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Mode coupling between nonpolar and polar phonons as the origin of improper ferroelectricity in hexagonal LuMnO$_3$

Seungwoo Song,$^{a}$ Jung-Hoon Lee,$^{a}$ and Hyun Myung Jang$^{a}$$^{ab}$

Currently, the most puzzling problem associated with the hexagonal LuMnO$_3$ ($h$-LMO) is a large temperature-gap between the structural phase transition to the polar $P6_3cm$ phase at $\sim$1290 K and the emergence of the spontaneous polarization at a substantially reduced temperature, $\sim$750 K. Interestingly, this large temperature-gap is not limited to $h$-LMO but is a universal phenomenon valid for other rare-earth manganites. We have examined this important issue by exploiting first-principles calculations. It is shown that the structural phase transition to the polar $P6_3cm$ phase from the nonpolar $P6_3/mmc$ phase of $h$-LMO is mediated by the freezing-in of the zone-boundary $K_3$ phonon. However, the ferroelectric polarization remains at a negligibly small value until the amplitude of $K_3$ phonon becomes a certain critical value above which the coupling of the polar $\Gamma^{-}_2$ mode with the nonpolar $K_3$ mode is practically turned on. This coupling-induced polarization explains the observed temperature-gap in $h$-LMO as well as other rare-earth manganites.

1. Introduction

Multiferroic materials exhibit simultaneous ferroic responses with cross-coupled electric, magnetic, and structural orders.$^1$ Over the past decade, there has been a resurgence of interest in understanding and technological applications of multiferroics.$^1,7$ Multiferroics have received a great deal of attention owing to their potential for enabling new device paradigms that are based on the cross-coupling between distinct order parameters.$^1,7$ Among numerous multiferroic materials, manganite-based oxides have been most extensively studied. Orthorhombic manganites such as TbMnO$_3$ and TbMn$_2$O$_5$ exhibit a strong tendency of the magnetoelectric (ME) coupling which stems from noncollinear spin-ordering-induced improper or pseudo-proper ferroelectricity.$^7,8$ In hexagonal manganites ($h$-RMnO$_3$), on the other hand, asymmetric movement of rare-earth (R) cations from the centrosymmetric position is known to be a prevailing factor in the manifestation of ferroelectricity.$^9,11$

Since the thermodynamic stability of $h$-RMnO$_3$ enhances with decreasing radius of R cation,$^{12,13}$ LuMnO$_3$ is expected to show the highest stability towards the hexagonal phase among 15 different lanthanide-based manganites. Currently, the most puzzling problem associated with the hexagonal LuMnO$_3$ ($h$-LMO) is the observed large temperature-gap between the structural phase transition to the polar $P6_3cm$ phase at $\sim$1290 K$^{14,15}$ and the emergence of the spontaneous polarization ($P_s$) at a substantially reduced temperature of $\sim$750 K.$^{16}$ It was reported that the appearance of $P_s$ is accompanied with the enhanced electron density between Lu and axial oxygen ions.$^{17}$ Interestingly, this large temperature-gap ($\Delta T_h$) is not limited to $h$-LMO but is a universal phenomenon valid for other rare-earth manganites. According to the previous report,$^{18}$ $\Delta T_h$ is in the rage of 250 and 540 K with the largest gap occurring in $h$-LMO: $\Delta T_h$ for $h$-YMnO$_3$, $h$-ErMnO$_3$, $h$-YbMnO$_3$, and $h$-LuMnO$_3$ ($h$-LMO) are 300 K, 477 K, 277 K, and 540 K, respectively.$^{18}$ Thus, it is of great scientific importance to elucidate the origin of this universal phenomenon.

In the present study, to resolve this puzzling issue, we have examined the ferroelectric origin of $h$-LMO by analyzing the phonon-amplitude-dependent Kohn-Sham (K-S) energy. On the basis of ab initio density-functional theory (DFT) calculations, we have shown that the structural phase transition to the polar $P6_3cm$ phase from the nonpolar $P6_3/mmc$ phase is mediated by the freezing-in of the zone-boundary $K_3$ phonon. However, the spontaneous ferroelectric polarization remains at a negligibly small value until the amplitude of $K_3$ phonon becomes a certain critical value above which the coupling of the polar $\Gamma^{-}_2$ mode with the nonpolar $K_3$ mode is practically turned on.

