by the corresponding

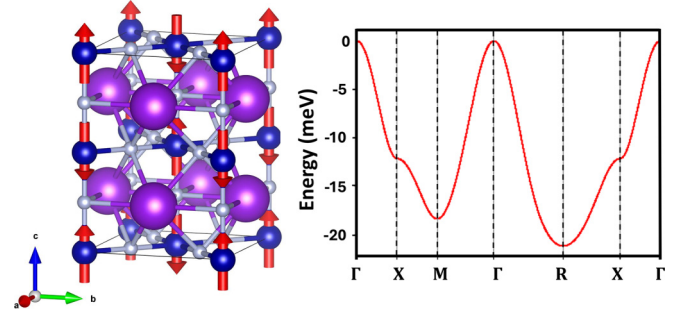


FIG. 1. (Left) Magnetic structure of KCoF_3 showing the ground state G-type antiferromagnetic ordering. The purple spheres represent K atoms, blue spheres represent Co atoms with alternating spin directions (indicated by red vectors), and light gray spheres represent F atoms forming octahedra around Co sites. The crystallographic axes are indicated in the bottom left corner. (Right) Calculated magnon dispersion along high-symmetry paths in the FM cubic Brillouin zone. The dispersion shows characteristic energy minima at the R point corresponding to the configuration shown in left panel. $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $M = (1/2, 1/2, 0)$, and $R = (1/2, 1/2, 1/2)$ in units of the cubic reciprocal lattice vectors.

magnetic space group symmetry as all of the AFM orders give a tetragonal magnetic space group when considering the magnetic moment direction (i.e., the magnetic moments are treated as pseudovectors and not as simple scalar values as done in collinear calculations, see Table I). We also stress that none of these AFM-related magnetic space groups allows for magnetoelectricity.

Our calculated total magnetic moment of the Co atoms is found to be $3.43 \mu_B$, which is in good agreement with the experimental value of $3.33 \mu_B$ [25] and we found it to be the same value irrespective of the magnetic ordering. This total calculated magnetic moment decomposes into a spin component of $2.50 \mu_B$ and an orbital contribution of $0.93 \mu_B$. The free Co^{2+} ion with d^7 configuration can theoretically host a magnetic moment of $3 \mu_B$ for both spin and orbital contributions, totalizing $6 \mu_B$ in spherical symmetry. This ideal value can be reduced through several effects: (i) the local rotational symmetry associated with the quenching of the orbitals can greatly reduce the free ion maximum value [33], (ii) the spin-orbit coupling allows for a magnetic moment transfer from the spin to the unquenched orbital magnetic

TABLE I. Relative energy with respect to the FM phase and lattice parameters of the common commensurate magnetic phases of the high symmetry KCoF_3 , along with the associated magnetic space groups (magnetic moment along the z direction). We can see that the magnetic ordering breaks the cubic symmetry when considering magnetic moment orientation within the noncollinear regime calculation and the inclusion of the spin-orbit coupling.

Magnetic phase	ΔE (meV/f.u.)	a	c	Mag S.G.
FM	0	4.077	4.012	$P4/mm'm'$
A-AFM	-32	4.079	4.002	P_64'/mmm'
C-AFM	-51	4.069	4.010	$P_2c4'/mm'm'$
G-AFM	-79	4.071	4.001	$P_14'/mm'm'$

moment, (iii) the magnon-phonon interaction itself is further enhanced owing to the unquenched orbital magnetic moment [34] and a residual orbital magnetic moment can be present in the cubic crystal field [35]. The orbital moment value we obtain in KCoF_3 is in line with the equivalent ones in octahedral coordination, e.g., CoO_4X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{S}, \text{Se}$) [33,36]. Although the highest reported value of Co^{2+} to our knowledge is found in $\text{SrTi}_{0.88}\text{Co}_{0.04}\text{Nb}_{0.08}\text{O}_3$ where the total magnetic moment is $5.95 \mu_B$, i.e., close to the free ion value [37]. Nonetheless, the orbital magnetic moment in KCoF_3 is larger than in the prototypical transition-metals of VI_3 ($0.59 \mu_B$) [38], Fe_3O_4 ($0.44 \mu_B$), or CrO_2 ($0.06 \mu_B$) [39]. The presence of an important orbital contribution to the magnetic moment can have an impact on, e.g., the magnon dispersion [40] as reported in a compound similar to KCoF_3 , RbCoF_3 [41].

According to Dubrovin *et al.* [42], the calculation of the phonon dispersion shows that there is no unstable mode in the cubic phase (see SM Fig. S.2 [26]), which means that the structure is found to be stable at the harmonic level. However, this does not explain the cubic to tetragonal transition reported experimentally.

B. Tetragonal phase

As we have written above, experimentally below the critical temperature of 115 K a lattice distortion driving KCoF_3 from a cubic phase to a tetragonal phase is simultaneous to the appearance of the magnetic order [17,18], similarly to KMnF_3 but for which it has been proved that the coincidence of the structural transition and the Néel temperature is essentially accidental [43]. However, no experimental report on the space group or atom positions below 115 K is reported, only the values of the cell parameters and their tetragonal splitting are reported [17,18]. Some authors mention that the transition can be purely elastic [44,45], but this is based on a more speculative theoretical analysis and it is not supported by any experimental work or theoretical calculations.

High spin Co d^7 orbitals in the octahedra environment should be Jahn-Teller active as the two electrons of the minority channel break the t_{2g} threefold degeneracy of the octahedral cubic crystal field [46]. This situation should correspond to the so-called first-order Jahn-Teller effect [17,47,48]. Previous first-principles collinear DFT calculations go into this direction, as Dubrovin *et al.* [42] report that the cubic phase in its G-AFM state has no unstable phonon in the whole Brillouin zone (Fig. 5 of Ref. [42]) and Varignon *et al.* [13] report that the tetragonal phase of KCoF_3 comes from a first order Jahn-Teller instability, which is associated with the cubic R zone boundary point pattern of distortion. As the first-order Jahn-Teller effect appears at the first order in an energy expansion, it is not seen through unstable phonons as the phonons correspond to a second order energy derivatives.

We confirm those results in our collinear calculations as we observe a sudden jump in energy once the cubic symmetry is broken through Jahn-Teller pattern of distortion (see SM Fig. S.1 [26]), and thus before any lattice distortion is allowed, which is a fingerprint of an electronic instability of the first order Jahn-Teller type [13]. The full relaxation of the cell gives the typical Jahn-Teller distortion of the R zone boundary point (R_3^- label with origin on the K atom [46]) with the tetragonal

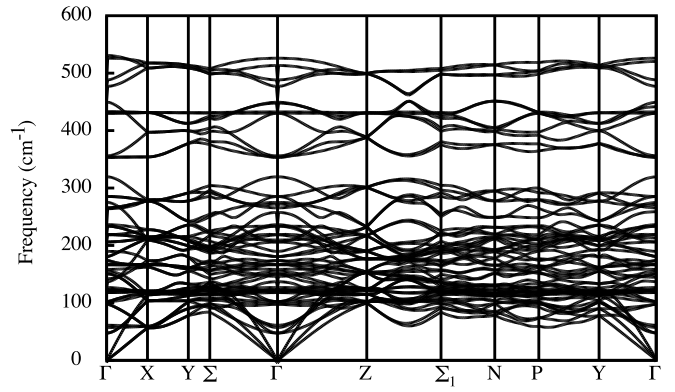


FIG. 2. Phonon dispersion curves of KCoF_3 in the calculated (collinear DFT regime) ground state G-AFM $I4/mcm$ phase. $\Gamma = (0, 0, 0)$, $X = (0, 0, 1/2)$, $Y = (-0.26, 0.26, 1/2)$, $\Sigma = (-0.38, 0.38, 0.38)$, $Z = (1/2, 1/2, -1/2)$, $\Sigma_1 = (0.38, 0.62, -0.38)$, $N = (0, 1/2, 0)$, and $P = (1/4, 1/4, 1/4)$ in units of the cubic reciprocal lattice vectors.

space group $I4/mcm$. The calculation of phonon dispersion in this relaxed lower energy phase (see Fig. 2) does not exhibit any unstable mode and if we break all symmetry operations and fully relax the crystal, the system stays in this $I4/mcm$ phase (illustrated in Fig. 3), such that we can conclude that this phase is locally stable.

In our search for local minima and including the spin-orbit coupling (noncollinear DFT calculation regime), we found (i) the $I4/mcm$ phase with a gain of energy of 23.1 meV/f.u. (with respect to the G-AFM high symmetry reference with spin-orbit coupling, see Fig. 4), (ii) a purely elastic distorted phase, with the space group $P2_1/c$, which reduces the energy by 0.7 meV/f.u., hence a gain of energy much smaller than the $I4/mcm$ phase, and (iii) another Jahn-Teller distortion phase associated with a M -point distortion (M_3^+ label giving the $I4/mcm$ space group [46]) and lowering the energy by 11.1 meV/f.u., again higher than the $I4/mcm$ phase. Hence, according to our calculations, the G-AFM $I4/mcm$ phase is the ground state of KCoF_3 and it comes from a first-order Jahn-Teller electronic instability combined with a lattice distortion associated with the R -point distortion [46].

In this ground state phase, we found that the magnetic crystal space group is $I4'/mcm'$, i.e., by using a magnetic easy-axis along the c -axis lattice vector direction, as reported experimentally [5,34]. This magnetic symmetry allows for the inverse piezomagnetic effect (tensor $\wedge^T$ coupling magnetiza-

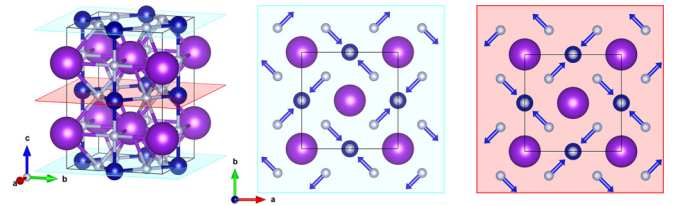


FIG. 3. Visualization of the atomic displacements associated with the R_3^- Jahn-Teller mode. (Left) Three-dimensional perspective of the crystal structure with two consecutive cobalt planes highlighted in cyan and red. (Center, right) Top-view projections of the cobalt planes illustrating the in-plane atomic motion patterns.

