

Ferroelectric ferrimagnetic LiFe_2F_6 : Charge-ordering-mediated magnetoelectricity

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Trirutile-type LiFe_2F_6 is a charge-ordered material with an $\text{Fe}^{2+}/\text{Fe}^{3+}$ configuration. Here, its physical properties, including magnetism, electronic structure, phase transition, and charge ordering, are studied theoretically. On one hand, the charge ordering leads to improper ferroelectricity with a large polarization. On the other hand, its magnetic ground state can be tuned from the antiferromagnetic to ferrimagnetic by moderate compressive strain. Thus, LiFe_2F_6 can be a rare multiferroic with both large magnetization and polarization. Most importantly, since the charge ordering is the common ingredient for both ferroelectricity and magnetization, the net magnetization may be fully switched by flipping the polarization, rendering intrinsically strong magnetoelectric effects and desirable functions.

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Introduction. Multiferroics, with spontaneous magnetic order and charge dipole order, are not only physically interesting as emergent systems but also potentially useful as functional materials [1–3]. Despite significant advances in the past decades, it remains challenging to obtain desirable physical properties, i.e., the coexistence of large polarization (**P**), large magnetization (**M**), and strong magnetoelectric coupling, at room temperature (*T*) [2,3].

Classified by the underlying physical mechanisms, there are several routes to access multiferroicity. For example, the origins of magnetism and ferroelectricity in BiFeO_3 are independent of each other, i.e., both **P** and antiferromagnetic **L** are primary order parameters. Thus, the coupling between **P** and **L** has to be indirect, mediated via the third ingredient, usually a structural distortion. In contrast, in magnetic ferroelectrics (the so-called type-II multiferroics), e.g., TbMnO_3 [4,5] and CuO [6–8], ferroelectricity directly originates from spiral magnetism, i.e., **L** is a primary order parameter but **P** is not. Such inequivalent roles make it rather difficult to control magnetism via electric methods, although it is easy to control **P** via magnetic fields.

To overcome the drawbacks of these two main branches, other new routes were explored in recent years. For example, the magnetic geometric ferroelectrics, e.g., hexagonal RMO_3 [9–12], $\text{Ca}_3\text{M}_2\text{O}_7$ [13], and BaMF_4 [14,15] (*R*: trivalent rare earth or Y; *M*: magnetic transition metal such as Mn or Fe), have drawn much attention. In these materials, ferroelectricity is generated by collaborative multiple nonpolar modes of lattice distortion, i.e., **P** is not a primary order parameter (thus different from the BiFeO_3 case). However, the origin of magnetism in these systems remains independent of **P**, and magnetoelectric coupling remains mediated via lattice distortion modes (similar to the BiFeO_3 case).

Besides these branches, there is one more possible route based on charge ordering (CO) to generate multiferroicity [16,17]. The first proposed material was Lu_2FeO_4 , which was reported to be ferroelectric induced by $\text{Fe}^{2+}/\text{Fe}^{3+}$ ordering between layers [18–22], but the following works questioned its ferroelectricity [23–25]. Other proposed CO multiferroics

include Fe_3O_4 [26] and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [27,28]. However, due to their very narrow band gaps (in fact, Fe_3O_4 is a half metal above the CO Verwey point 124 K [29,30]), the low resistivity and thus serious current leakage make the experimental evidence of their ferroelectricity not fully convincing.

Recently, a new mechanism for magnetoelectric coupling based on the carrier-mediated field effect was proposed, which can be abstractly expressed as $(\nabla \cdot \mathbf{P})(\mathbf{M} \cdot \mathbf{L})$ [31]. However, it is challenging in experiments to fabricate few-layer [111]-oriented BiFeO_3 , as designed in Ref. [31].

Besides multiferroic oxides, there are many possible hidden multiferroics in fluorides, which can provide a fertile field to find materials with the desired properties [14,15,32,33]. In this Rapid Communication, we will predict a different bulk multiferroic, trirutile-type LiFe_2F_6 [34], which can realize the desired multiferroicity based on a CO mechanism but avoids the fabrication of artificial heterostructures. Although it was synthesized nearly half a century ago [35] and recently investigated as an electrode material in lithium ion batteries [36–38], the possible multiferroicity of LiFe_2F_6 has not yet been touched.