2. Computational details

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We have performed DFT calculations on the basis of the generalized gradient approximation (GGA)\textsuperscript{19} and GGA+U method\textsuperscript{20} implemented with projector augmented wave pseudopotential\textsuperscript{21} using the Vienna ab initio Simulation Package.\textsuperscript{22} All the DFT calculations were performed by adopting (i) a 5x5x3 Monkhorst-Pack \textit{k}-point mesh\textsuperscript{23} centered at \(\Gamma\), (ii) a 500-eV plane-wave cutoff energy, and (iii) the tetrahedron method with Blöchl corrections for the Brillouin-zone integrations.\textsuperscript{24} We explicitly treated nine valence electrons for Lu(5\textit{p}^5\textit{d}^5\textit{s}^2), seven for Mn(3\textit{d}^5\textit{s}^2), and six for O(2\textit{s}^22\textit{p}^4). Lu 4\textit{f} electrons were treated as a frozen core. The structural optimizations were performed for the 30-atom-cell which corresponds to a hexagonal unit cell consisting of six formula units. The ions were relaxed until the Hellmann-Feynmann energy as a function of the unit-cell volume and finding its parameters for each phase were obtained by calculating the Kohn-Sham (K-S) energy per formula unit for the spin configurations (a), (b), (c), and (d), respectively. This suggests that \(h\)-LMO is nearly characterized by multiply degenerate ground-state spin configurations. In our subsequent calculations, we adopted a noncollinear triangular AFM spin configuration as schematically depicted in Fig. 2. It is shown that the K-S energy is essentially independent of the spin configuration adopted: 0.00018, 0.00017, 0.00005, and 0.0 eV per formula unit for the spin configurations (a), (b), (c), and (d), respectively. Several conceivable spin structures were considered as the ground-state Mn-spin configuration in the triangular sublattice of \(h\)-RMnO\textsubscript{3}\textsuperscript{31} Accordingly, we have computed the Kohn-Sham (K-S) energy of \(h\)-LMO for the four distinct noncollinear spin configurations as schematically depicted in Fig. 2. It is shown that the K-S energy is essentially independent of the spin configuration adopted: 0.00018, 0.00017, 0.00005, and 0.0 eV per formula unit for the spin configurations (a), (b), (c), and (d), respectively. This suggests that \(h\)-LMO is nearly characterized by multiply degenerate ground-state spin configurations. In our subsequent calculations, we adopted a noncollinear triangular AFM spin configuration as schematically depicted in Fig. 2. This triangular spin configuration is largely consistent with a typical spin structure adopted for frustrated triangular AFM spins in hexagonal manganites, \(h\)-RMnO\textsubscript{3}.\textsuperscript{32,33} In this case, one would expect a nearly zero residual magnetic moment along the in-plane \(a\)-\(b\) direction. According to our DFT calculations, however, Mn\textsuperscript{3+} spins are slightly canted with a non-zero moment of 0.004 \(\mu_B\) (Bohr magneton) per formula unit along the out-of-plane \(c\)-direction.

### 3. Results and discussion

**Crystal and spin structures**

We obtained the refined crystal structures of \(P6/\text{mmc}\) and \(P6\text{cm}\) phases of \(h\)-LMO using the conjugated gradient algorithm for iterative calculations.\textsuperscript{29} The optimized lattice parameters for each phase were obtained by calculating the K-S energy as a function of the unit-cell volume and finding its minimum which corresponds to the K-S energy in the absence of external pressure. The optimized parameters are: \(a = 6.1441\ \text{Å}, c = 11.5143\ \text{Å}\) for \(P6/\text{cm}\) and \(a = 6.1400\ \text{Å}, c = 11.4859\ \text{Å}\) for \(P6/\text{mmc}\) with the difference in the equilibrium K-S energy of 1.06 eV per unit cell. As shown in Fig. 1(a), both types of hexagonal structures consist of the stacking of two layers: one layer of corner-linked MnO\textsubscript{3} bipyramids and the other layer of Lu\textsuperscript{3+} ions. In contrast to the paraelectric \(P6/\text{mmc}\) phase, however, the ferroelectric \(P6\text{cm}\) unit cell of \(h\)-RMnO\textsubscript{3} is characterized by the existence of three distinct RO\textsubscript{3} off-centering units having trigonal \(D_{3d}\) site symmetry.\textsuperscript{10,30} We found that this is also true for \(h\)-LMO. Among three distinct types of Lu ions in a given unit cell of the polar \(P6\text{cm}\) phase, two Lu ions shift downward along the \(c\)-axis while the third ion moves upward for the downward polarization [Fig. 1(b)]. As the three local dipoles do not cancel each other, the net ferroelectric polarization develops along the \(c\)-axis. On the other hand, the net off-centering distortion in the MnO\textsubscript{3} unit having \(D_{3h}\) site symmetry is relatively negligible [Fig. 1(b)], indicating this bipyramidal unit is not responsible for the manifestation of ferroelectricity in \(h\)-LMO or \(h\)-RMnO\textsubscript{3}, in general.\textsuperscript{10,30}