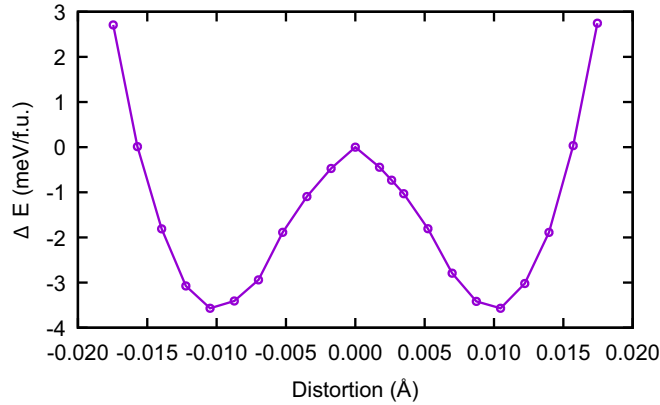


FIG. 4. Energy evolution under the first-order type Jahn-Teller rigid distortion in KCoF_3 in the G-AFM magnetic state including SOC but at fixed cell parameter (the one of the high symmetry reference, see SM for Table S.I [26]). The zero energy is taken from the $P_14/m\bar{m}'m'$ high symmetry phase including SOC (Table S.I in SM [26]). Under the full cell relaxation, a total gain of 23.1 meV/f.u. is obtained, showing that the elastic contribution is important as at frozen cell parameter as shown in this figure the gain of energy is a bit less than 4 meV/f.u.

tion direction to strain). Consequently, the total free energy cannot be easily separated into intrinsic magnetocrystalline anisotropy and magnetoelastic contributions without complex simultaneous relaxation of lattice and magnetization, which is beyond the scope of the present study on dynamical charges.

The only internal degree of freedom falls on the basal F atom at the 8h Wyckoff site ($x, x + \frac{1}{2}, 0$), with $x = 0.03$ Å. The distortion corresponds to the typical Jahn-Teller distortion from the R point [46], i.e., an in-plane stretching of the octahedra in antiphase with both in- and out-of-plane neighboring octahedra (see inset of Fig. 5). We would like to mention here that the cubic phase cannot stay in cubic symmetries with the G-AFM magnetic phase while including the spin-orbit coupling. Indeed, the magnetic space group is the tetragonal $P_14/m\bar{m}'m'$ (for a magnetic easy-axis along c [5]) such that the electronic instability is always relaxed. In this situation with the spin-orbit coupling on, we cannot probe the sudden jump in energy due to the electronic instability [13] (see Fig. 4) but we can recover it when doing the collinear calculations (see Fig. S.1 in SM [26]). The energy well is closer to a smooth double well, but we can still observe a dominant linear evolution of the energy around the zero distortion as if two single wells would be present [13].

Let us address the implication of the Jahn-Teller electronic instability on the magnetism of KCoF_3 . In Fig. 5 we show the evolution of the Co atom orbital angular momentum versus the Jahn-Teller distortion. The orbital magnetic moment of Co atoms has a large value in the cubic phase of about $0.95 \mu_B$. Then, once the Jahn-Teller distortion is frozen into the structure, we find this orbital magnetic moment to first decrease strongly for small distortions (up to roughly 0.03 – 0.04 Å) and beyond this range of distortion amplitudes it slowly stabilizes to about $1/3$ of the initial value (see Fig. 5). We would like to stress that the energy minimum of the $I4'/m\bar{c}m'$ Jahn-Teller ground state phase (i.e., at around 0.01 Å) is reached much

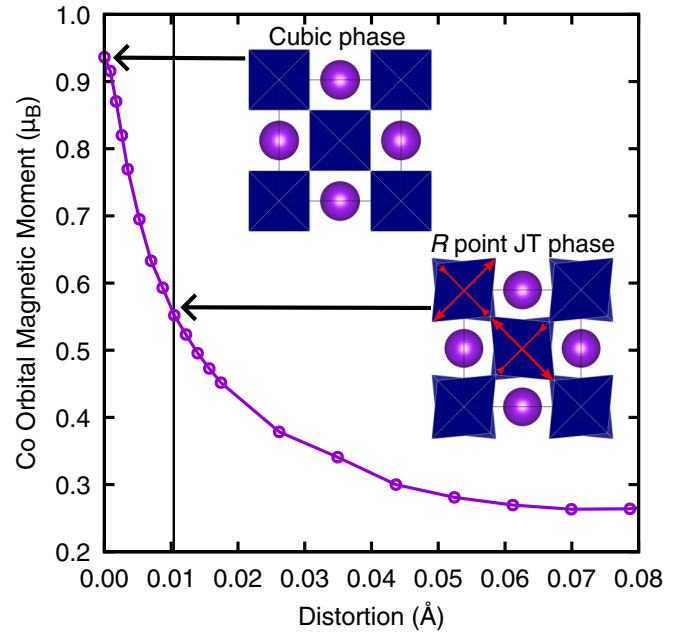


FIG. 5. Evolution of Co orbital magnetic moment of KCoF_3 with respect to the Jahn-Teller distortion amplitude in its G-AFM magnetic ground state. The relaxed Jahn-Teller distortion amplitude (0.01 Å) is reported by the vertical dashed line.

earlier than the orbital magnetization stabilization, giving a value of the orbital magnetic moment of $0.55 \mu_B$ (vertical dashed line in Fig. 5). However, within the same regime of distortion amplitude, the spin contribution to the magnetic moment does not vary significantly (0.4%).

Hence, we can see from this analysis that the orbital magnetic moment is strongly sensitive to the Jahn-Teller pattern of atomic distortions, so that we will scrutinize in the next section how each individual atom displacement affects the magnetic moment and magnetism of KCoF_3 .

C. Dynamical magnetic charges

One way to check how individual atomic motion can affect the magnetism of a crystal is through the DMC (see Appendix A). In Table II, we report our calculated DMC tensor elements

TABLE II. DMC tensor elements of each inequivalent atoms displayed in the crystal basis in the $I4'/m\bar{c}m'$ phase of KCoF_3 based on the symmetry analysis. The Symm. column gives the magnetic point group of the Wyckoff site given in the second column (see also Table S.VI in SM [26]) and the fourth column gives the nonzero DMC tensor elements. In the last two columns, the corresponding calculated values for both spin (S) and orbital (L) contributions are given in $10^{-2} \mu_B/\text{\AA}$. The values <3 are those lower than the precision of the calculations.

Atom	Wyc.	Symm.	Nonzero components	S	L
K	4a	$4'22'$	$Z_{xx}^{*m} = -Z_{yy}^{*m}$	-54	-62
Co	4d	$m.m'm'$	—	—	—
F _{api}	4b	$-4'2m'$	$Z_{xx}^{*m} = Z_{yy}^{*m}, Z_{zz}^{*m}$	90, <3	96, -10
F _{bas}	8h	$m.2'm'$	$Z_{xz}^{*m} = Z_{yz}^{*m}, Z_{zx}^{*m} = Z_{zy}^{*m}$	30, <3	24, <3

for each nonequivalent atom and by decomposing the spin (S column in the table) and orbital (L column in the table) magnetic moment contributions. We can first see that the DMC associated with the Co atom is zero, a surprising result considering that one could expect that the magnetic atom would carry the highest DMC values [20,49]. However, a symmetry analysis confirms this result as the 4d Wyckoff position where the Co atoms lie, which corresponds to the $m.m'm'$ magnetic point group, should be strictly zero by symmetry.

The K atom at the 4a Wyckoff position corresponds to the $4'22'$ magnetic point group, which allows for the xx and yy DMC tensor components to be nonzero and with $Z_{xx}^{*m} = -Z_{yy}^{*m}$. This is exactly what we obtain from our DFT calculations where the spin contribution ($-54 \times 10^{-2} \mu_B/\text{\AA}$) is smaller than the orbital contribution ($-62 \times 10^{-2} \mu_B/\text{\AA}$), and giving a total of $-116 \times 10^{-2} \mu_B/\text{\AA}$.

The apical F atom at the 4b Wyckoff site is associated with the $-4'2m'$ magnetic point group, which allows the diagonal xx , yy and zz DMC tensor components to be nonzero and where $Z_{xx}^{*m} = Z_{yy}^{*m} \neq Z_{zz}^{*m}$. Here again, our DFT calculations reproduce those nonzero DMC matrix elements where the xx/yy components are high ($90 \times 10^{-2} \mu_B/\text{\AA}$ and $96 \times 10^{-2} \mu_B/\text{\AA}$ for the spin and orbital contributions respectively, making a total of $186 \times 10^{-2} \mu_B/\text{\AA}$) and the zz component comparatively small ($<3 \times 10^{-2} \mu_B/\text{\AA}$ for the spin part and $-10 \times 10^{-2} \mu_B/\text{\AA}$ for the orbital part).

At last, the basal fluorine located at the 8h Wyckoff position allows for the yz and zy off-diagonal DMC elements to be nonzero and with $Z_{xz}^{*m} = Z_{yz}^{*m} \neq Z_{zx}^{*m} = Z_{zy}^{*m}$. Our DFT results also find a nonzero and large value for the yz component ($30 \times 10^{-2} \mu_B/\text{\AA}$ for the spin part and $24 \times 10^{-2} \mu_B/\text{\AA}$ for the orbital part) and a negligible value for the zy component.

We can first note that the spin and orbital contributions are roughly on par for all atoms, meaning that the orbital magnetization contribution with SOC cannot be neglected for this crystal. The second note is that the DMC values of KCoF₃ are rather large when comparing with other crystals with 3d transition metal cations. The largest value obtained is for the F atom at the 4b Wyckoff site ($186 \times 10^{-2} \mu_B/\text{\AA}$), which is about six times larger than the one reported for BiCoO₃ ($31 \times 10^{-2} \mu_B/\text{\AA}$) [20] and two orders of magnitude higher than in Cr₂O₃ ($6 \times 10^{-2} \mu_B/\text{\AA}$) [49,50]. This is smaller but of the same order of magnitude than the artificially designed magnetoelectric KITPite compound (CaAlMn₃O₇ [49]) with a calculated value reported of $341 \times 10^{-2} \mu_B/\text{\AA}$ (see Table III). The largest reported DMC values are for the hexagonal perovskites HoMnO₃ and LuFeO₃, with a value of 445 and $665 \times 10^{-2} \mu_B/\text{\AA}$, respectively (Table III). Those large values in hexagonal perovskites originate from geometric spin frustration and magnetostriction effects [51], while KCoF₃ stands out as an exceptional case because its important DMC values are not from these conventional mechanisms. The large DMC values in KCoF₃ arise from a different pathway involving orbital degrees of freedom and Jahn-Teller distortions, which represent a potential alternative route to explore substantial dynamical magnetic charges in cubic perovskite systems.

To help visualizing the DMC's, we represent the DMC site tensor of each Wyckoff position using a vector field approach [see Figs. 7(a)–7(c)] [20]. This vector field is de-

TABLE III. Nonexhaustive table of comparison of previously reported DMC values (in $10^{-2} \mu_B/\text{\AA}$), for which atom and for which tensor element (the largest over all other atoms is reported). Beside the reference magnetoelectric crystal Cr₂O₃, we report the largest cases we could find in the literature. Indexes api and bas refer to the apical, respectively, basal positions in their respective structures.