Model system. LiFe_2F_6 forms a tetragonal crystal structure [see Fig. 1(a)]. At high temperature, the high symmetric structure (HSS) without CO is $P4_2/mnm$ (No. 136). A Mössbauer spectrum measurement found the existence of Fe^{2+} and Fe^{3+} in LiFe_2F_6 above room-*T* [39,40], although the configuration of Fe^{2+} and Fe^{3+} could not be determined at that time. Later, Fourquet *et al.* studied a LiFe_2F_6 single crystal using x-ray diffraction, which revealed a low symmetric structure (LSS, No. 102, $P4_2nm$) for the CO state [40]. Actually, the structural difference between HSS and LSS is quite subtle. In practice, the LSS can be also refined to HSS if the tolerance is increased a little bit.

The most relevant collinear orders of Fe spins include the so-called A^+ , A^- , F^- , and F^+ , as defined in Ref. [41] [see Figs. 1(c)–1(f)]. Neutron powder diffraction revealed an A^+ antiferromagnetism [Fig. 1(c)] below 105 K [41,42].

Method. To reveal the multiferroicity of LiFe_2F_6 , density functional theory (DFT) calculations are performed using the projector augmented wave (PAW) pseudopotentials as implemented in the Vienna *ab initio* simulation package

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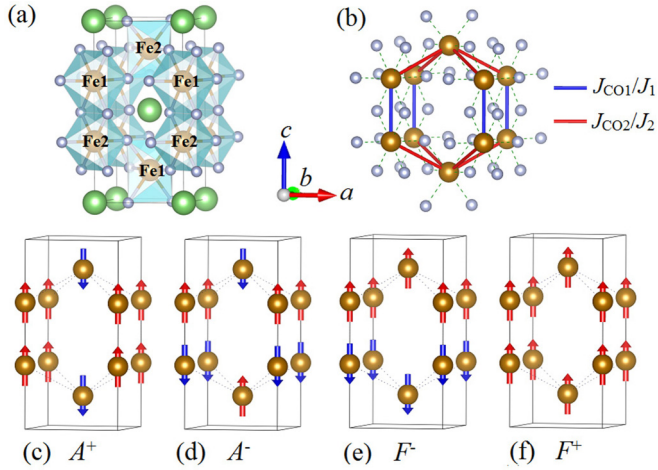


FIG. 1. (a) Crystalline structure of LiFe_2F_6 . Brown: Fe; green: Li; silver: F. HSS: $\text{Fe1} = \text{Fe2}$. LSS: $\text{Fe1} \neq \text{Fe2}$. (b) The framework of Fe-F ions and the charge/magnetic exchange paths for J_{CO1}/J_1 and J_{CO2}/J_2 . (c)–(f) Sketch of different magnetic orders of Fe spins. F and A (+ and –) stand for ferromagnetic and antiferromagnetic coupling between next-nearest-neighbor (nearest-neighbor) moments, respectively.

(VASP) code [43,44]. To acquire an accurate description of the crystalline structure and electron correlation, the revised Perdew-Burke-Ernzerhof for solids (PBEsol) functional and the generalized gradient approximation plus U (GGA+ U) method are adopted [45,46]. In addition, the hybrid functional calculations based on the Heyd-Scuseria-Ernzerhof (HSE06) exchange are used to check the band gap [47–49]. The standard Berry phase method is employed to estimate the ferroelectric $\mathbf{P}$ [50,51]. The nudged elastic band (NEB) method [52] is adopted to simulate the flipping of $\mathbf{P}$ and estimate the upper limit of the energy barriers.

The cutoff of the plane wave basis was fixed to 650 eV, a quite high value due to the element Li. The Monkhorst-Pack k -point mesh is set to be $6 \times 6 \times 3$ for the minimal cell. Both the lattice constants and atomic positions are fully relaxed until the force on each atom is below 0.01 eV/Å. To account for the influence of strain, the in-plane lattice constants are fixed while the length of the c axis is optimized, as well as the atomic positions.