To identify the transition path responsible for the appearance of the polar \(P6\text{cm}\) ferroelectric ground state, we have decomposed the atomic displacements that relate the prototypic \(P6\text{mmc}\) phase to the low-temperature polar \(P6\text{cm}\) phase into the symmetry-adapted modes of the prototypic phase in \(h\)-LMO, namely, \(\Gamma_{2g}^3\), \(K_3\), and \(K_\theta\). The computed atomic displacement eigenvectors for the three relevant phonons are schematically shown in Fig. 3(b). The relative strength of each mode in the ferroelectric structure can be quantified by evaluating its amplitude.\textsuperscript{34} The calculated mode amplitudes \(Q_a\) for all three relevant phonons, \(\Gamma_{2g}^3\), \(K_3\), and \(K_\theta\) are presented in Table I. The relative sizes of the symmetry-adapted mode amplitudes can be used to judge the path responsible for the transition to
the P6$_3$cm ferroelectric ground-state structure. According to the computed amplitudes, $Q_{K1}$ is negligibly smaller than $Q_{K3}$ or $Q_{\Gamma_3}$ (Table I). Thus, a transition sequence of P6$_3$/mmc-P6$_3$cm (the second path mediated by the nonlocal K$_1$ phonon) can be ruled out. First-principles calculations of the Kohn-Sham energy as a function of the fractional amplitude further distinguish between the first path and the third path. As shown in Fig. 4(a), the prototypic P6$_3$/mmc phase is stable with respect to the fractional displacement for the polar $\Gamma_3$ mode. This indicates that the transition to the intermediate ferroelectric P6$_3$mc phase [i.e., the first path in Fig. 3(a)] is highly unlikely to occur. On the contrary, the prototypic P6$_3$/mmc phase is unstable with respect to the fractional displacement for the K$_3$ mode ($Q_{K3}$) and the computed K-S energy exhibits a double-well potential, which demonstrates the relative stability of the ferroelectric P6$_3$cm phase over the nonpolar P6$_3$/mmc phase [Fig. 4(b)]. Thus, the manifestation of the P6$_3$cm hexagonal ferroelectricity in h-LMO can be attributed to the direct one-step transition to the P6$_3$cm ferroelectric ground state from the prototypic nonpolar P6$_3$/mmc state via the third transition path [Fig. 3(a)].

**Polarization induced by phonon mode coupling**

The third transition path, however, is mediated by the freezing-in of the nonpolar K$_3$ phonon. On the other hand, the globally polar P6$_3$cm structure requires a condensation of the polar $\Gamma_3$ phonon. This suggests a coupling of the nonpolar K$_3$ mode with the polar $\Gamma_3$ mode, producing a non-zero equilibrium value of $Q_{\Gamma_3}$. We have then considered the phonon part of the free-energy density ($\mathcal{F}_p$) to quantitatively assess the degree of this mode-mode coupling. Expanding the Landau free-energy invariant to the fourth order in $Q_{K3}$ and $Q_{\Gamma_3}$ with the coupling between them, we obtain:

$$\mathcal{F}_p(Q_{K3}, Q_{\Gamma_3}) = a_{20}Q_{K3}^2 + a_{22}Q_{\Gamma_3}^2 + \beta_{40}Q_{K3}^4 + \beta_{42}Q_{\Gamma_3}^4 + y_{31}Q_{K3}Q_{\Gamma_3} + y_{32}Q_{K3}^2Q_{\Gamma_3}^2$$