Material	Atom	Element	Largest DMC value	Reference
Cr ₂ O ₃	Cr	xy	6	[49,50]
BiCoO ₃	Co	xx	31	[20]
KCoF ₃	F _{api}	xx	186	Present
CaAlMn ₃ O ₇	Mn	xx	341	[49]
HoMnO ₃	O _{bas}	xx	445	[51]
LuFeO ₃	O _{bas}	xx	665	[51]

fined by the linear transformation $\mathbf{y} = \mathbf{A}\mathbf{x}$, where $\mathbf{y}$ denotes the resulting vector field, $\mathbf{A}$ is the DMC tensor acting as the Jacobian matrix, and $\mathbf{x}$ represents the atomic displacement vector. The DMC tensor, serving as the linear operator, maps displacements to corresponding changes in magnetization, thereby providing a complete characterization of the site-specific magnetoelectric coupling (moving a single atom is polar by construction in ionic crystals and if this atom motion is associated to a change in magnetization, it works as a magnetoelectric response). Due to the reciprocal nature of magnetoelectricity, this tensor representation can also be interpreted in the inverse sense: it describes the atomic displacement induced by an external magnetic field applied in a given direction. Specifically, if a magnetic field is applied along the x axis, the corresponding atomic displacement response can be determined by examining the direction of the associated vector field arrows along the x axis of the tensor. This representation proves to be particularly valuable for analyzing the symmetry-constrained magnetoelectric

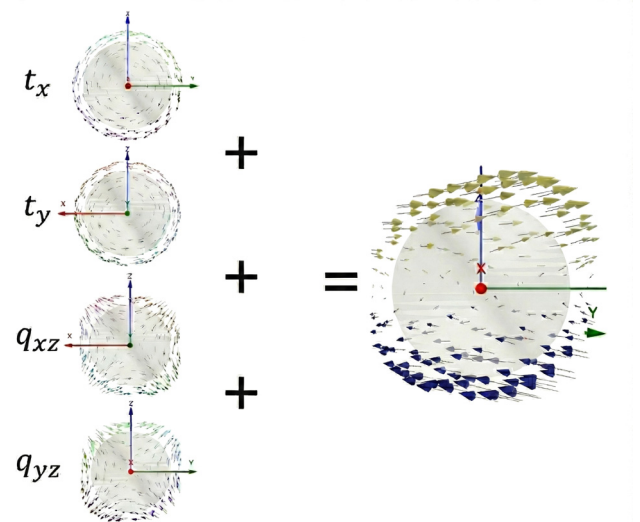


FIG. 6. Schematic representation of the DMC decomposition into multipole components of the F_{base} at the 8h Wyckoff site. See Appendix B for the t and q multipole notations.

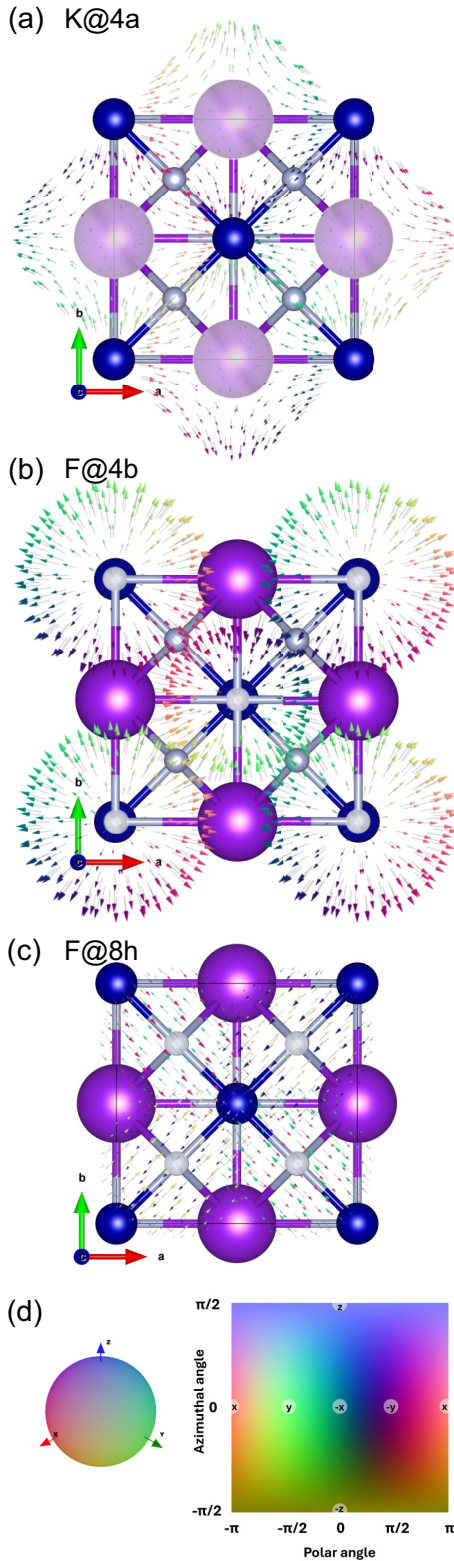


FIG. 7. Visualization of the different DMC vectorial representation of (a) the K atoms at the 4a Wyckoff position, (b) the F atoms at the 4b Wyckoff position, respectively, and (c) the F atoms at the 8h Wyckoff positions. The associated colormap representation is shown in panel (d).

response in crystalline materials, establishing a clear connection between polar lattice dynamics and magnetic properties.

In addition, the plotted vector field is color-mapped [Fig. 7(d)] by converting each vector's coordinates into RGB values. This directional color-coded technique enhances the perception of the vector field's structure allowing for immediate visual identification of atoms with similar/opposite vector orientations.

Additionally, the resulting vector field can be decomposed into irreducible tensor representations [21,52,53] that directly correspond to magnetoelectric multipoles: a scalar trace component corresponds to the magnetic monopole contribution, a fully antisymmetric tensor corresponds to the toroidal moment, and a symmetric traceless tensor corresponds to the magnetic quadrupole term (see Appendix B for the mathematical formalism and Fig. 6 for a visual aspect). Each of these magnetoelectric multipoles represents distinct physical mechanisms for magnetoelectric coupling, with the monopole a term relating to isotropic effects, the quadrupole q capturing anisotropic interactions, and the toroidal moment t describing vortexlike response of the magnetization to electric field stimuli. Fig. 6 illustrates this decomposition for the basal Fluorine atom at the 8h Wyckoff site. This analysis disentangles the complex total response into its irreducible symmetry-adapted components, revealing that the magnetoelectric properties at this site are governed by a combination of toroidal and quadrupolar moments. Visually, the toroidal contribution manifests as a distinct curl (vortex) field, indicating a rotational character in the coupling between lattice displacement and induced magnetization. Conversely, the quadrupolar contribution appears as a shear field, reflecting the anisotropic nature of the response.

The DMC magnetization texture generated by the individual Wyckoff sites constitutes a continuous global vector field that strictly obeys the crystal symmetry. This continuity implies that the symmetry-allowed magnetization at any point in the unit cell, including unoccupied Wyckoff positions, must naturally align with the overall “flow” of the vector field established by the occupied sites. This coherence confirms that the derived DMC tensors provide a consistent and robust description of the magnetic symmetry throughout the crystal volume.

Figure 7 provides a vectorial representation of the dynamical magnetic charge tensors for the occupied Wyckoff sites. In these plots, the vector field describes the local magnetoelectric response: the arrows indicate the direction and relative magnitude of the magnetization induced by an atomic displacement along the corresponding radial direction. Due to the reciprocal nature of the coupling, this visualization can equivalently be interpreted as the displacement direction of the atom by an external magnetic field. A particularly high-symmetry case is observed for the apical Fluorine at Wyckoff site 4b; the associated vector field is quasi purely divergent, physically, this indicates that the induced magnetization is mostly parallel to the atomic displacement vector regardless of the direction of motion ($\mathbf{M} \parallel \mathbf{u}$), a signature of a monopolar response.

The calculation of the DMC in the cubic phase is not possible using our “frozen-phonon” technique. Indeed, moving atoms one by one breaks the symmetry that allows the first-order Jahn-Teller electronic instability to relax for some cases, with the consequence that it is not anymore in the linear response regime.

D. Antimagnetoelectric response in KCoF_3

The magnetic space group of the ground state phase of KCoF_3 with the magnetic moment along the z direction is $I4'/mcm'$, does not allow for a magnetoelectric response. However, as the DMCs are nonzero, the contribution to the antimagnetoelectric response stemming from the spin lattice, respectively orbital-lattice couplings is nonzero. Assisted by the visualization tool for examining atomic responses to external fields of Fig. 7, it is more apparent why polar modes do not induce a magnetization. Indeed, atoms occupying equivalent Wyckoff positions with opposite DMC (like in KCoF_3) and moving in the same direction with the same amplitude will necessarily cancel each other regarding the induced magnetization, and resulting in an antimagnetoelectric behavior.

By splitting the response through magnetic sublattice, we have found that each sublattice carries a total response of 105 ps/m per formula unit (f.u.), i.e., 210 ps/m per spin channel (the unit cell contains 2 f.u. with spin up and two f.u. with spin down), which is split between the spin lattice $\alpha^{S,\text{latt}} = 50$ ps/m per f.u. and the orbital-lattice $\alpha^{L,\text{latt}} = 55$ ps/m per f.u. contributions. Hence, the local equivalent magnetoelectric response is rather large.

IV. DISCUSSION

To check how general is the possibility to have nonzero DMCs and to have antimagnetoelectric, we have looked from symmetry analysis how they are in the most common $Pnma$ perovskite phase within the ferromagnetic, C-, A-, and G-type AFM magnetic orders. We report these results in Table S.V of the SM [26]. Although none of those phases are magnetoelectric, we can see that all of the possible magnetic space groups that can be built from the $Pnma$ perovskites are antimagnetoelectric as they all have one or more of the Wyckoff sites that host a nonzero DMC tensor. The DMC is strictly forbidden in the paramagnetic parent group ($Pnma1'$), i.e., when there is no magnetic order. The same result is observed if one does the same general analysis in both Jahn-Teller phases from R and M zone boundary points or with octahedra rotation in one, two or three directions (not shown). Hence, we can see that the antimagnetoelectric property is actually very common in perovskites even for those that are nonfunctional.

V. CONCLUSIONS

In summary, we have studied from first-principles DFT calculations the cubic to tetragonal phase transition of KCoF_3 by looking at the phonons, energy landscape with respect to atom displacements and the magnetic ground state and the associated DMC. We could confirm that the phase transition is from a first-order Jahn-Teller electronic instability and that the associated ground state phase is antimagnetoelectric. We found that the DMCs of Co are zero and that the ones of K and F atoms are very large, the largest value being reached by the apical fluorine anion when moving it along the x or y direction perpendicular to the tetragonal axis. All of the large values are evenly split between spin and orbital magnetization, which

sum to make particularly large values. We could demonstrate from symmetry arguments the shape of the DMC tensors of each atom and that the DMC of Co cation should indeed be zero, even though it is the source of magnetism in KCoF_3 crystal.

