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Hongwei Wang  
*Temple University*

Igor V. Solovyev  
*National Institute of Materials Science*

Wenbin Wang  
*Fudan University*

Xiao Wang  
*Bryn Mawr College*

Philip J. Ryan  
*Argonne National Laboratory*

See next page for additional authors

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Structural and electronic origin of the magnetic structures in hexagonal LuFeO$_3$

Hongwei Wang,$^{1,2}$ Igor V. Solovyev,$^3$ Wenbin Wang,$^4$ Xiao Wang,$^5$ Philip J. Ryan,$^6$ David J. Keavney,$^6$ Jong-Woo Kim,$^6$ Thomas Z. Ward,$^7$ Leyi Zhu,$^8$ Jian Shen,$^4$ X. M. Cheng,$^5$ Lixin He,$^2$ Xiaoshan Xu,$^{5,7,9,*}$ and Xifan Wu$^{1,4,*}$

$^1$Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, USA
$^2$Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China
$^3$Computational Materials Science Unit, National Institute for Materials Science, I-2-1 Sengen, Tsukuba 305-0047, Japan
$^4$Department of Physics, Fudan Institute for Materials Science, Shanghai 200433, People’s Republic of China
$^5$Department of Physics, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010, USA
$^6$Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA
$^7$Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
$^8$Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
$^9$Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, USA

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Using combined theoretical and experimental approaches, we studied the structural and electronic origin of the magnetic structure in hexagonal LuFeO$_3$. Besides showing the strong exchange coupling that is consistent with the high magnetic ordering temperature, the previously observed spin reorientation transition is explained by the theoretically calculated magnetic phase diagram. The structural origin of this spin reorientation that is responsible for the appearance of spontaneous magnetization, is identified by theory and verified by x-ray diffraction and absorption experiments.

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I. INTRODUCTION

While the ferroelectricity in materials is naturally connected to structural distortions that break the spatial inversion symmetry [1,2], the relation between spontaneous magnetization and structure is not obvious because no spatial symmetry is broken by ferromagnetism (FM). Nevertheless, magnetic orderings in a material are tied to the structure, and the ties are particularly important in multiferroic materials [3] in which structural distortions may mediate couplings between ferroelectricity and ferromagnetism or even generate ferroelectric ferromagnets, which are extremely rare [4].

The recently discovered room temperature multiferroic, i.e., hexagonal LuFeO$_3$ (hLFO) [5], provides a rare case of multiferroic material in which spontaneous electric and magnetic polarizations coexist. On one hand, ferroelectricity appears below $T_c = 1050$ K resulting from a $P_{63/mmc} \rightarrow P_{63}cm$ structure distortion, which can be decomposed in terms of three phonon modes [Fig. 1(a)] [5,6]. On the other hand, spin frustration in hLFO presents rich magnetic phases [7]. Intriguingly, below the Neél temperature $T_N = 440$ K, magnetic order in hLFO transits again from $B_2$ to $A_2$ [Fig. 1(b)] at $T_R = 130$ K [5] by a spin reorientation (SR), resulting in a weak ferromagnetism due to the Dzyaloshinskii-Moriya and single-ion anisotropy mechanism [8–12]. Similar to hexagonal YMnO$_3$, the $K_3$ phonon is believed to be the driving force that induces the instability of $\Gamma_7^-$ that is responsible for the ferroelectricity [13–15]. However, the origin of the SR is still elusive. Since the SR is the direct cause of spontaneous magnetization, elucidating the origin may provide a way to effectively tune $T_R$, or even a novel route for realizing a coexistence of spontaneous electric and magnetic polarizations above room temperature [16–18].

*Authors to whom correspondence should be addressed: xifanwu@temple.edu and xiaoshan.xu@unl.edu

Previous studies in hexagonal manganites (h-RMO, isomorphic to hLFO) indicate rich magnetic phases due to the SR that is strongly coupled to the crystal structure [3,19,20]. However, the multiple degrees of freedom involved (spin and orbital degrees of freedom of the electrons and the lattice) complicate the problem in h-RMO [21]. The complexity may be reduced in h-LFO, in which Fe$^{3+}$ can be considered a spin-only ion with nearly spherical 3$d^5$ electronic configuration. Therefore, a better understanding of the SR in hLFO is possible, particularly in terms of the phonon modes [Fig. 1(b)]; it may also be an important step in understanding the more complex SR in h-RMO [21], in which the single-ion anisotropy is expected to play a more important role.