(1)

where the last two terms take care of the symmetry-allowed coupling between these two phonon modes. Identifying the phonon part of the K-S energy (with respect to the centrosymmetric P6$_3$/mmc state where Q = 0) with $\mathcal{F}_p$, one can obtain optimized expansion coefficients by exploiting the K-S energy calculations. For this, we performed a series of K-S energy calculations as a function of $Q_{\Gamma_3}$ under the condition of $Q_{K3} = 0$ (i.e., in the absence of coupling). Similarly, we carried out K-S energy calculations as a function of $Q_{K3}$ under the condition of $Q_{\Gamma_3} = 0$. The following four expansion coefficients were then obtained by nonlinear fitting: $a_{22} = +0.2089$ eV, $\beta_{40} = +0.0116$ eV, and $a_{20} = -2.7916$ eV, $\beta_{42} = +0.0508$ eV. The two coupling coefficients were subsequently fit using the computed $Q_{\Gamma_3}$-dependent K-S energy for various values of $Q_{K3}$ (Fig. 5): $y_{31} = -0.5367$ eV, $y_{32} = +0.6138$ eV.

It is interesting to notice that the K-S energy plotted as a function of $Q_{K3}$ does not show its minimum at $Q_{K3} = \pm 1$ [red squares in Fig. 4(b)]. We are now able to explain this apparent anomaly using the optimized coefficients obtained previously. $E_{K3}$ in Fig. 4(b) with $Q_{\Gamma_3} = 0$ can be identified by $a_{20}Q_{K3}^2 + \beta_{40}Q_{K3}^4$ from Eq. (1). The two minima in $E_{K3}$ can be obtained by imposing the equilibrium condition, i.e., $\left(\partial E_{K3}/\partial Q_{K3}\right)_{Q_{\Gamma_3}=0} = 0$. Thus, the corresponding $Q_{K3}$ values are ($Q_{K3}$)$_{\min} = \pm \sqrt{-a_{20}/2\beta_{40}} = \pm 0.83 < 1$. This suggests that the transition to the $\Gamma_3$ mode coupling is needed for a complete transformation to the polar P6$_3$cm structure from the prototypic P6$_3$/mmc structure via the third transition path.

Having obtained a clue for the $K_3 \leftrightarrow \Gamma_3$ mode coupling, we are now able to critically examine the role of this phonon coupling in the manifestation of the ferroelectric polarization. The mode coupling can be realized by plotting $E_{K3}$ as a function of $Q_{\Gamma_3}$ for various values of $Q_{K3}$. It is interesting to notice that the equilibrium position of $Q_{\Gamma_3}$ shifts to a positive value and continues to increase with increasing $Q_{K3}$ (Fig. 5). According to the computed result, the $K_3$ mode does not destabilize the polar $\Gamma_3$ mode, but pushes $Q_{\Gamma_3}$ to a non-zero equilibrium position, playing a role of ‘a geometric field’ since the coupling-induced polarization can be shown to be proportional to either $Q_{K3}$ or $\beta_{42}$ depending on the magnitude of $Q_{K3}$. Thus, one can identify the $K_3$ mode as the primary order parameter and the transverse optical (TO) $\Gamma_3$ mode as a secondary parameter. All these computed results clearly indicate that the ferroelectric polarization ($P_s$) which is proportional to $Q_{\Gamma_3}$ is triggered by the coupling of the nonpolar unstable $K_3$ mode with the polar $\Gamma_3$ mode.

Having identified the role of the $K_3 \leftrightarrow \Gamma_3$ mode coupling in the manifestation of $P_s$, let us go back to our puzzling question: What is the microscopic origin of the observed large temperature-gap between the structural transition to the polar P6$_3$cm phase (at ~1290 K) and the emergence of $P_s$ (at ~750 K)? To elucidate this question, we have divided the $Q_{K3}$-dependent $P_s$ into two distinct regions by imposing the equilibrium condition to Eq. (1) with respect to $Q_{\Gamma_3}$, i.e., $\left(\partial \mathcal{F}_p/\partial Q_{\Gamma_3}\right)_{Q_{K3}=0} = 0$. If $Q_{K3} \ll (a_{22}/y_{32})^{1/2}$, the following inequality relation is obviously valid: $a_{20} > 2\beta_{40}Q_{\Gamma_3}$. Under this condition, $P_s$ remains at a very small value (Region I) and we establish the following expression for $Q_{\Gamma_3}$.

(Region I) $Q_{\Gamma_3} = -\gamma_{31}/2a_{20}Q_{K3}^2$ (2)

On the other hand, if $Q_{K3} \gg (a_{22}/y_{32})^{1/2}$ (Region II), $Q_{\Gamma_3}$ is simply proportional to $Q_{K3}$.