The presence of a Jahn-Teller orbital ordering seems to be an important condition to obtain large DMC; however, this would require a more systematic and deeper analysis, which is beyond the scope of the present paper. We can however discuss here the possible reasons of why the DMCs are large in KCoF_3 . The strong correlation between the Jahn-Teller distortion and the emergence of a large DMC can be understood through the intimate coupling of electronic orbitals, lattice degrees of freedom, and spin-orbit interactions. The Jahn-Teller effect is, by definition, a manifestation of strong electron-phonon coupling, where a structural distortion lifts the electronic degeneracy of the magnetic ion's d -orbitals (in this case, Co^{2+}) to lower the system's total energy. This distortion not only modifies the crystal field environment but also partially quenches the orbital angular momentum. Consequently, the orbital component of the magnetic moment becomes highly sensitive to the positions of the surrounding ligands (F^- ions). A dynamical atomic displacement, which corresponds to a phonon excitation, modulates the Jahn-Teller distortion pattern. This dynamic modulation of the local crystal field, in turn, induces a change in the orbital magnetization. Through spin-orbit coupling, this orbital fluctuation is directly coupled to the spin degrees of freedom, inducing a corresponding change in the spin magnetization. The DMC is thus significantly enhanced because the Jahn-Teller mechanism could be a direct and efficient pathway for a lattice vibration to dynamically control both the orbital and spin magnetic moments. This would require testing this hypothesis in several compounds with and without Jahn-Teller distortions to verify it.

We could also show from symmetry arguments that the antimagnetoelectric response is present in most of the nonfunctional phases of perovskites and that it could be a more general property of magnetic materials that goes beyond the scope of multiferroic (having magnetic and polar orders together) or magnetoelectric crystals. We hope that our work will encourage further studies and use of the DMC in magnetic materials.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: DYNAMICAL MAGNETIC CHARGES

First, let us reassess the importance of the spin and orbital magnetic moments coupled to an electric field. The linear magnetoelectric effect, which is the coupling between the electric and magnetic degrees of freedom in materials, can be simply traced from the net magnetization $\mathbf{M}$ (polarization $\mathbf{P}$) induced by the applied electric (magnetic) field's amplitude:

$$\alpha_{ij} = \mu_0 \left. \frac{\delta M_j}{\delta \mathcal{E}_i} \right|_{\mathcal{H}} = \left. \frac{\delta P_i}{\delta \mathcal{H}_j} \right|_{\mathcal{E}}. \quad (\text{A1})$$

From the theoretical standpoint, the second-rank tensor α_{ij} can be decomposed into three contributions: electronic, lattice and strain, $\alpha^{\text{tot}} = \alpha^{\text{elec}} + \alpha^{\text{latt}} + \alpha^{\text{str}}$, each of which arising from the coupling with either the spin, $\mathbf{S}$, or the orbital, $\mathbf{L}$, degrees of freedom. While the electronic component (α^{elec}) response requires the presence of a spontaneous polarization to be nonzero, it is not the case for the latter two. In fact, lattice-mediated terms can give rise to a significant response in the vicinity of a ferroelectric phase transition [19,54]. Furthermore, the full magnetoelectric response can be strongly enhanced as a results of an unquenched orbital magnetic moment due to a strong lattice-orbital coupling [55–57]. We remind from a previous work [19,20] that the lattice-mediated contribution to the magnetoelectric tensor takes the following form:

$$\alpha_{ij}^{\text{latt}} = \frac{\mu_0}{\Omega} \sum_{n=1}^{N_{\text{IR}}} \frac{S_{n,ij}}{\omega_n^2}, \quad (\text{A2})$$

where ω_n the phonon *angular* frequencies corresponding to the N_{IR} infrared-active phonon modes, and $S_{n,ij}$ is the magnetoelectric mode-oscillator strength tensor, defined as follows:

$$S_{n,ij} = \left(\sum_{\kappa, i'} Z_{\kappa, ii}^* u_{n, \kappa, i'} \right) \times \left(\sum_{\kappa, j'} Z_{\kappa, j' j}^* u_{n, \kappa, j'} \right), \quad (\text{A3})$$

where κ identifies the atom in the unit cell, $u_{n, \kappa, j}$ the normalized eigendisplacement, Z_{κ}^* and Z_{κ}^{m} the Born effective charge and DMC, respectively, defined as

$$Z_{\kappa, ij}^* = \Omega \frac{\partial P_i}{\partial \tau_{\kappa, j}} = \frac{\partial^2 E}{\partial \mathcal{E}_i \partial \tau_{\kappa, j}}, \quad (\text{A4})$$

i.e., the net polarization along direction i induced by a displacement τ of atom κ along direction j , and

$$Z_{\kappa, ij}^{\text{m}} = \Omega \frac{\partial M_i}{\partial \tau_{\kappa, j}} = \frac{\partial^2 E}{\partial \mathcal{H}_i \partial \tau_{\kappa, j}}, \quad (\text{A5})$$

which corresponds to the net magnetization along the direction i , induced by a displacement τ of atom κ along direction j [19,49], or equivalently in the DFPT framework, the change in energy of a system under an applied magnetic field $\mathcal{H}$ along direction i and a displacement τ of atom κ along direction j .

Those DMCs have been used recently to explain the antiferromagnetoelectric case [21] where the global magnetoelectric

response is zero but the local one is not, similarly to antiferromagnetism with nonzero atom magnetic moments that are antialigned from site to site and giving zero total magnetization [20].

While DMCs were defined through magnetoelectric, magnetodielectric and multiferroic materials [19,20,49,58], in this work we show that large DMC can exists in nonfunctional materials. We study the antiferromagnetoelectric effect in the antiferromagnetically ordered KCoF_3 perovskite crystal in the presence of a Jahn-Teller instability by means of *ab initio* calculations.

APPENDIX B: MAGNETOELECTRIC MULTIPOLES

Magnetoelectric (ME) multipoles emerge as fundamental descriptors of magnetic structures lacking combined space-inversion (P) and time-reversal (T) symmetry, i.e., PT -noninvariant systems [59–61]. They originate from the spatial inhomogeneity of the magnetization density $\mathbf{M}(\mathbf{r})$ within a magnetic unit cell, formally arising from the first spatial moment tensor of magnetization, $\mathcal{M}_{ij} = \int r_i M_j(\mathbf{r}) d^3r$, where the integral is typically taken over the unit cell [59,60]. This tensor $\mathcal{M}_{ij}$ inherently captures the PT -odd character because the position vector $\mathbf{r}$ is P -odd, T -even, while the magnetization $\mathbf{M}$ is P -even, T -odd, making their product $r_i M_j$ odd under both P and T transformations. Consequently, ME multipoles are intrinsically linked to linear magnetoelectric phenomena, characterized by the ME tensor α_{ij} [59]. The microscopic ME multipoles defined via $\mathcal{M}_{ij}$ provide a direct connection to the macroscopic response tensor α_{ij} .

The tensor $\mathcal{M}_{ij}$ can be decomposed into its irreducible components, corresponding to distinct ME multipoles [59,60]:

(i) The ME monopole (also related to the anapole), associated with the trace of $\mathcal{M}$, $\text{Tr}(\mathcal{M}) = \int \mathbf{r} \cdot \mathbf{M}(\mathbf{r}) d^3r$. It represents a pointlike source of PT -odd characteristics.

(ii) The magnetic toroidal moment $\mathbf{T}$, an axial vector derived from the antisymmetric part of $\mathcal{M}_{ij}$: $T_k = \frac{1}{2} \epsilon_{ijk} \mathcal{M}_{ij} = \frac{1}{2} \int (\mathbf{r} \times \mathbf{M}(\mathbf{r}))_k d^3r$. Physically, it corresponds to vortexlike arrangements of magnetic moments, breaking both P and T symmetries individually [59,60]. It couples to the curl of an electric field or the time derivative of a magnetic field.

(iii) The ME quadrupole tensor Q_{ij}^{ME} , obtained from the symmetric traceless part of $\mathcal{M}_{ij}$: $Q_{ij}^{\text{ME}} = \frac{1}{2} \int (r_i M_j + r_j M_i - \frac{2}{3} \delta_{ij} \mathbf{r} \cdot \mathbf{M}) d^3r$.

The magnetoelectric multipoles collectively reconstitute the tensor $\mathcal{M}_{ij}$ shown in Eq. (B1). This tensor directly corresponds to the magnetoelectric tensor α_{ij} when constrained by the magnetic point group symmetry of the unit cell, which determines both the allowed Wyckoff positions and their corresponding magnetic moment orientations. Furthermore, $\mathcal{M}_{ij}$ represents the dynamical magnetic charge when further restricted by the local symmetries at specific Wyckoff sites:

$$\mathcal{M}_{ij} = \begin{pmatrix} a + \frac{1}{2} q_{x^2-y^2} - \frac{1}{2} q_z^2 & t_z + q_{xy} & t_y + q_{xz} \\ -t_z + q_{xy} & a - \frac{1}{2} q_{x^2-y^2} - \frac{1}{2} q_z^2 & -t_x + q_{yz} \\ -t_y + q_{xz} & t_x + q_{yz} & a + q_z^2 \end{pmatrix}. \quad (\text{B1})$$

While initially explored primarily in noncentrosymmetric magnetic insulators, the significance of ME multipoles is increasingly recognized even in metallic systems where itinerant electrons might be expected to screen electric fields [59,60] and in nonmagnetoelectric systems. They serve as crucial primary or secondary order parameters for complex magnetic phases, particularly “hidden orders” where the net magnetic dipole moment vanishes but a nonzero ME multipole exists [59–62]. Their presence can distinguish between magnetic structures that are degenerate at the dipole level but differ in their ME multipolar content, i.e., Fe_2O_3 and Cr_2O_3 [21], leading to distinct macroscopic properties like nonreciprocal transport, optical effects (e.g., directional dichroism), and specific contributions to magne-

toelectric responses [59,60]. Theoretically, their identification and calculation often rely on symmetry analysis (group theory) and first-principles electronic structure methods [59,62]. Experimentally, detecting ME multipoles can be challenging as their signatures are often weaker than those of magnetic dipoles. Techniques sensitive to PT -symmetry breaking, such as optical second harmonic generation, nonlinear optical effects, resonant and nonresonant x-ray diffraction (exploiting specific symmetries or dichroism), Compton scattering [62], and detailed analysis of polarized neutron scattering data (going beyond the standard magnetic structure factor), are employed for their investigation [60,61]. To the best of our knowledge, there is no experimental measurement of DMC and/or ME multipoles.