With energy coefficients extracted from DFT, model calculations are employed to simulate the phase transitions via the Monte Carlo (MC) method. Although intrinsic magnetoelectricity exists in LiFe_2F_6 (to be studied later), their *phase transitions* are physical decoupled, which can be simulated independently. Our MC simulation can estimate the magnetic Néel temperature (T_N) and CO transition temperature (T_{CO}), which are important properties for multiferroics. The charge degree of freedom is mapped to a charge lattice model, characterized by a coefficient C between -1 and 1 (stands for $\text{Fe}^{(2.5+\frac{C}{2})+}$),

$$H_{\text{charge}} = -J_{\text{CO1}} \sum_{\langle i,j \rangle} C_i \cdot C_j - J_{\text{CO2}} \sum_{[i,k]} C_i \cdot C_k. \quad (1)$$

The spin degree of freedom is mapped to a Heisenberg model, characterized by $\mathbf{S}$,

$$H_{\text{spin}} = -J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{[i,j]} \mathbf{S}_i \cdot \mathbf{S}_j - A \sum_i (\mathbf{S}_i^e)^2, \quad (2)$$

where J_{CO1}/J_1 is the interaction between the nearest-neighbor ($\langle \rangle$) charges/spins along the c axis while J_{CO2}/J_2 stand for the next-nearest-neighbor ($[]$) ones [see Fig. 1(b)]. Considering the experimental fact that the CO transition is above room- T while the magnetic transition is about 105 K [39–41], here $J_{\text{CO1}}/J_{\text{CO2}}/C$ can be approximated to be spin independent when studying the CO transition, and $J_1/J_2/\mathbf{S}$ can all be fixed as constants ($|\mathbf{S}|$ is normalized to 1) when studying the magnetic transition. $\mathbf{S}_i^e$ is the projection of spin to the magnetic easy (or hard) axis on the i site, and A is the magnetocrystalline anisotropy coefficient.

In MC simulations, periodic boundary conditions are used with lattice sizes $L \times L \times L$ ($L = 8$). Larger sized lattices (e.g., $L = 16$ or 32) have also been tested to check the finite size effects, which are negligible. Specific heats (C_v) and the charge/spin structure factor $C(\mathbf{k})/S(\mathbf{k})$ (Fourier transform of the real space correlation function) [53–55] are measured as a function of T to characterize phase transitions.

Results and discussion. The choice of U_{eff} for Fe's $3d$ orbitals may be important to obtain the correct physical properties in DFT calculations. Here, the value of U_{eff} is tested from 0 to 6 eV, as presented in detail in the Supplemental Material [56]. It is found that $U_{\text{eff}} = 4$ eV can lead to the best results, and most consistent with available experimental data, regarding the magnetism, CO, and lattice constants. This value also agrees with the previous empirical value used for Fe-based oxides with octahedra [31,57]. Thus $U_{\text{eff}} = 4$ eV will be used in the following by default.

DFT calculated data for unstrained LiFe_2F_6 are summarized in Table I. Among all candidate states, the lowest energy one is always the A^+ (despite the structural choice), in agreement with the neutron study [41]. In addition, the calculated lattice constants for LSS with A^+ magnetism are quite close to the experimental ones [35,40]. Furthermore, the CO state is obtained only for the LSS, evidenced by the disproportion of local magnetic moments and Bader charges (shown in Table I), while the HSS always gives a charge uniform (CU) result. For all calculated magnetic states, the energy of LSS is always lower than that of HSS. Therefore, our DFT calculation on LiFe_2F_6 gives fully consistent results as compared with available experimental data [35,40], which provides a solid starting point for the following calculations.

For the ground A^+ state, LiFe_2F_6 is insulating, with a moderate band gap of 0.8 eV. Such a band gap has been further checked using the hybrid functional calculation based on the HSE06 exchange [47–49], which leads to 1.0 eV [56]. Thus, comparing with other CO materials, LiFe_2F_6 is insulating enough to perform ferroelectric measurements. According to the density of states (DOS) (Fig. 2), the bands near the Fermi level are mostly contributed by Fe's $3d$ orbitals. In particular, the topmost valence band is contributed by Fe^{2+} 's upper Hubbard band of the d_{xy} orbital (if the ab -plane Fe-F bond is taken as the z axis of the F octahedron), as visualized in

TABLE I. The optimized structural parameters (a/c in the tetragonal notation), local magnetic moment (M_1 for Fe1 and M_2 for Fe2) within the default PAW sphere, Bader charge (B_1 for Fe1 and B_2 for Fe2), energy difference (ΔE), band gap, net magnetization (M), and ferroelectric polarization (P) for various magnetic structures. The experimental values (Expt. for short) of lattice constants are also listed for comparison. The A^+ of LSS is taken as the reference for energy.