(Region II) $Q_{\Gamma_3} = -\gamma_{31}/2y_{32}Q_{K3}$ (3)

As $Q_{K3}$ is the primary order parameter, we have computed the $Q_{K3}$-dependent $P_s$ by exploiting the Berry phase method. For this, we have to evaluate the equilibrium value of $Q_{\Gamma_3}$ first by computing the $Q_{\Gamma_3}$-dependent K-S energy for each selected value of $Q_{K3}$. As shown in Fig. 6, $P_s$ remains at a very small value owing to the $Q_{K3}^3$-dependence in Region I. For $Q_{K3}$ greater than a certain critical value (Region II), the coupling of the polar $\Gamma_3$ mode with the nonpolar $K_3$ mode is practically turned on and $P_s$, thus $Q_{\Gamma_3}$, is linearly proportional to $Q_{K3}$. The existence of Region I having a small $P_s$ (Fig. 6) explains the
observed large temperature-gap between the structural phase transition at ~1290 K and the para-to-ferroelectric transition at ~750 K. Thus, h-LMO undergoes a structural transition to \( P6_3/cm \) polar symmetry below ~1290 K but its \( P_4 \) remains at a very small value down to ~750 K (Region I). As the \( Q_{K3} \rightarrow Q_{E3} \) crossover occurs at ~750 K, h-LMO enters into Region II and its \( P_4 \) is practically turned on owing to the \( K_3 \leftrightarrow \Gamma_2 \) mode coupling. This type of mode-coupling arguments can be extended to other hexagonal rare-earth manganites that exhibit a large temperature-gap (\( \Delta T_a \)) such as \( h\text{-Ymno}_3 \), \( h\text{-ErMnO}_3 \), and \( h\text{-YbMnO}_3 \).\[18\]

**Asymmetric Lu-O bonding and ferroelectricity**

We then examined the asymmetric chemical bonding directly related to an off-centering ferroelectric distortion along the \( c \)-axis. For this purpose, we have compared the computed electron localization function (ELF) of the paraelectric \( P6_3/mmc \) phase with that of the \( P6_3/cm \) phase as the ELF is known to be an informative tool to distinguish different bonding interactions.\[11\] As shown in Fig. 7(a), the computed ELF value of the region between the Lu ion and the axial \( O_\Lambda \) is negligible in the \( P6_3/mmc \) phase, which demonstrates a dominant ionic bonding character in the Lu-O\(_\Lambda\) bond. Upon the transition to the ferroelectric \( P6_3/cm \) phase, the Lu ion moves to an asymmetric position and there occurs asymmetric bonding interaction between the Lu ion and one of the two \( O_\Lambda \) ions along the \( c \)-axis. This results in a spontaneous breaking of the centrosymmetric state. Contrary to this, there is no noticeable variation in the computed ELF for both Lu-O\(_s\) and Mn-O\(_s\) bonds.

To clearly visualize the change in the localized electron density associated with the \( P6_3/mmc-P6_3/cm \) phase transition, we also present the difference in the electron localization function (\( \delta\text{ELF}(r) \)) between the ferroelectric and paraelectric states.\[10,13\] As presented in Fig. 7(b), the \( \delta\text{ELF}(r) \) contour clearly shows asymmetric movements of Lu and \( O_\Lambda \) ions and a strong asymmetric electron localization along the \( c \)-axis upon the transition to the ferroelectric \( P6_3/cm \) state. All these computed results thus suggest that the asymmetric Lu-O\(_\Lambda\) bonding interaction is directly related to the paraelectric-to-ferroelectric transition in h-LMO.

The computed Born effective charge (BEC) tensors interestingly support the asymmetric covalent-bonding interaction between Lu and \( O_\Lambda \) in the ferroelectric \( P6_3/cm \) phase. As shown in Table II, the BEC tensor of Lu ion for the in-plane (\( xx \) or \( yy \)) direction decreases while the BEC tensor for the out-of-plane (\( zz \)) direction increases markedly upon the transition to the polar \( P6_3/cm \) phase. The same tendency is also obtained for the BEC tensor of \( O_\Lambda \) (Table II). Thus, the enhanced \( zz \)-component of the BEC tensor correlates well with the enhanced asymmetric covalent bonding between Lu and \( O_\Lambda \) along the \( c \)-axis upon the transition to the ferroelectric \( P6_3/cm \) structure.