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- [1] V. Gnezdilov, J. Deisenhofer, P. Lemmens, D. Wulferding, O. Afanasiev, P. Ghigna, A. Loidl, and A. Yermenko, Phononic and magnetic excitations in the quasi-one-dimensional heisenberg antiferromagnet KCuF_3 , *Low Temp. Phys.* **38**, 419 (2012).
 - [2] J. C. T. Lee, S. Yuan, S. Lal, Y. I. Joe, Y. Gan, S. Smadici, K. Finkelstein, Y. Feng, A. Rusydi, P. M. Goldbart, S. Lance Cooper, and P. Abbamonte, Two-stage orbital order and dynamical spin frustration in KCuF_3 , *Nat. Phys.* **8**, 63 (2012).
 - [3] J.-S. Zhou, J. Alonso, J. Han, M. Fernández-Díaz, J.-G. Cheng, and J. Goodenough, Jahn-Teller distortion in perovskite KCuF_3 under high pressure, *J. Fluorine Chem.* **132**, 1117 (2011).
 - [4] K. Hirakawa, K. Hirakawa, and T. Hashimoto, Magnetic properties of potassium iron group fluorides KMF_3 , *J. Phys. Soc. Jpn.* **15**, 2063 (1960).
 - [5] A. Oleaga, A. Salazar, and D. Skrzypek, Critical behaviour of magnetic transitions in KCoF_3 and KNiF_3 perovskites, *J. Alloys Compd.* **629**, 178 (2015).
 - [6] K. Hirakawa and Y. Kurogi, One-dimensional antiferromagnetic properties of KCuF_3 , *Prog. Theor. Phys. Suppl.* **46**, 147 (1970).
 - [7] K. Koterass, S. Biesenkamp, P. Barone, Z. Mazej, G. c. v. Tavčar, T. C. Hansen, J. Lorenzana, W. Grochala, and M. Braden, Rearrangement of orbitals in KAgF_3 due to the Kugel-Khomskii mechanism: A neutron diffraction and density functional theory study, *Phys. Rev. B* **111**, 115156 (2025).
 - [8] J. Li, L. Xu, M. Garcia-Fernandez, A. Nag, H. C. Robarts, A. C. Walters, X. Liu, J. Zhou, K. Wohlfeld, J. van den Brink, H. Ding, and K.-J. Zhou, Unraveling the orbital physics in a canonical orbital system KCuF_3 , *Phys. Rev. Lett.* **126**, 106401 (2021).
 - [9] L. Clark and P. Lightfoot, Magnetic properties of transition metal fluoride perovskites, in *Photonic and Electronic Properties of Fluoride Materials*, edited by A. Tressaud and K. Poeppelmeier (Elsevier, Boston, MA, 2016), pp. 261–284.
 - [10] V. V. Iglamov and M. V. Eremin, Orbital order fluctuations in KCuF_3 , *Opt. Spectrosc.* **116**, 828 (2014).
 - [11] D. Legut and U. D. Wdowik, Vibrational properties and the stability of the KCuF_3 phases, *J. Phys.: Condens. Matter* **25**, 115404 (2013).
 - [12] S. Yuan, M. Kim, J. T. Seeley, J. C. T. Lee, S. Lal, P. Abbamonte, and S. L. Cooper, Inelastic light scattering measurements of a pressure-induced quantum liquid in KCuF_3 , *Phys. Rev. Lett.* **109**, 217402 (2012).
 - [13] J. Varignon, M. Bibes, and A. Zunger, Origins versus fingerprints of the Jahn-Teller effect in d -electron ABX_3 perovskites, *Phys. Rev. Res.* **1**, 033131 (2019).
 - [14] E. Pavarini, E. Koch, and A. I. Lichtenstein, Mechanism for orbital ordering in KCuF_3 , *Phys. Rev. Lett.* **101**, 266405 (2008).
 - [15] I. Leonov, N. Binggeli, D. Korotin, V. I. Anisimov, N. Stojić, and D. Vollhardt, Structural relaxation due to electronic correlations in the paramagnetic insulator KCuF_3 , *Phys. Rev. Lett.* **101**, 096405 (2008).
 - [16] I. Leonov, D. Korotin, N. Binggeli, V. I. Anisimov, and D. Vollhardt, Computation of correlation-induced atomic displacements and structural transformations in paramagnetic KCuF_3 and LaMnO_3 , *Phys. Rev. B* **81**, 075109 (2010).
 - [17] A. Okazaki and Y. Suemune, The crystal structures of KMnF_3 , KFeF_3 , KCoF_3 , KNiF_3 and KCuF_3 above and below their Néel temperatures, *J. Phys. Soc. Jpn.* **16**, 671 (1961).
 - [18] A. Okazaki, Y. Suemune, and T. Fuchikami, The crystal structures of KMnF_3 , KFeF_3 , KCoF_3 , KNiF_3 and KCuF_3 , *J. Phys. Soc. Jpn.* **14**, 1823 (1959).
 - [19] J. Íñiguez, First-principles approach to lattice-mediated magnetoelectric effects, *Phys. Rev. Lett.* **101**, 117201 (2008).
 - [20] M. Braun, B. Guster, A. Urru, H. Kabbour, and E. Bousquet, Large dynamical magnetic effective charges and antimagnetoelectricity from spin and orbital origin in multiferroic BiCoO_3 , *Phys. Rev. B* **110**, 144442 (2024).
 - [21] X. H. Verbeek, A. Urru, and N. A. Spaldin, Hidden orders and (anti-)magnetoelectric effects in Cr_2O_3 and α - Fe_2O_3 , *Phys. Rev. Res.* **5**, L042018 (2023).
 - [22] X. Gonze, The ABINIT project: Impact, environment and recent developments, *Comput. Phys. Commun.* **248**, 107042 (2020).
 - [23] M. Torrent, F. Jollet, F. Bottin, G. Zerah, and X. Gonze, Implementation of the projector augmented-wave method in the ABINIT code: Application to the study of iron under pressure, *Comput. Mater. Sci.* **42**, 337 (2008).
 - [24] F. Jollet, M. Torrent, and N. Holzwarth, Generation of projector augmented-wave atomic data: A 71 element validated table in the XML format, *Comput. Phys. Commun.* **185**, 1246 (2014).

- [25] V. Scatturin, L. Corliss, N. Elliott, and J. Hastings, Magnetic structures of 3d transition metal double fluorides, *KMeF₃*, *Acta Crystallogr.* **14**, 19 (1961).
- [26] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/wsc9-2llg> for tables regarding Hubbard parameter energy dependence, Born effective charges in the cubic phase, respectively in the Jahn-Teller phase, magnetic space groups associated with the parent *Pnma* group, and two figures: energy evolution under the rigid distortion in the collinear case, the phonon dispersion in the FM cubic phase, and an extended discussion on SOC vs spin frustrated DMC.
- [27] X. Gonze and C. Lee, Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory, *Phys. Rev. B* **55**, 10355 (1997).
- [28] A. H. Romero, D. C. Allan, B. Amadon, G. Antonius, T. Applencourt, L. Baguet, J. Bieder, F. Bottin, J. Bouchet, E. Bousquet, F. Bruneval, G. Brunin, D. Caliste, M. Côté, J. Denier, C. Dreyer, P. Ghosez, M. Giantomassi, Y. Gillet, O. Gingras, *et al.*, ABINIT: Overview and focus on selected capabilities, *J. Chem. Phys.* **152**, 124102 (2020).
- [29] Q. Zhang, J. Yan, Y. Zhang, and Y. Ke, Exact muffin tin orbital based first-principles method for electronic-structure and electron-transport simulation of device materials, *Phys. Rev. B* **100**, 075134 (2019).
- [30] J. W. Zwanziger, M. Torrent, and X. Gonze, Orbital magnetism and chemical shielding in the projector augmented-wave formalism, *Phys. Rev. B* **107**, 165157 (2023).
- [31] X. He, N. Helbig, M. J. Verstraete, and E. Bousquet, TB2J: A Python package for computing magnetic interaction parameters, *Comput. Phys. Commun.* **264**, 107938 (2021).
- [32] S. Wang, W. Li, G. Wang, D. Dong, J. Shi, X. Li, P. Li, and W. Tang, Crystal structure and electrical transport property of KMF_3 ($M = \text{Mn, Co, and Ni}$), *Powder Diffr.* **28**, S3 (2013).
- [33] H.-J. Koo, R. K. Kremer, and M.-H. Whangbo, Orbital magnetic moments of the high-spin Co^{2+} ions at axially-elongated octahedral sites: Unquenched as reported from experiment or quenched as predicted by theory? *Inorg. Chem.* **59**, 18319 (2020).
- [34] T. Isu and K. Motizuki, Theory of nuclear magnetic relaxation in KCoF_3 having residual orbital moment, *J. Phys. Soc. Jpn.* **45**, 806 (1978).
- [35] J. Kanamori, Theory of the magnetic properties of ferrous and cobaltous oxides, I, *Prog. Theor. Phys.* **17**, 177 (1957).
- [36] M.-H. Whangbo, R. K. Kremer, and H.-J. Koo, Unusually high magnetic moments reported for the high-spin Co^{2+} ions at axially elongated CoO_4X_2 ($X = \text{Cl, Br, S, Se}$) octahedral sites: Overestimated magnetic moments caused by underestimated magnetic form factors, *J. Phys. Chem. C* **126**, 16563 (2022).
- [37] Y. M. Oey and R. Cava, The effective magnetic moments of Co^{2+} and Co^{3+} in SrTiO_3 investigated by temperature-dependent magnetic susceptibility, *Mater. Res. Bull.* **122**, 110667 (2020).
- [38] D. Hovančík, J. Pospíšil, K. Carva, V. Sechovský, and C. Piamonteze, Large orbital magnetic moment in VI_3 , *Nano Lett.* **23**, 1175 (2023).
- [39] D. Huang, C. Chang, J. Chen, H.-J. Lin, S. Chung, H.-T. Jeng, G. Guo, W. Wu, S. Shyu, and C. Chen, Orbital moments of CrO_2 and Fe_3O_4 studied by MCD in soft x-ray absorption, *J. Electron Spectrosc. Relat. Phenom.* **137-140**, 633 (2004).
- [40] R. R. Neumann, A. Mook, J. Henk, and I. Mertig, Orbital magnetic moment of magnons, *Phys. Rev. Lett.* **125**, 117209 (2020).
- [41] J. Nouet, D. J. Toms, and J. F. Scott, Light scattering from magnons and excitons in RbCoF_3 , *Phys. Rev. B* **7**, 4874 (1973).
- [42] R. M. Dubrovin, A. C. Garcia-Castro, N. V. Siverin, N. N. Novikova, K. N. Boldyrev, A. H. Romero, and R. V. Pisarev, Incipient geometric lattice instability of cubic fluoroperovskites, *Phys. Rev. B* **104**, 144304 (2021).
- [43] M. A. Carpenter, E. K. H. Salje, and C. J. Howard, Magnetoelastic coupling and multiferroic ferroelastic/magnetic phase transitions in the perovskite KMnF_3 , *Phys. Rev. B* **85**, 224430 (2012).
- [44] J. Kanamori, Crystal distortion in magnetic compounds, *J. Appl. Phys.* **31**, S14 (1960).
- [45] J. F. Scott, Soft-mode spectroscopy: Experimental studies of structural phase transitions, *Rev. Mod. Phys.* **46**, 83 (1974).
- [46] M. M. Schmitt, Y. Zhang, A. Mercy, and P. Ghosez, Electron-lattice interplay in LaMnO_3 from canonical Jahn-Teller distortion notations, *Phys. Rev. B* **101**, 214304 (2020).
- [47] K. I. Kugel' and D. I. Khomskii, The Jahn-Teller effect and magnetism: Transition metal compounds, *Sov. Phys. Usp.* **25**, 231 (1982).
- [48] Edited by I. B. Bersuker, *The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry* (Springer, New York, NY, 1984).
- [49] M. Ye and D. Vanderbilt, Dynamical magnetic charges and linear magnetoelectricity, *Phys. Rev. B* **89**, 064301 (2014).
- [50] N. Tillack, J. R. Yates, and P. G. Radaelli, *Ab initio* cycloidal and chiral magnetoelectric responses in Cr_2O_3 , *Phys. Rev. B* **94**, 100405(R) (2016).
- [51] M. Ye and D. Vanderbilt, Magnetic charges and magnetoelectricity in hexagonal rare-earth manganites and ferrites, *Phys. Rev. B* **92**, 035107 (2015).
- [52] A. Urru and N. A. Spaldin, Magnetic octupole tensor decomposition and second-order magnetoelectric effect, *Ann. Phys.* **447**, 168964 (2022).
- [53] N. A. Spaldin, M. Fechner, E. Bousquet, A. Balatsky, and L. Nordström, Monopole-based formalism for the diagonal magnetoelectric response, *Phys. Rev. B* **88**, 094429 (2013).
- [54] E. Bousquet and N. Spaldin, Induced magnetoelectric response in *Pnma* perovskites, *Phys. Rev. Lett.* **107**, 197603 (2011).
- [55] A. Malashevich, S. Coh, I. Souza, and D. Vanderbilt, Full magnetoelectric response of Cr_2O_3 from first principles, *Phys. Rev. B* **86**, 094430 (2012).
- [56] A. Scaramucci, E. Bousquet, M. Fechner, M. Mostovoy, and N. A. Spaldin, Linear magnetoelectric effect by orbital magnetism, *Phys. Rev. Lett.* **109**, 197203 (2012).
- [57] I. V. Solovyev and T. V. Kolodiaznyi, Origin of magnetoelectric effect in $\text{Co}_4\text{Nb}_2\text{O}_9$ and $\text{Co}_4\text{Ta}_2\text{O}_9$: The lessons learned from the comparison of first-principles-based theoretical models and experimental data, *Phys. Rev. B* **94**, 094427 (2016).
- [58] K. Kimura, P. Babkevich, M. Sera, M. Toyoda, K. Yamauchi, G. S. Tucker, J. Martius, T. Fennell, P. Manuel, D. D. Khalyavin, R. D. Johnson, T. Nakano, Y. Nozue, H. M. Rønnow, and T. Kimura, Magnetodielectric detection of magnetic quadrupole order in $\text{Ba}(\text{TiO})\text{Cu}_4(\text{PO}_4)_4$ with Cu_4O_{12} square cupolas, *Nat. Commun.* **7**, 13039 (2016).