To address the above issues, we perform combined theoretical and experimental studies of the exchange interactions and their couplings to the structural instabilities in hLFO. We apply an extended Kugel-Khomskii (KK) model for superexchange (SE) interactions [22] based on localized Wannier functions (LWFs) [23,24]. While the antiferromagnetic (AFM) exchange coupling is dominated by the intralayer superexchange, the model clearly shows that the singly occupied $d_z^2$ orbital in hLFO greatly increases the exchange coupling compared with the empty $d_z^2$ in LuMnO$_3$ (LMO). The interlayer exchange, although much weaker in magnitude, is key to the SR. Our first-principles calculations show that SR is strongly coupled to the $K_1$ phonon mode and only weakly dependent on $K_3$ mode. Our theory indicates that the atomic displacements of $K_1$ mode is responsible for the SR. This scenario is then confirmed by our x-ray diffraction and x-ray absorption experiments.

II. COMPUTATIONAL METHODS AND EXPERIMENTAL TECHNIQUES

Our extended KK model [22,25] is built on the basis of LWFs generated from density functional theory (DFT) calculations. The screened Coulomb interactions between LWFs are computed in the constrained random-phase approximation.
Lu, 0, 0) (50 nm), and h-LFO films (50 nm thick) were grown on Al2O3 formed within DFT.

In hexagonal ferrites, the exchange interaction between the Fe sites can be written as

\[ H_{ex} = H_{ex}^{in} + H_{ex}^{out} \]  

(1)

where \( H_{ex}^{in} \) is the intralayer exchange interaction and \( H_{ex}^{out} \) is the interlayer exchange interaction considering only the nearest neighbors.

As shown in Fig. 2, the intralayer SE interaction \( H_{ex}^{in} = \sum_{i,j} J_{i,j}^{in} S_{i}^{ex} \cdot S_{j}^{ex} \) between two nearest neighbor (NN) Fe atoms at site \( i \) and \( j \) are mediated by corner sharing oxygen atoms. In order to elucidate the electronic structural origin, we employ the extended KK model, and the SE coupling can be expressed as

\[ J_{i,j}^{in} = \sum_{a,a'} J_{a,a'}^{FM} + \sum_{a,a'} J_{a,a'}^{FM} \]  

(2)

The first term in Eq. (2) describes the AFM-type coupling resulting from virtual hopping processes between two half-filled \( d \) bands; while the second term depicts the competing FM-type coupling from hoppings from a half-filled \( d \) orbital \( (a) \) to empty ones \( (\beta) \) [25]. The computed individual exchange interaction as well as the overall SE coupling \( J_{ex}^{in} \) for both hLFO and hLMO are presented in Table I. The total exchange couplings \( J_{ex}^{in} \) from the direct fit of the total DFT energies are also shown.

According to the local environment (Fig. 1), the \( 3d \) orbitals in Fe and Mn are split into \( e^2(\text{zz}) \), \( e^2(\text{zz}^2) \), \( \text{xy} \) levels by the crystal field, with increasing energy respectively [30,31]. It can be seen that the largest SE interactions are contributed by the diagonal hopping processes involving \( d \) orbitals of \( e^2 \) symmetry. This is consistent with the physical expectation that SE is of intralayer nature while \( d_{z} \) and \( d_{z} \) are the only \( d \) orbitals lying mostly inside the \( ab \) plane. Centered on the magnetic ions, these \( d \)-like LWFs are also connected with the first neighboring magnetic atoms through hybridization with the shared oxygen atoms on the bipyramids. As a result, a strong oxygen \( p \) character is found on the lobe of the LWFs, pointing to each of the three neighboring oxygen atoms. Considering such \( d \)-like LWFs on the hexagonal lattices, a large AFM hopping integral is thus expected along the path of Fe[Fe]l-O-Fe[Mn] [32]. Based on the same orbital symmetry argument, it can be easily seen that the diagonal hopping is relatively smaller for \( a^2_1(\text{zz}) \) character and almost zero for \( e^2 \) character. This is because \( d_{z} \) and \( d_{z} \)

![Fig. 1](image1)

**FIG. 1.** (Color online) (a) Displacement patterns of the FeO5 local environment (trigonal bipyramidal) in the three phonon modes that freeze in the \( P6_3/mmc \rightarrow P6_3cm \) structural transition in hexagonal ferrites (h-RFeO3). The arrows indicate the relative displacement of the atoms. \( \bar{K} \) is the wave vector of the modes in the reciprocal space of the \( P6_3/mmc \) structure. (b) Four independent spin structures \( (A_1, A_2, B_1, B_2) \) of the 120-degree magnetic orders viewed along the \( c \) axis. The arrows indicate the spins \( (\vec{S}^z_{b}) \) on the Fe sites. The Fe sites shown in the polyhedra are in the \( Z_{fe} = 0 \) layer while all the other Fe sites are in the \( Z_{fe} = 1 \) layers. In the \( B (A) \) phase, \( \vec{S}^z_1 \) is parallel (antiparallel) to \( \vec{S}^z_2 \).