	a/c (Å)	M_1/M_2 (μ_B)	B_1/B_2 (e)	ΔE (meV/Fe)	Gap (eV)	M (μ_B/Fe)	P ($\mu\text{C}/\text{cm}^2$)
$P4_2/mnm$							
F^+	4.674/9.091	4.13/4.13	12.19/12.19	83.05	0.3	4.5	
F^-	4.657/9.283	4.21/4.20	12.19/12.19	124.98	Metallic	0	
A^+	4.671/9.082	4.09/4.10	12.19/12.19	45.75	0.4	0	
A^-	4.658/9.263	4.19/4.12	12.20/12.20	87.70	Metallic	0	
Expt. [35]	4.673/9.29						
$P4_2nm$							
F^+	4.674/9.249	3.79/4.37	12.46/12.01	40.98	0.7	4.5	13.6
F^-	4.669/9.304	3.78/4.38	12.47/12.01	40.98	0.8	0	13.3
A^+	4.666/9.253	3.25/4.35	12.46/12.02	0.00	0.8	0	13.0
A^-	4.666/9.291	3.72/4.35	12.47/12.02	0.50	0.7	0.5	12.4
Expt. [40]	4.679/9.324						

the insets of Fig. 2. The DOS for the first excited state A^- is shown in Fig. 2(b), which owns a net $\mathbf{M} = 0.5\mu_B/\text{Fe}$.

The point groups of HSS and LSS are $4/mmm$ (nonpolar) and $4mm$ (polar), respectively. Thus, the CO transition is also the nonpolar/polar transition (i.e., ferroelectric Curie temperature $T_C = T_{\text{CO}}$). The dipole moment formed by the $\text{Fe}^{2+}\text{-Fe}^{3+}$ pair can be estimated using the intuitive point charge model, which gives $12.4 \mu\text{C}/\text{cm}^2$. For comparison, the Berry phase method leads to $13.0 \mu\text{C}/\text{cm}^2$ along the c axis for the A^+ state. Such an agreement implies an ideal CO driven ferroelectricity. For such an electronic ferroelectric state, the switching of $\mathbf{P}$ can be realized by fast electron hopping between Fe^{2+} and Fe^{3+} , instead of the ion's slow displacements in most conventional ferroelectrics.

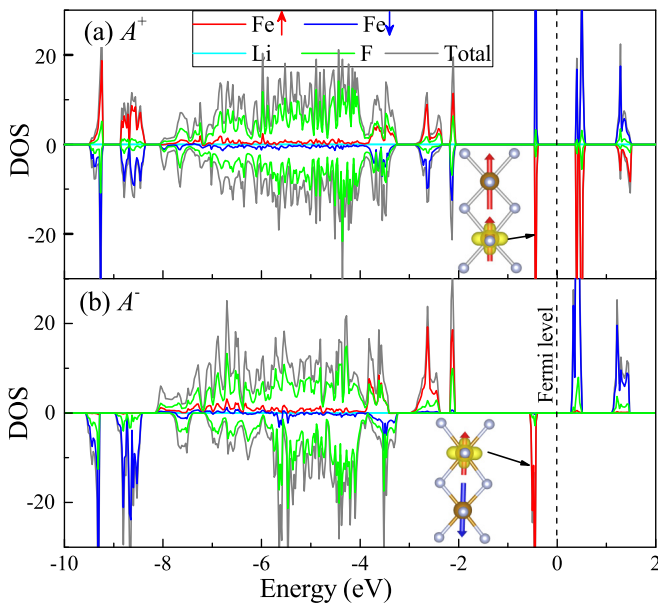


FIG. 2. DOS and atom-projected DOS (PDOS) of LiFe_2F_6 for the LSS. (a) A^+ ; (b) A^- . $\uparrow/\downarrow$ denote the spin directions. Inset: The electron cloud of the topmost valence band.