- [59] F. Thöle and N. A. Spaldin, Magnetoelectric multipoles in metals, *Philos. Trans. R. Soc. A* **376**, 20170450 (2018).
- [60] M. Yatsushiro, H. Kusunose, and S. Hayami, Multipole classification in 122 magnetic point groups for unified understanding of multiferroic responses and transport phenomena, *Phys. Rev. B* **104**, 054412 (2021).
- [61] S. Bhowal, S. P. Collins, and N. A. Spaldin, Hidden k -space magnetoelectric multipoles in nonmagnetic ferroelectrics, *Phys. Rev. Lett.* **128**, 116402 (2022).
- [62] S. Bhowal and N. A. Spaldin, Revealing hidden magnetoelectric multipoles using compton scattering: Case study of ferroelectric GeTe, *Phys. Rev. Res.* **3**, 033185 (2021).

Supplementary Material: First-principles study of KCoF_3 : Jahn-Teller effect, dynamical magnetic charges, magnetoelectric multipoles and antimagetoelectricity

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I. SUPPLEMENTARY TABLES

TABLE S.I. Relative energy difference (ΔE) between the cubic and the Jahn-Teller and the elastic phase with respect to the Hubbard U value. The corresponding lattice parameters of each case is listed as well. All lengths are expressed in Bohr.

#	Cubic			JT - Q^{2-}				Monoclinic			
U	a	b	c	a	b	c	ΔE (meV/f.u.)	a α	b β	c γ	ΔE (meV/f.u.)
4.0	10.695	10.695	15.658	10.880	10.880	15.124	-23.1	10.885 90	10.885 90	15.123 88.00	-0.7
4.5	10.696	10.696	15.658	10.887	10.887	15.137	-22.1	10.887 90	10.892 90	15.133 88.03	-0.7
5.0	10.709	10.709	15.658	10.890	10.890	15.130	-21.1	10.893 90	10.897 90	15.137 88.05	-0.7
6.0	10.719	10.719	15.663	10.898	10.898	15.158	-19.5	10.899 90	10.901 90	15.163 88.15	-0.7
8.0	10.727	10.727	15.667	10.910	10.910	15.206	-17.2	10.915 90	10.911 90	15.191 88.21	-1.1
10.0	10.765	10.765	15.677	10.923	10.923	15.232	-14.8	10.926 90	10.928 90	15.224 88.33	-0.7

TABLE S.II. Calculated Born effective charges tensor components (in unit of the elemental charge e) in the FM phase of KCoF_3 in the cubic geometry. Columns refer to derivatives with respect to the electric field and lines to derivatives with respect to atomic positions, in atomic units.

Atom	Born Effective Charge (e)			
	$\partial/\partial\mathcal{E}_x$	$\partial/\partial\mathcal{E}_y$	$\partial/\partial\mathcal{E}_z$	
K	$\partial/\partial\tau_x$	1.19	0	0
	$\partial/\partial\tau_y$	0	1.19	0
	$\partial/\partial\tau_z$	0	0	1.21
Co	$\partial/\partial\tau_x$	2.01	0.	0
	$\partial/\partial\tau_y$	0	2.01	0
	$\partial/\partial\tau_z$	0	0	2.39
F_{api}	$\partial/\partial\tau_x$	-0.82	0	0
	$\partial/\partial\tau_y$	0	-0.82	0
	$\partial/\partial\tau_z$	0	0	-1.64
F_{bas}	$\partial/\partial\tau_x$	-0.63	0.	0
	$\partial/\partial\tau_y$	0	-1.67	0
	$\partial/\partial\tau_z$	0	0	-0.82

TABLE S.III. Calculated Born effective charges tensor components (in unit of the elemental charge e) in the G-AFM phase of KCoF_3 in the R-point Jahn-Teller distorted geometry. Columns refer to derivatives with respect to the electric field and lines to derivatives with respect to atomic positions, in atomic units.

Atom	Born Effective Charge (e)			
	$\partial/\partial\mathcal{E}_x$	$\partial/\partial\mathcal{E}_y$	$\partial/\partial\mathcal{E}_z$	
K	$\partial/\partial\tau_x$	1.20	0	0
	$\partial/\partial\tau_y$	0	1.20	0
	$\partial/\partial\tau_z$	0	0	1.21
Co	$\partial/\partial\tau_x$	2.13	-0.18	0
	$\partial/\partial\tau_y$	-0.18	2.13	0
	$\partial/\partial\tau_z$	0	0	2.31
F_{api}	$\partial/\partial\tau_x$	-0.78	0	0
	$\partial/\partial\tau_y$	0	-0.78	0
	$\partial/\partial\tau_z$	0	0	-1.84
F_{bas}	$\partial/\partial\tau_x$	-1.26	0.49	0
	$\partial/\partial\tau_y$	0.49	-1.26	0
	$\partial/\partial\tau_z$	0	0	-0.83

TABLE S.IV. Mode effective charges of the polar phonon modes of KCoF_3 in the JT phase.

$\omega(\text{meV})$	Character	Mode effective charge		
		x	y	z
15	A_{2u}	0	0	2.78
15	E_u	0	-2.79	0
15	E_u	2.79	0	0
21	E_u	0	-0.11	0
21	E_u	-0.11	0	0
26	A_{2u}	0	0	-3.29
27	E_u	0	-2.93	0
27	E_u	-2.93	0	0
33	E_u	-0.94	0	0
33	E_u	0	0.94	0
54	E_u	-0.001	4.081	0
54	E_u	-4.081	-0.001	0
56	A_{2u}	0	0	-4.27

TABLE S.V: Magnetic space groups associated with the parent space group $Pnma$ (#62). The table lists the BNS number and Wyckoff positions filled in standard perovskites (ABX_3).

Group Name (BNS #)	Wyckoff Pos.	Representative Site ($x, y, z \mid m_x, m_y, m_z$)	Site Sym.	Tensor Shape [Z_{ij}^{*m}]
$Pnma1'$ (#62.442)	4b	(0, 0, 1/2 0, 0, 0)	-11'	$\emptyset$
	4c	(x, 1/4, z 0, 0, 0)	.m.1'	$\emptyset$
	8d	(x, y, z 0, 0, 0)	11'	$\emptyset$
$Pn'ma$ (#62.443)	4b	(0, 0, 1/2 0, 0, 0)	-1'	$\begin{bmatrix} Z_{xx}^{*m} & Z_{xy}^{*m} & Z_{xz}^{*m} \\ Z_{yx}^{*m} & Z_{yy}^{*m} & Z_{yz}^{*m} \\ Z_{zx}^{*m} & Z_{zy}^{*m} & Z_{zz}^{*m} \\ 0 & Z_{xy}^{*m} & 0 \\ Z_{yx}^{*m} & 0 & Z_{yz}^{*m} \\ 0 & Z_{zy}^{*m} & 0 \\ Z_{xx}^{*m} & Z_{xy}^{*m} & Z_{xz}^{*m} \\ Z_{yx}^{*m} & Z_{yy}^{*m} & Z_{yz}^{*m} \\ Z_{zx}^{*m} & Z_{zy}^{*m} & Z_{zz}^{*m} \end{bmatrix}$
	4c	(x, 1/4, z 0, m_y , 0)	.m.	$\begin{bmatrix} Z_{xx}^{*m} & Z_{xy}^{*m} & Z_{xz}^{*m} \\ 0 & Z_{yy}^{*m} & 0 \\ Z_{yx}^{*m} & 0 & Z_{yz}^{*m} \\ 0 & Z_{zy}^{*m} & 0 \\ Z_{xx}^{*m} & Z_{xy}^{*m} & Z_{xz}^{*m} \\ Z_{yx}^{*m} & Z_{yy}^{*m} & Z_{yz}^{*m} \\ Z_{zx}^{*m} & Z_{zy}^{*m} & Z_{zz}^{*m} \end{bmatrix}$
	8d	(x, y, z m_x, m_y, m_z)	1	$\begin{bmatrix} Z_{xx}^{*m} & Z_{xy}^{*m} & Z_{xz}^{*m} \\ Z_{yx}^{*m} & Z_{yy}^{*m} & Z_{yz}^{*m} \\ Z_{zx}^{*m} & Z_{zy}^{*m} & Z_{zz}^{*m} \\ Z_{xx}^{*m} & 0 & Z_{xz}^{*m} \\ 0 & Z_{yy}^{*m} & 0 \\ Z_{yx}^{*m} & 0 & Z_{yz}^{*m} \\ Z_{zx}^{*m} & 0 & Z_{zz}^{*m} \end{bmatrix}$
$Pnm'a$ (#62.444)	4b	(0, 0, 1/2 0, 0, 0)	-1'	$\begin{bmatrix} Z_{xx}^{*m} & Z_{xy}^{*m} & Z_{xz}^{*m} \\ Z_{yx}^{*m} & Z_{yy}^{*m} & Z_{yz}^{*m} \\ Z_{zx}^{*m} & Z_{zy}^{*m} & Z_{zz}^{*m} \\ Z_{xx}^{*m} & 0 & Z_{xz}^{*m} \\ 0 & Z_{yy}^{*m} & 0 \\ Z_{yx}^{*m} & 0 & Z_{yz}^{*m} \\ Z_{zx}^{*m} & 0 & Z_{zz}^{*m} \end{bmatrix}$
	4c	(x, 1/4, z m_x , 0, m_z)	.m'.	$\begin{bmatrix} Z_{xx}^{*m} & Z_{xy}^{*m} & Z_{xz}^{*m} \\ 0 & Z_{yy}^{*m} & 0 \\ Z_{yx}^{*m} & 0 & Z_{yz}^{*m} \\ 0 & Z_{zy}^{*m} & 0 \\ Z_{xx}^{*m} & 0 & Z_{xz}^{*m} \\ 0 & Z_{yy}^{*m} & 0 \\ Z_{yx}^{*m} & 0 & Z_{yz}^{*m} \\ 0 & 0 & 0 \end{bmatrix}$