Having demonstrated asymmetric Lu-O\(_\Lambda\) covalent-bonding interaction associated with the transition to the \( P6_3/cm \) state, we now address the following issue: What kind of orbital interaction is involved in the asymmetric Lu\(^{3+}\)-O\(_\Lambda\) bonding? To answer this question, we have considered two distinct possibilities of the Lu\(^{3+}\)-O\(_\Lambda\) bonding interaction. As schematically shown in Fig. 8(a), these are (i) empty \( 5d_2^0\text{(Lu)}\)-2\( p_3\text{(O}_\Lambda\text{)} \) interaction and (ii) empty \( 6s\text{(Lu)}\)-2\( p_3\text{(O}_\Lambda\text{)} \) interaction. Both types of hybridization induce asymmetric covalent bonding along the \( c \)-axis of \( P6_3/cm \). In this way, the central Lu ion is now able to make an asymmetric covalent bond with one of the two neighboring \( O_\Lambda \) ions (but not simultaneously with two neighboring \( O_\Lambda \) ions), which results in a spontaneous breaking of the centrosymmetric state.

We have then examined partial density of states (PDOS) for several atomic orbitals relevant to the asymmetric covalent-bonding interaction. As shown in Fig. 8(b), there is little tendency of the orbital hybridization between \( 6s\text{(Lu)} \) and \( 2p_3\text{(O}_\Lambda\text{)} \) for both paraelectric \( (P6_3/mmc) \) and ferroelectric \( (P6_3/cm) \) states. Contrary to this, there is a strong overlapping of the Lu \( 5d_2^0\)-orbital PDOS with the \( O_\Lambda \) \( 2p_3 \)-orbital PDOS in the valence-bonding energy region (between -1.5 and 0 eV below the valence-band top). This overlapping is remarkably enhanced upon the transition to the polar \( P6_3/cm \) state. Thus, the \( 5d_2^0\text{(Lu)}\)-2\( p_3\text{(O}_\Lambda\text{)} \) hybridization is primarily responsible for the asymmetric covalent-bonding interaction along the \( c \)-axis of \( P6_3/cm \). However, the \( 5d_2^0\text{(Lu)}\)-2\( p_3\text{(O}_\Lambda\text{)} \) asymmetric covalent bonding cannot be the main driving force of ferroelectricity in h-LMO since the prototypic \( P6_3/mmc \) phase is stable with respect to the fractional displacement for the polar \( \Gamma_2 \) mode (\( Q_{I_2} \)) [Fig. 4(a)]. On the contrary, the \( 5d_2^0\text{(Lu)}\)-2\( p_3\text{(O}_\Lambda\text{)} \) hybridization allows the \( K_3 \) mode to be unstable through antipolar distortions along the \( c \)-axis [Fig. 4(b)]. This pushes \( Q_{I_2} \) to a non-zero equilibrium position through the \( K_3 \leftrightarrow \Gamma_2 \) mode coupling [Fig. 5]. Thus, the orbital hybridization plays an indirect role in the manifestation of the hexagonal ferroelectricity in h-LMO.

## 4. Conclusions

In conclusion, the phase transition to the polar \( P6_3/cm \) structure is mediated by the freezing-in of the zone-boundary \( K_3 \) phonon. However, the ferroelectric polarization remains at a negligibly small value until \( Q_{K3} \) becomes a certain critical value above which the coupling of the polar \( \Gamma_2 \) mode with the nonpolar \( K_3 \) mode is practically turned on. This mode-coupling-induced polarization explains the observed temperature-gap in h-LMO as well as other rare-earth manganites.

### Acknowledgements

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Notes and references


TABLE I. Decomposition of the atomic displacements (Å) into the symmetry-adapted modes of the prototypic P6_3/mmc phase in h-LMO. The mode amplitudes, Q, are shown in Å.

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TABLE II. The computed Born effective charge tensors (Z^*_{\kappa\alpha\beta}; scalar) of Lu and O for the paraelectric P6_3/mmc and ferroelectric P6_3/cm phases of h-LMO. The Born effective charge is defined by Z^*_{\kappa\alpha\beta} = \left[\frac{\Omega(\partial P_{\alpha} / \partial x_\kappa)_{\mu_{\kappa\beta}}}{e}\right]_{E=0}^v, where \Omega is the unit-cell volume [m^3], P is the total field-induced polarization [C/m^2], \mu_{\kappa} is the displacement of the \kappa-th atom [m], and e is the elementary charge [C].