![Fig. 2](image2)

**FIG. 2.** (Color online) (a) Representative \( d_{xy} \), \( d_{z} \), and \( d_{z} \)-like LWFs viewed from [001] direction. (b) Illustrations of two independent SSE paths \( J_1 \) and \( J_2 \) between Fe0 at \( z/c = 0 \) and three neighboring iron ions Fe1, Fe2, and Fe3 at \( z/c = 1/2 \). (c) Atomic displacements of the \( K_1 \) phonon mode. (d) Atomic displacements of the \( K_3 \) phonon mode, viewed from [001] direction.

### Table I. Individual and total intralayer exchange interaction (meV) in both hLFO and hLMO [25].

| J_{a,a'}^{FM} | J_{a,a'}^{FM} | J_{a,a'}^{FM} | J_{a,a'}^{FM} | J_{a,a'}^{FM} | J_{a,a'}^{FM} | J_{a,a'}^{FM} | J_{a,a'}^{FM} |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| hLFO           | 0.85           | 0.45           | 45.7           | 3.2            | 1.4           | 0.4            | 45.2           | 49.7           |
| d_{xy}         | 0.68           | 0.93           | 0.88           | 1.04           | 0.0           | 0.05          | 0.0            | 0.0            |
| d_{z}          | 1.25           | 5.05           | 3.58           | 1.27           | 0.27          | 0.27          | 0.27           | 0.27           |
| d_{z}          | 0.56           | 0.09           | 0.14           | 0.01           | 0.06          | 0.06          | 0.06           | 0.06           |
| d_{z}          | 0.32           | 1.00           | 0.65           | 0.37           | 0.37          | 0.37          | 0.37           | 0.37           |
| d_{z}          | 10.15          | 5.81           | -0.64          | 1.17           | 0.78          | 29.3          | 30.7           | 30.7           |
| d_{z}          | 1.28           | 10.9           | -2.71          | 0.85           | 0.12          | 0.12          | 0.12           | 0.12           |
| d_{z}          | 0.41           | 0.17           | -0.43          | 0.01           | 0.08          | 0.08          | 0.08           | 0.08           |
| d_{z}          | 0.39           | 0.85           | -0.19          | 0.31           | 0.04          | 0.04          | 0.04           | 0.04           |
of the value at 300 K, while the other two phonon displacements are kept as zero. Inset: theoretical phase diagram as functions of mode amplitudes of $K_1$ and $K_3$, and $\Gamma_2^c$ phonon mode, where $\delta Q = Q - Q_0$ and $Q_0$ is the value at 300 K, while the other two phonon displacements are kept as zero. Inset: theoretical phase diagram as functions of mode amplitudes of $K_1$ and $K_3$, and $\Gamma_2^c$ phonon mode, where $\delta Q = Q - Q_0$ and $Q_0$ are fixed at the experimental values [25].

Having established the electronic origin of the large intralayer exchange coupling, we now focus on the interlayer exchange coupling $H_{\text{ex}}^c = \sum_{\text{Fe}} J_{\text{Fe}-\text{Fe}}^c \cdot \vec{S}_{\text{Fe}} \cdot \vec{S}_{\text{Fe}}^{\pm \uparrow \downarrow}$ in hLFO. This is the key to understanding the mechanism of SR and weak FM moment below $T_K$ [5]. In contrast to the SE nature of intralayer exchange, the interlayer Fe ions are coupled by the super-super-exchange (SSE) interaction [33], in which one Fe atom at $Z_{\text{Fe}} = 0$ is in exchange interaction with three first neighbor Fe atoms at $Z_{\text{Fe}} = c/2$ mediated by two apical oxygen atoms ($O_{\text{ap}}$). Due to the $P6_3cm$ structure in Fig. 3(b), the three SSE paths can be further simplified by two independent SSE coupling strengths: $J_1$ through $\text{Fe}^{0\downarrow}_3$, $\text{O}^{\uparrow\downarrow}$, $\text{Fe}^{\uparrow\downarrow}_1$, $\text{Fe}^{\uparrow\downarrow}_2$, $\text{Fe}^{\uparrow\downarrow}_3$, $\text{O}^{\uparrow\downarrow}$, $\text{Fe}^{0\uparrow}_1$, and $\text{Fe}^{0\uparrow}_2$. As a result, the $H_{\text{ex}}^c$ spin Hamiltonian in Eq. (1) can be rewritten as $H_{\text{ex}}^{c} = \sum_{\text{Fe}} \left( J_1^c \cdot S_{\text{Fe}} \cdot S_{\text{Fe}}^c \right)$. Obviously, the sign of $\Delta J$ determines the preferred alignment between $S_{\text{Fe}}$ and $S_{\text{Fe}}^c$: parallel (B phase) if $\Delta J < 0$; antiparallel (A phase) if $\Delta J > 0$; no alignment if $\Delta J = 0$, which is the case for $P6_3/mmc$ structure.