Continued on next page

TABLE S.V – continued from previous page

Group Name	Pos.	Representative Site	Sym.	Tensor Shape
	8d	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>Pnma'</i> (#62.445)	4b	$(0, 0, 1/2 \mid 0, 0, 0)$	$-1'$	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	4c	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \end{bmatrix}$
	8d	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>Pn'm'a</i> (#62.446)	4b	$(0, 0, 1/2 \mid m_x, m_y, m_z)$	-1	$\emptyset$
	4c	$(x, 1/4, z \mid m_x, 0, m_z)$	$.m'.$	$\begin{bmatrix} Z^{*m}_{xx} & 0 & Z^{*m}_{xz} \\ 0 & Z^{*m}_{yy} & 0 \\ Z^{*m}_{zx} & 0 & Z^{*m}_{zz} \end{bmatrix}$
	8d	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>Pnm'a'</i> (#62.447)	4b	$(0, 0, 1/2 \mid m_x, m_y, m_z)$	-1	$\emptyset$
	4c	$(x, 1/4, z \mid m_x, 0, m_z)$	$.m'.$	$\begin{bmatrix} Z^{*m}_{xx} & 0 & Z^{*m}_{xz} \\ 0 & Z^{*m}_{yy} & 0 \\ Z^{*m}_{zx} & 0 & Z^{*m}_{zz} \end{bmatrix}$
	8d	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>Pn'm'a'</i> (#62.448)	4b	$(0, 0, 1/2 \mid m_x, m_y, m_z)$	-1	$\emptyset$
	4c	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \end{bmatrix}$
	8d	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>Pn'm'a'</i> (#62.449)	4b	$(0, 0, 1/2 \mid 0, 0, 0)$	$-1'$	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	4c	$(x, 1/4, z \mid m_x, 0, m_z)$	$.m'.$	$\begin{bmatrix} Z^{*m}_{xx} & 0 & Z^{*m}_{xz} \\ 0 & Z^{*m}_{yy} & 0 \\ Z^{*m}_{zx} & 0 & Z^{*m}_{zz} \end{bmatrix}$
	8d	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>P_anma</i> (#62.450)	8c	$(3/4, 1/2, 1/2 \mid 0, 0, 0)$	$-1'$	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	8d	$(0, 1/2, 1/2 \mid m_x, m_y, m_z)$	-1	$\emptyset$
	8f	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \end{bmatrix}$
	16g	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>P_bnma</i> (#62.451)	4b	$(0, 0, 0 \mid m_x, 0, m_z)$	$.2'/m'.$	$\emptyset$
	4d	$(0, 0, 1/2 \mid m_x, 0, m_z)$	$.2'/m'.$	$\emptyset$
	8g	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \end{bmatrix}$
	16i	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
<i>P_cnma</i> (#62.452)	8a	$(0, 0, 3/4 \mid 0, 0, 0)$	$-1'$	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	8b	$(0, 0, 0 \mid m_x, m_y, m_z)$	-1	$\emptyset$

Continued on next page

TABLE S.V – continued from previous page

Group Name	Pos.	Representative Site	Sym.	Tensor Shape
	8d	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	16e	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	8d	$(0, 0, 0 \mid m_x, m_y, m_z)$	-1	$\emptyset$
$P_{An}ma$ (#62.453)	8f	$(x, 3/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	16h	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	8d	$(1/4, 0, 1/4 \mid 0, 0, 0)$	-1'	$\begin{bmatrix} Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \\ 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
$P_{Bn}ma$ (#62.454)	8g	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	16h	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	8c	$(0, 0, 0 \mid m_x, m_y, m_z)$	-1	$\emptyset$
$P_{Cn}ma$ (#62.455)	8f	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	16g	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	4a	$(0, 0, 0 \mid 0, m_y, m_z)$	$2'/m'..$	$\emptyset$
	4b	$(0, 0, 1/2 \mid 0, m_y, m_z)$	$2'/m'..$	$\emptyset$
$P_{In}ma$ (#62.456)	8i	$(x, 1/4, z \mid 0, m_y, 0)$	$.m.$	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$
	16j	$(x, y, z \mid m_x, m_y, m_z)$	1	$\begin{bmatrix} 0 & Z^{*m}_{xy} & 0 \\ Z^{*m}_{yx} & 0 & Z^{*m}_{yz} \\ 0 & Z^{*m}_{zy} & 0 \\ Z^{*m}_{xx} & Z^{*m}_{xy} & Z^{*m}_{xz} \\ Z^{*m}_{yx} & Z^{*m}_{yy} & Z^{*m}_{yz} \\ Z^{*m}_{zx} & Z^{*m}_{zy} & Z^{*m}_{zz} \end{bmatrix}$

TABLE S.VI: Wyckoff Positions, Site Symmetries, and DMC shapes for Space Group #140.545. Only Wyckoff positions filled in standard perovskites are listed.

Group Name (BNS #)	Wyckoff Pos.	Representative Site $(x, y, z \mid m_x, m_y, m_z)$	Site Sym.	Tensor Shape $[Z^{*m}_{ij}]$
	4a	$(0, 0, 1/4 \mid 0, 0, 0)$	$4'22'$	$\begin{bmatrix} -Z^{*m}_{xx} & 0 & 0 \\ 0 & Z^{*m}_{xx} & 0 \\ 0 & 0 & 0 \\ Z^{*m}_{xx} & 0 & 0 \\ 0 & Z^{*m}_{xx} & 0 \\ 0 & 0 & Z^{*m}_{zz} \end{bmatrix}$
$I4'/mcm'$ (#140.545)	4b	$(0, 1/2, 1/4 \mid 0, 0, 0)$	$-4'2m'$	$\begin{bmatrix} Z^{*m}_{xx} & 0 & 0 \\ 0 & Z^{*m}_{xx} & 0 \\ 0 & 0 & Z^{*m}_{zz} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
	4d	$(0, 0, 0 \mid 0, 0, m_z)$	$m.m'm'$	$\emptyset$
	8h	$(x, x + 1/2, 0 \mid 0, 0, m_z)$	$m.2'm'$	$\begin{bmatrix} 0 & 0 & Z^{*m}_{xz} \\ 0 & 0 & Z^{*m}_{xz} \\ 0 & 0 & Z^{*m}_{xz} \\ Z^{*m}_{zx} & Z^{*m}_{zx} & 0 \end{bmatrix}$

II. SUPPLEMENTARY FIGURES

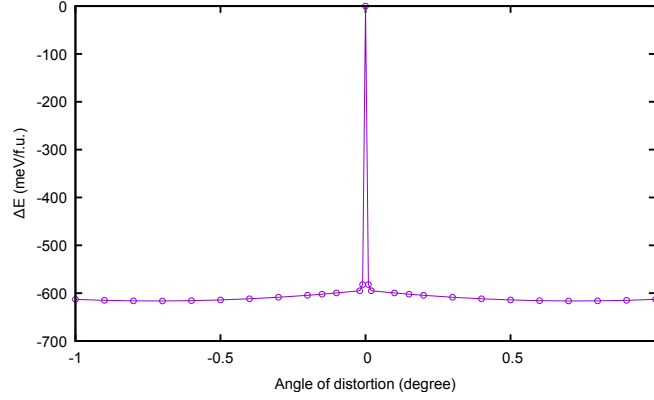


FIG. S.1. Energy evolution under the first-order type Jahn-Teller rigid distortion in KCoF_3 in the *collinear treatment* of the G-AFM magnetic state. The energy gain is comparable with the work of Varignon et al. [1] (See Fig. 7).

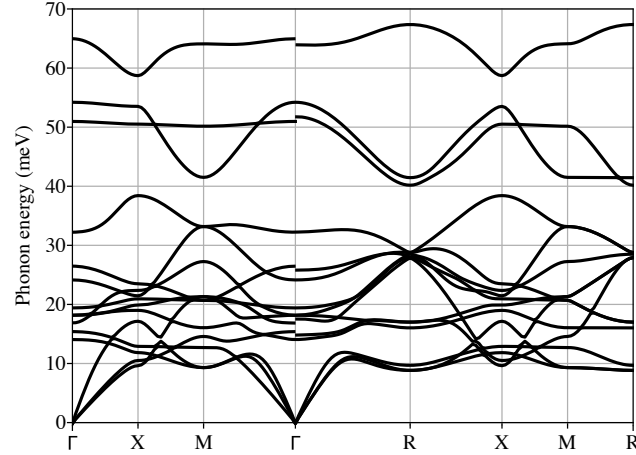


FIG. S.2. Phonon dispersion of KCoF_3 in the collinear treatment of the FM undistorted phase. This is in line with the G-AFM phonon dispersion calculation of Dubrovin et al. [2] where they also observe no unstable phonon mode.

III. EXTENDED DISCUSSION

Contrary to spin-frustrated systems, such as triangular lattice configurations, KCoF_3 exhibits large dynamical magnetic effective charges (DMCs) of comparable magnitude but relies on a fundamentally different mechanism due to its structure symmetry, which precludes spin frustration. The absence of such geometric spin frustration in KCoF_3 necessitates an alternative mechanism for generating large DMCs. We expand on this topic in Fig. S.3.