By comparing the DFT energies of high and low symmetric A^- (or F^-) states of CO/CU states, the combination $2J_{\text{CO}2} + \frac{J_{\text{CO}1}}{2}$ can be extracted for the charge lattice model. Note that it is impossible to stabilize any other CO pattern in the DFT self-consistent calculation. Thus, it is insufficient to obtain the individual values of $J_{\text{CO}1}$ and $J_{\text{CO}2}$. However, with this coefficient $2J_{\text{CO}2} + \frac{J_{\text{CO}1}}{2}$, our MC simulation on the lattice model can confirm that the ground state is indeed CO and the T_{CO} can be rather high. For example, T_{CO} is roughly estimated as 493 K [Fig. 3(a)] when $J_{\text{CO}2} = J_{\text{CO}1}$. The contour plots of charge distribution at room- T and high- T can be seen in Figs. 3(b) and 3(c). T_{CO} decreases with an increasing ratio of

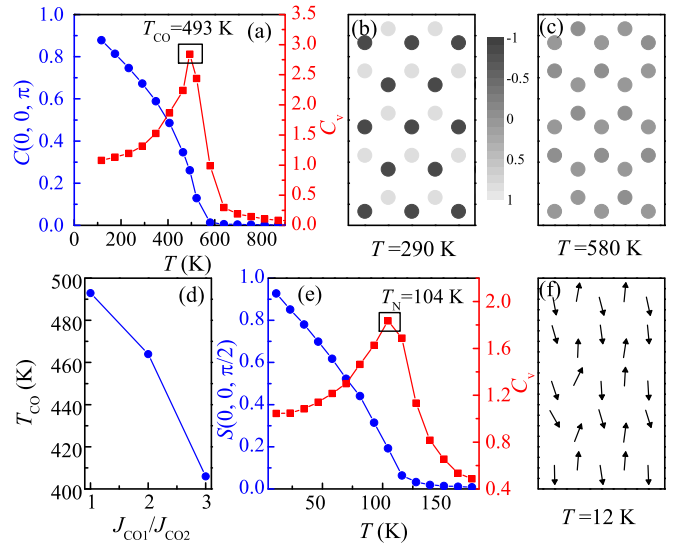


FIG. 3. MC results for models of LiFe_2F_6 . (a) The charge structure factor $C(\mathbf{k})$ and specific heat C_v as a function of T . (b), (c) Contour plots for charge distribution (characterized by C) at room- T and high- T . (d) T_{CO} as a function of $\frac{J_{\text{CO}1}}{J_{\text{CO}2}}$. (e) The spin structure factor $S(\mathbf{k})$ and specific heat C_v as a function of T . (f) The real space spin pattern of a MC snapshot obtained at low temperature. Here, the vectors $\mathbf{k}$ in $C(\mathbf{k})$ and $S(\mathbf{k})$ are reciprocal vectors of corresponding real space orders, in unit of $(1/a, 1/a, 4/c)$.

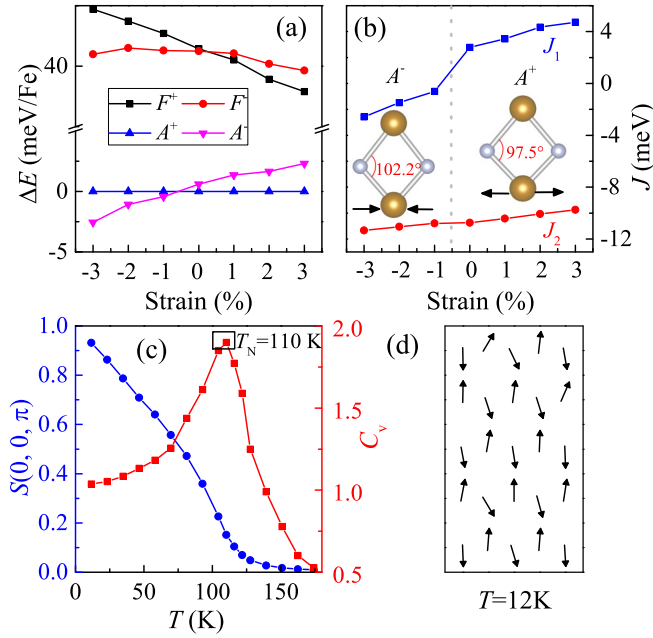


FIG. 4. Results for strained $LiFe_2F_6$. (a) Energies of the F^+ , F^- , A^+ , and A^- states as a function of strain. The energy of the A^+ state is the reference. (b) Strain-dependent exchanges for the Heisenberg model. Inset: Sketch of the bond angle of Fe^{2+} -F- Fe^{3+} for the J_1 path. (c) MC results for the case under -3% strain: The spin structure factor $S(\mathbf{k})$ for A^- order and specific heat C_v as a function of T . (d) The real space spin pattern (MC snapshot) at low- T .