Since the nonzero $\Delta J$ comes from the structural distortion ($P6_3/mmc \rightarrow P6_3cm$), the low temperature spin reorientation must have a structural origin. Here we investigate the dependence of $\Delta J$ on the three phonon modes $K_1$, $K_3$, and $\Gamma_2^c$ that are responsible for the structural distortion [25]. We use DFT to calculate the $\Delta J$ as functions of phonon mode displacements ($Q_p$, where $p = K_1$, $K_3$, and $\Gamma_2^c$) and the results are shown in Fig. 3(a). It can be seen that $\Delta J$ depends on the displacement of each phonon mode rather differently.

Clearly, the $K_1$ phonon mode has the largest effect on SR. This can be identified by the steepest slope of $\Delta J$ when $K_1$ is increased perturbatively, yielding a linear coefficient $\frac{\Delta J}{\Delta K_1} \sim 1.9$ meV/Å. This suggests a strong tendency of $K_1$ in driving hLFO from B phase ($\Delta J < 0$) into A phase ($\Delta J > 0$). Indeed this is also consistent with the physical expectation of atomic displacements under the $K_1$ mode. The $K_3$ phonon is a Brillouin zone (BZ) boundary mode and is of pure in-plane nature. The atomic displacements of the $K_1$ phonon mostly involve the $O_{\text{ap}}$ of FeO$_5$ (Fig. 1). As shown in Fig. 3(c), the effects of the $K_1$ are as follows: $O_{\text{ap}}$ of Fe$^{0\downarrow}_1$ moves away from that of Fe$^{\uparrow\downarrow}_1$, causing $J_1^c$ to decrease; and $O_{\text{ap}}$ of Fe$^{0\uparrow}_1$ moves closer to that of Fe$^{\uparrow\downarrow}_2$ and Fe$^{\uparrow\downarrow}_3$, causing $J_2^c$ to increase. As a result, $K_1$ is strongly coupled to $\Delta J$.

The $K_3$ phonon mode can be described by the rotation of FeO$_5$ [Fig. 1(a)] also located at BZ boundary. The atomic displacements of the $K_3$ mode include all the $O_{\text{ap}}$ of the FeO$_5$. However, due to its rotational nature, the atomic displacement of the $O_{\text{ap}}$ alternate their directions along $c$ as shown in Fig. 2(d). As a result, the overall lengths of $J_1^c$ and $J_2^c$ paths are barely changed except that the Fe atom is slightly moved away from its equilibrium positions in $P6_3/mmc$ symmetry. Compared with the direct tunability of $\Delta J$ by the $K_1$ mode, the $K_3$ phonon is expected to be a second-order effect in SR. Indeed, our DFT calculation predicts a much weaker variation of $\Delta J$ with increased $K_3$ phonon mode amplitude, in which the linear coefficient $\frac{\Delta J}{\Delta K_3} \sim 0.3$ meV/Å is about one order of magnitude smaller than that of $K_1$. Similar to that of $K_1$ mode, the slope is also positive, favoring the SR from B to A phase.

Finally, we focus on the coupling between $\Gamma_2^c$ and $\Delta J$. $\Gamma_2^c$ is the ferroelectric phonon mode at zone center. The atomic displacements of this mode involve all the Lu, O, and Fe atoms moving along $c$. However, the displacements of the two $O_{\text{ap}}$ of one bipyramid are exactly the same. As a result, the SSE paths in $J_1^c$ and $J_2^c$ are changed uniformly. Not surprisingly, our theory predicts a zero dependence of $\Delta J$ on $\Gamma_2^c$ mode amplitude. It indicates that this ferroelectric distortion alone does not play any role in SR.
The significantly different coupling strengths of $\Delta J$ with the phonon modes suggests the primary role of the $K_1$ phonon mode in SR of hLFO. Indeed, when the $K_1$ mode is frozen into the experimental structural coordinates at $T = 300$ K perturbatively, $J'_1$ and $J'_2$ rapidly increase and decrease respectively, and SR occurs at the crossing point as shown in Fig. 3(b) separating the $B$ from $A$ phases. Below, we show that $Q_{K_1}$ saturates close to $T_R$, while $Q_{K_1}$ changes significantly from 300 to 20 K using XRD and XAS measurements.