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*Figure Captions*

**FIG. 1** (Color online). Crystal and off-centering structures of $h$-LuMnO$_3$ ($h$-LMO). (a) The crystal structure of the paraelectric $P6_3/mmc$ phase is compared with that of the ferroelectric $P6_{3}cm$ phase. (b) The three distinct LuO$_3$ units and the MnO$_3$ bipyramidal unit in the ferroelectric state. Asymmetry in the computed bond distance between Lu and O$_3$ indicates a non-zero off-centering displacement in the LuO$_3$ unit along the c-axis. The three green-colored arrows indicate the direction of the off-centering displacement in each LuO$_3$ unit.

**FIG. 2** (Color online). A schematic representation of the four distinct noncollinear spin configurations used in our calculations of the spin-structure-dependent Kohn-Sham energy. Herein, the arrows at the blue-colored Mn ions denote the directions of the Mn-magnetic moments on the a-b plane at $z = 0$ while the arrows at the green-colored Mn ions represent the directions on the a-b plane at $z = 1/2$.

**FIG. 3** (Color online). (a) Group theoretically allowed three possible phase transition paths from prototypic $P6_3/mmc$ to ferroelectric $P6_{3}cm$. (b) The computed atomic displacement eigenvectors (denoted by green arrows) schematically represented for the three relevant phonons, $\Gamma_2^-$, $K_1$, and $K_2$.

**FIG. 4** (Color online). (a) The Kohn-Sham energy plotted as a function of the fractional amplitude $Q_{\Gamma_2^-}$ under the condition of $Q_{K_3} = 0$. The reference state of $Q_{\Gamma_2^-} = 0$ denotes the prototypic $P6_3/mmc$ phase. Herein, $Q_{\Gamma_2^-} = 1$ corresponds to 0.276 Å. The computed atomic displacement eigenvectors in the ferroelectrically active LuO$_3$ unit are displayed in the right-hand side (blue arrows) for the polar $\Gamma_2^-$ mode. (b) The Kohn-Sham energy plotted as a function of $Q_{K_3}$ under the condition of $Q_{\Gamma_2^-} = 0$. Herein, $Q_{K_3} = 1$ corresponds to 1.104 Å. The computed atomic displacement eigenvectors in the two distinct LuO$_3$ units, Lu1 ($= $ Lu2) and Lu3, are displayed in the right-hand side (blue arrows) for the nonpolar $K_3$ mode.

**FIG. 5** (Color online). The Kohn-Sham energy plotted as a function of $Q_{\Gamma_2^-}$ for various values of $Q_{K_3}$. The computed result shows that the $K_3$ mode pushes $Q_{\Gamma_2^-}$ to a non-zero equilibrium position, playing a role of ‘a geometric field.’

**FIG. 6** (Color online). The computed $Q_{\Gamma_2^-}$ and polarization plotted as a function of $Q_{K_3}$.

**FIG. 7** (Color online). (a) A comparison of the three-dimensional ELF contour of the paraelectric $P6_3/mmc$ phase (left) with that of the ferroelectric $P6_{3}cm$ phase (right). A left-hand-side bar represents the electron-isosurface gradation adopted in the ELF contour with the isosurface level of 0.06e/Å$^3$. Red arrows appeared in the $P6_{3}cm$ phase denote the direction of the off-centering displacement from the centrosymmetric position upon the transition to the polar $P6_{3}cm$ phase. (b) The difference in the computed ELF between the ferroelectric $P6_{3}cm$ phase and the paraelectric $P6_3/mmc$ phase in $h$-LMO. The $\delta$ELF contour on (110)$_h$ is presented in the figure.

**FIG. 8** (Color online). (a) Schematic diagrams of the two distinct possibilities of the Lu$^{3+}$-O$_h$ bonding interaction in $h$-LMO: (i) 5$d^2$(Lu)-2$p_x$(O$_A$) orbital interaction and (ii) 6$s$(Lu)-2$p_x$(O$_A$) orbital interaction. (b) A comparison of the orbital-resolved partial density of states for 5$d^2$(Lu), 6$s$(Lu), 2$p_x$ or 2$p_y$(O$_A$) and 2$p_z$(O$_A$) orbitals of the paraelectric $P6_3/mmc$ phase with those of the ferroelectric $P6_{3}cm$ phase.
FIG. 3

(a)

(b)

FIG. 4

(a)

(b)