$\frac{J_{CO1}}{J_{CO2}}$ [Fig. 3(d)] but is still higher than 400 K when $\frac{J_{CO1}}{J_{CO2}} = 3$, and the type of CO does not change with $\frac{J_{CO1}}{J_{CO2}}$.

By comparing the energies of different magnetic orders with an *identical structure*, the exchange interactions of the Heisenberg model are obtained as $J_1 = 2.8$ meV and $J_2 = -10.7$ meV [56]. By incorporating spin-orbit coupling (SOC) in the DFT calculation and comparing the energies of different spin axes [56], the magnetocrystalline easy axis is found to be along the c axis, in agreement with the neutron study [41], and the calculated $A = 0.158$ meV/Fe. The MC-simulated T_N is about 104 K [Fig. 3(e)], in good agreement with the experimental value (105 K) [41]. Such an agreement further confirms that $U_{eff} = 4$ eV is the best choice. Below T_N , the real space spin pattern taken from the MC snapshot, as shown Fig. 3(f), indicates the A^+ pattern.

However, the ground A^+ state is antiferromagnetic without a net spontaneous $\mathbf{M}$. Instead, the first excited state A^- is ferrimagnetic, leading to $0.5\mu_B/\text{Fe}$ resulting from the $Fe^{2+}(\downarrow)$ - $Fe^{3+}(\uparrow)$ pair. Since the energy of the A^- state is only slightly higher (0.50 meV/Fe) than that of A^+ , it is hopeful to tune the sign of superexchange J_1 and then the magnetic ground state.

Strain is a routinely useful method to tune the physical properties of materials [58]. For example, strained $EuTiO_3$ becomes ferromagnetic and ferroelectric, although originally it is paraelectric and antiferromagnetic [59,60].

Indeed, a magnetic transition from A^+ and A^- can be realized by applying biaxial strain to $LiFe_2F_6$. Figure 4(a) shows the energy differences as a function of strain (defined as

$\delta = \frac{a'}{a} - 1$, where a' is the strained in-plane lattice constant). Once the compressive strain is beyond -0.5% , the A^- state eventually has the lowest energy, and hence becomes the ground state. By fitting the DFT energy using the Heisenberg model, the coefficients J_1 and J_2 are extracted as a function of strain, as shown in Fig. 4(b). It is clear that the sign of J_1 is changed by strain, while J_2 is very robust. The sign change of J_1 is associated with the change of bond angle of the J_1 path (Fe^{2+} -F- Fe^{3+}), which increases from 97.5° ($\delta = 3\%$) to 102.2° ($\delta = -3\%$), as shown in the inset of Fig. 4(b). For the $\delta = -3\%$ case, the single-axis magnetocrystalline anisotropy remains along the c axis ($A = 0.254$ meV/Fe) and the exchange interactions become $J_1 = -2.6$ meV, $J_2 = -11.3$ meV, which lead to $T_N = 110$ K for the A^- state [Figs. 4(c) and 4(d)]. Although this ferrimagnetism is still below room- T , it is beyond the boiling point of liquid nitrogen and much higher than the ferromagnetic T_C (4 K) in strained $EuTiO_3$ [60].

Since both $\mathbf{P}$ and $\mathbf{M}$ are in proportional to the CO parameter C , this common origin guarantees the intrinsically strong magnetoelectricity and equivalent levels of $\mathbf{M}$ and $\mathbf{P}$. If the antiferromagnetic $\mathbf{L}$ is conserved, the tuning of C can change $\mathbf{P}$ and $\mathbf{M}$ simultaneously. Based on this mechanism, the ferrimagnetic $\mathbf{M}$ can be switched up/down accompanying $\mathbf{P}$ via the electric method, giving the desired electric-control-magnetism function expressed as $(C \cdot \mathbf{c})(\mathbf{M} \cdot \mathbf{L})$, where $\mathbf{c}$ is the vector along the polarization direction.