As shown in Fig. 4(a), the temperature dependence of the normalized intensity ratio between (104) and (004) peaks appears to saturate when temperature is lowered to $T_R$. We attribute the saturation to the slow variation of the $K_3$ phonon at low temperature, because $K_3$ is expected to have a dominant effect here, according to the simulated intensity ratio [Fig. 4(a) inset] [34], while the zone center mode $\Gamma_2$ is expected to have no effect. The saturation of the $K_3$ mode can be further confirmed by the temperature dependence of the lattice constant $c$ which follows closely that of the intensity ratio, as shown in Fig. 4(a). The displacement of the $K_3$ mode includes a rotation of the FeO$_5$ trigonal bipyramid, which changes the shape of the unit cell by enlarging $a$ and reducing $c$ [7]; the change of $c$ ($\Delta c$) is proportional to $\Delta Q_{K_3}$ for small change of $Q_{K_3}$. The matching temperature dependence in Fig. 4(a) suggests that the change of $c$ is indeed caused by the $K_3$ mode which saturates at low temperature.

XAS measurements suggest that the $K_1$ mode undergoes a gradual change at low temperature. Previously, we assigned the Fe-3$d$ crystal levels using the XAS at room temperature [25,30]. As shown in Fig. 4(b), the temperature dependences of the energy levels all show broad peak-like features with the maxima close to $T_R$. The crystal field levels of Fe-3$d$ are expected to be sensitive to the shape of FeO$_5$. As shown in Fig. 1(a), the $K_3$ mode causes a rotation of the FeO$_5$ while the $K_1$ or $\Gamma_2$ modes cause distortions of the FeO$_5$, so the energy-level shifts observed in Fig. 4(c) are most likely generated by the change of $Q_{K_1}$ or $Q_{\Gamma_2}$. Figure 4(c) shows a simulation [25] of the energy-level change of the crystal field levels as functions of $Q_{K_1}$ or $Q_{\Gamma_2}$ with respect to the value when all the mode displacements are zero. According to the simulation, the $K_1$ mode generates a maximum at $Q_{K_1} = 0$ while $Q_{\Gamma_2}$ generates a minimum at $Q_{\Gamma_2} = 0$; this is because the $K_1$ mode moves both O$_{ap}$ atoms away from the Fe sites and makes the FeO$_5$ larger while the $\Gamma_2$ mode pushes one O$_{ap}$ atom close to the Fe site. Comparing the simulation and the observation, we infer that the $K_1$ mode changes gradually when the temperature is lowered, in order to generate the maximum [25]; this is consistent with the theoretical prediction in which $Q_{K_1}$ changes when the temperature is lowered and causes the transition from antiferromagnetism in the $B_2$ phase to weak ferromagnetism in the $A_2$ phase.

### IV. CONCLUSION

The roles of all three structural distortions are elucidated in hLFO; the instability of the $K_3$ mode is the driving force of the $P6_3/mmc \rightarrow P6_3cm$ structural transition; the improper ferroelectricity of the $\Gamma_2$ mode is induced by the frozen $K_3$ mode [13,15]; and the competing effect between $K_1$ and $K_3$ modes determines the magnetic ordering and drives the magnetic phase transition. If the $K_1$ mode can be tuned by interface engineering [35–37], the $T_R$ can be increased, achieving the spontaneous electric and magnetic polarizations and their couplings at room temperature.

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FIG. 4. (Color online) Structural changes indicated by the XRD and XAS. (a) The XRD intensity ratio between the (104) and (004) peaks (normalized to the 30 K value) and the change of lattice constant $c$ (with respect to the 30 K value) as functions of the temperature (the representative error bars are shown). Inset: the simulated intensity ratio between the (104) and (004) peaks as functions of phonon displacements. (b) The change of Fe-3$d$ crystal field levels (relative to the 300 K values) as functions of the temperature (the error bars for $e'$ levels are shown); the bold line is a guide to the eye to highlight the common peak-like feature. (c) Simulated change of Fe-3$d$ levels as functions of phonon displacements [25].
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