The Jahn-Teller (JT) effect can induce orbital ordering (OO) in perovskite fluorides, but its manifestation and impact on magnetic couplings depend critically on the specific electronic configuration involved. In KCoF_3 , hosting high-spin Co^{2+} ($3d^7, t_{2g}^5 e_g^2$), the JT activity arises from the orbital degeneracy within the t_{2g} manifold. This leads to a potentially subtle form of OO involving the t_{2g} orbitals, driven by relatively weak JT distortions primarily modifying the Co-F bond lengths. As the dominant G-type antiferromagnetic (AFM) superexchange ($\text{Co}(e_g) - \text{F}(p) - \text{Co}(e_g)$) involves the non-degenerate e_g levels, this t_{2g} -based OO primarily serves to quantitatively fine-tune the exchange strength and, along with significant spin-orbit coupling, contributes to magnetic anisotropy, rather than dictating the overall magnetic structure. This contrasts sharply with archetypal JT systems like KCuF_3 , containing Cu^{2+}

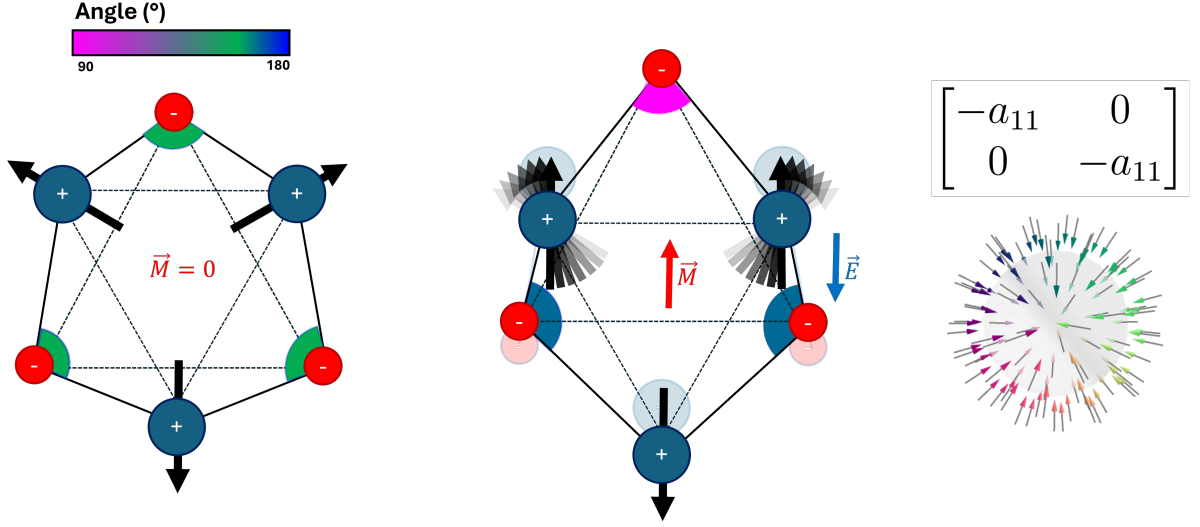


FIG. S.3. The illustration above of the frustrated spin configuration in a triangular lattice formed by magnetic atoms within a hexagonal structure. (Left) In the absence of an external electric field, the system exhibits spin frustration, resulting in zero net magnetization ($\vec{M} = 0$). (Center) Under an applied electric field ($\vec{E}$), ionic displacements along polar modes induce symmetry breaking, leading to a net magnetization ($\vec{M} \neq 0$) and modified spin orientations. (Right) Visualization of the resulting magnetoelectric coupling tensor in the form of a ME monopole.

($3d^9, t_{2g}^6 e_g^3$). Here, the strong e_g JT instability drives a pronounced, cooperative OO involving the e_g holes, which is well-established experimentally. This distinct pattern of occupied e_g orbitals, stabilized by significant modulations in Cu-F bond lengths, directly imposes a strong anisotropy onto the magnetic superexchange pathways, fundamentally determining the resulting quasi-one-dimensional or A-type AFM structures observed in KCuF_3 . Thus, while both systems can exhibit OO, the electronic manifold (t_{2g} vs e_g) dictates the robustness of the ordering and whether it fundamentally governs or merely modifies the magnetic interactions. Intriguingly, even though the resulting G-type AFM configuration in KCoF_3 can also be predicted by calculations performed on the idealized, non-JT-distorted cubic structure, the JT effect, via its associated lattice distortions and subtle t_{2g} orbital ordering, can still exert a significant influence on emergent phenomena such as magnetoelectric (ME) couplings.

A. Impact of Jahn-Teller (JT) Distortion and Electric Fields on KCoF_3 Super-Exchange Angles

Notably, while Jahn-Teller (JT) distortions alone do not directly modify super-exchange angles in the absence of an electric field, their interplay with field-induced polar phonon modes becomes critical. When an electric field drives ionic displacements along a polar mode (cation and anion sublattices shifting oppositely), the JT effect amplifies deviations from the ideal 180° Co-F-Co bond angles at the origin of the antiferromagnetic coupling following the Goodenough-Kanamori-Anderson rule. A key distinction arises between symmetric and JT-distorted configurations:

- **Symmetric structure:** The field redistributes bond angles into *two degenerate pairs*: two angles increase by $\Delta\theta$, while the other two decrease by $\Delta\theta$, maintaining pairwise equivalence.
- **JT-distorted structure:** The intrinsic symmetry breaking lifts this degeneracy, resulting in *four distinct angles* with unequal deviations ($\Delta\theta_1 \neq \Delta\theta_2 \neq \Delta\theta_3 \neq \Delta\theta_4$).

This loss of pairwise equivalence creates spatially nonuniform magnetic exchange interactions. The resulting exchange striction break local spin-environment symmetry, providing a mechanism for emergent dynamical magnetic charges.

Orbital ordering (OO) directly impacts the Born effective charge tensor (Z^*) which comprises ionic and electronic contributions, with the latter reflecting the dynamic redistribution of valence charge density accompanying ionic motion. By preferentially occupying specific orbitals (e.g., d -orbitals in transition metal ions), OO inherently breaks the local electronic symmetry, rendering the valence electron cloud anisotropic. Consequently, the electronic response to an ionic displacement $\mathbf{u}$ becomes direction-dependent; the change in polarization $\mathbf{P}$ resulting from displacing the ion parallel to the lobes of an occupied orbital differs from that induced by perpendicular displacement. Displacing the

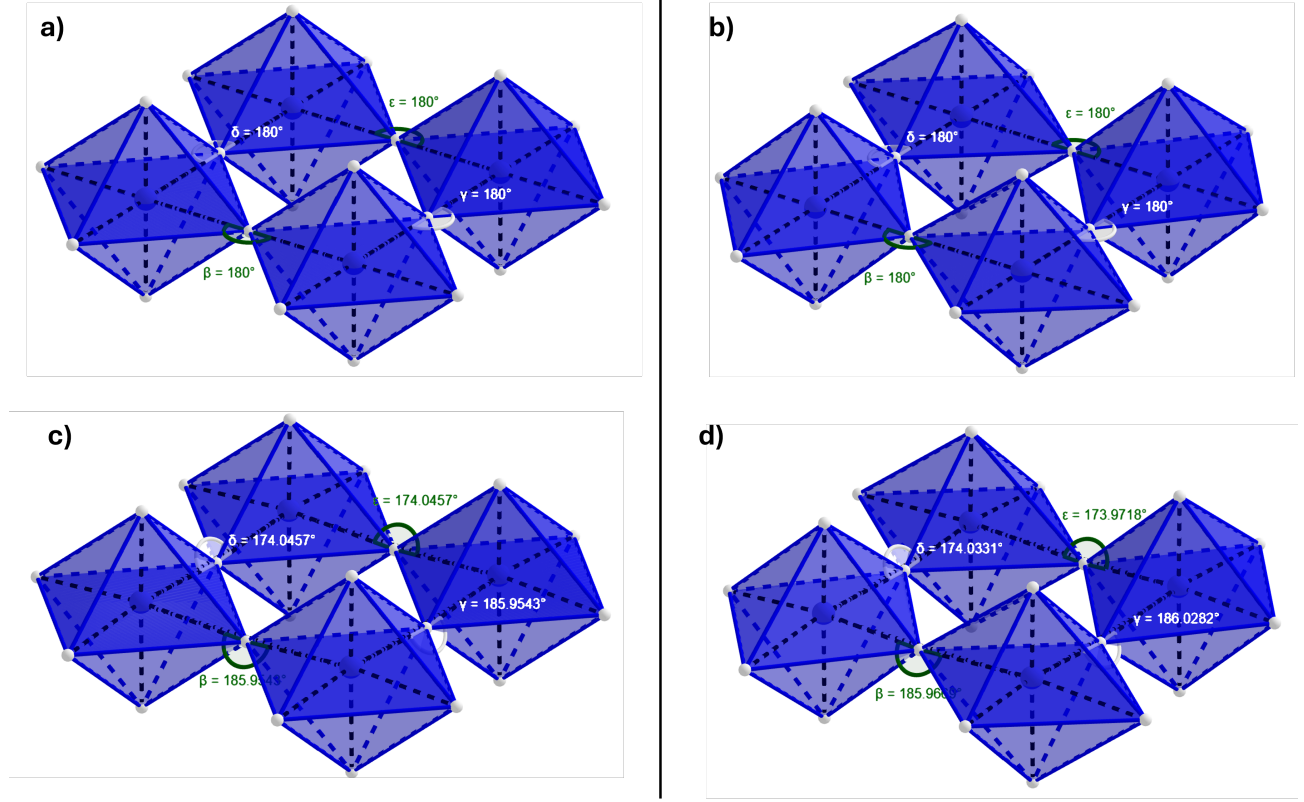


FIG. S.4. Impact of Jahn-Teller (JT) Distortion and Electric Fields on KCoF_3 Super-Exchange Angles (a, c) Symmetric atomic arrangements without JT distortion. (b, d) JT-distorted configurations altering Co-F-Co bond angles. An electric field applied along the crystallographic cell's diagonal (cases c, d) modifies structural symmetry compared to field-free cases (a, b).

ion along the direction where an occupied orbital lobe points will stretch or compress that lobe and modify its overlap with ligands differently than displacing it perpendicularly. This anisotropic electronic redistribution manifests directly as an anisotropy in the Z^* tensor, introducing off-diagonal components or making diagonal components unequal, even for ions residing on high-symmetry sites in the average crystal structure. Furthermore, OO modifies the specific orbital hybridization pathways involved in dynamic charge transfer with ligands, thereby altering the magnitude of the electronic contributions to Z^* components compared to a system without orbital ordering i.e the pristine cubic perovskite.

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- [1] J. Varignon, M. Bibes, and A. Zunger, Origins versus fingerprints of the Jahn-Teller effect in d -electron ABX_3 perovskites, *Phys. Rev. Res.* **1**, 033131 (2019).
 - [2] R. M. Dubrovín, A. C. García-Castro, N. V. Siverin, N. N. Novikova, K. N. Boldyrev, A. H. Romero, and R. V. Pisarev, Incipient geometric lattice instability of cubic fluoroperovskites, *Phys. Rev. B* **104**, 144304 (2021).