In traditional ferroelectrics, e.g., $BaTiO_3$, the switching of $\mathbf{P}$ is by simply moving the ions. However, in electronic ferroelectrics such as $LiFe_2F_6$, the process of ferroelectric switching may be different. A possible route is that the extra electron of Fe^{2+} directly hops to Fe^{3+} via quantum tunneling (electron first), which should be quite fast microscopically. The magnetic order is kept in this tunneling process and then the structure (e.g., F octahedra) gradually relaxes according to the new CO pattern. Both $\mathbf{P}$ and $\mathbf{M}$ can be switched from positive to negative.

Another possible process is to change the structure first, as what happens in proper ferroelectrics. Starting from the $+P$ LSS, the material climbs an energy barrier to the HSS ($P = 0$) first, then to the $-P$ LSS finally. The electron of Fe^{2+} moves smoothly, accompanying the structural change. This process can be simulated using the NEB method, as done in Fig. 5.

If the real material adopts the second route (structure first), there is another uncertainty regarding the magnetism. For the intermediate HSS, the A^+ state is always lower in energy than A^- due to magnetostriction, even under the compressive condition. Therefore, it is uncertain that the switching process will become LSS + A^- to HSS + A^+ to LSS + A^- (this process cannot be simulated by the NEB method). If so, the antiferromagnetic A^- order is broken in the middle process, and thus the flipping of $\mathbf{M}$ becomes uncertain. However, since the switching in such an electronic ferroelectric material is a kinetic process rather than equilibrium process, it is questionable whether the HSS + A^+ can really happen since it needs a relative long time for magnetostrictive relaxation (see the Supplemental Material [56] for more discussions). In the current stage, our theoretical methods cannot simulate the dynamics of magnetoelectric switching in $LiFe_2F_6$.

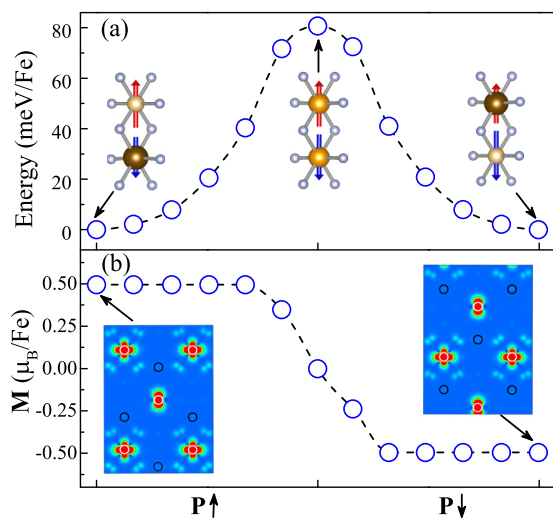


FIG. 5. Sketch of CO-mediated magnetoelectricity in strained (-3%) LiFe_2F_6 . (a) Switch of ferroelectric $\mathbf{P}$ simulated by the NEB method. The simulated energy barrier for switching should be considered as the upper limit in the real experiment, while other paths/processes with lower barriers are possible. Insets: Initial, intermediate, and final structures. (b) The corresponding switch of magnetic $\mathbf{M}$ obtained in the NEB process. Insets: The corresponding profiles (viewed from the $[110]$ direction) of the partial charge density for the topmost valence band. White/black circle: $\text{Fe}^{2+}/\text{Fe}^{3+}$.

Thus further experiments are encouraged to verify the real process.

Another ferroelectric ferrimagnetic material, $\text{Zn}_2\text{FeOsO}_6$, was predicted recently [61]. However, it is a proper ferroelectric material and thus conceptually different from LiFe_2F_6 . From the viewpoint of potential applications, the element Os is very expensive and toxic, and $\text{Zn}_2\text{FeOsO}_6$ is still to be synthesized.

Conclusion. The physical properties of LiFe_2F_6 were theoretically investigated. The A^+ -type antiferromagnetism was confirmed to be the ground state. The charge ordering of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ configuration can lead to room-temperature ferroelectricity. More interestingly, the ferrimagnetic A^- state with a net magnetization $0.5\mu_B/\text{Fe}$ can be stabilized by moderate compressive strain. In this single-phase multiferroic system with both large polarization and magnetization, the intrinsic and strong magnetoelectric coupling can be mediated by charge ordering. It is expected to flip the net magnetization together with the polarization by an electric voltage, which provides the desired magnetoelectric function in practice. Further study on other LiM_2F_6 (M is a $+2/+3$ transition-metal ion) systems is encouraged to pursue more multiferroics with better performance.

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