

Asymmetric Ho $5d$ -O $2p$ hybridization as the origin of hexagonal ferroelectricity in multiferroic HoMnO₃

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(Received 15 July 2011; revised manuscript received 29 September 2011; published 27 October 2011)

HoMnO₃ (HMO) is one of the most extensively studied hexagonal manganites owing to its strong tendency of the magnetoelectric coupling. In spite of extensive studies on its multiferroic properties, however, little progress has been made in our understanding on the electronic origin of the hexagonal ferroelectricity in HMO. Considering this, we have examined the bonding mechanism that gives rise to an off-centering ferroelectric distortion along the c axis of the hexagonal $P6_3cm$ unit cell by exploiting density-functional theory calculations. We have shown that the asymmetric $5d_{z^2}(\text{Ho})$ - $2p_z(\text{O}_A)$ hybridization is primarily responsible for the manifestation of this structural ferroelectricity in HMO.

DOI: [10.1103/PhysRevB.84.153106](https://doi.org/10.1103/PhysRevB.84.153106)

PACS number(s): 77.80.-e, 71.15.Mb, 71.20.-b, 75.50.Ee

Multiferroic materials exhibit simultaneous ferroic properties with coupled electric, magnetic, and structural orders. 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.^{1–4} Among numerous multiferroics, manganite-based oxides have been most extensively studied. Orthorhombic manganites such as TbMnO₃ and TbMn₂O₅ exhibit a strong tendency of the magnetoelectric (ME) coupling, which stems from noncollinear spin-ordering-induced improper or pseudoproper ferroelectricity.^{4,5} In hexagonal manganites (h -RMnO₃), on the other hand, an asymmetric movement of R (rare-earth) ions from the centrosymmetric position is known to be a prevailing factor in the manifestation of ferroelectricity.^{6–8}

Among hexagonal manganites, YMnO₃ is a prototype of the h -RMnO₃ family and is currently being extensively investigated. However, there have been some conflicting reports on the nature of ferroelectricity in multiferroic YMnO₃ (YMO hereafter). According to a pioneering work by Van Aken *et al.*,⁷ the Y-O bonds are predominantly ionic and orbital hybridization, thus covalency plays a minor role in the displacive ferroelectric transition to the $P6_3cm$ symmetry.⁷ However, more recent studies all reveal that the d^0 -ness of the Y³⁺ ion ($4d^0$) with a strong hybridization with the O $2p$ orbital is the main driving force of the hexagonal ferroelectricity.^{9–11}

Considering the ferroelectricity driven by Y d^0 -ness in YMO,^{9,10} it is of great scientific importance to clearly elucidate the role of d^0 -ness in the manifestation of ferroelectricity in other types of hexagonal manganites. HoMnO₃ (HMO) is one of most extensively studied hexagonal manganites owing to its strong tendency of the ME coupling as exemplified by the reversible switching of magnetic orders by an external electric field.²

In spite of extensive studies on the ME coupling and associated multiferroic properties,^{12–14} however, little progress has been made in our understanding on the electronic origin of the structural ferroelectricity in hexagonal HMO. In view of this, it is of great scientific interest to identify the main driving force of the ferroelectricity in the hexagonal HMO. Accordingly, we have clarified the bonding mechanism

responsible for the manifestation of ferroelectricity in HMO by exploiting first-principles density-functional theory (DFT) calculations. To do this, we have first examined the following issue: ionic-bonding-driven versus covalent-bonding-driven ferroelectricity. We have then identified the orbital-interaction mechanism primarily responsible for the hexagonal ferroelectricity in HMO, namely, asymmetric Ho $5d_{z^2}$ -O $2p_z$ covalent bonding along the c axis of the hexagonal HMO.

To quantitatively understand the ferroelectricity and associated orbital interactions, we performed first-principles density-functional theory (DFT) calculations on the basis of the generalized gradient approximations (GGA) implemented with the projector augmented wave (PAW)¹⁵ pseudopotential using the Vienna *ab initio* simulation package (VASP).¹⁶ We adopted (i) a $5 \times 5 \times 3$ Monkhorst-Pack k -point mesh centered at Γ in our DFT calculations,¹⁷ (ii) a 500-eV plane-wave cutoff energy, and (iii) the tetrahedron method with the Blöchl corrections for the Brillouin-zone integrations.¹⁸ The Hubbard U_{eff} of 4.5 eV for Mn and the cutoff energy of 500 eV were chosen on the basis of empirical corrections. We explicitly treated eight valence electrons for Ho ($5p^6 6s^2$), seven for Mn ($3d^5 4s^2$), and six for O ($2s^2 2p^4$). Ho $4f$ 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 lattice parameters used in our calculations were taken from the reported experimental values.¹⁹

In Fig. 1(a), we show the optimized crystal structure of the ferroelectric $P6_3cm$ unit cell of HMO. Similar to YMO, this hexagonal structure is characterized by (i) the HoO₈ unit having trigonal D_{3d} site symmetry and (ii) the MnO₅ trigonal bipyramid with D_{3h} site symmetry. More specifically, the structure consists of the stacking of two layers: one layer of corner-linked MnO₅ bipyramids and the other layer of Ho³⁺ ions. As shown in Fig. 1(b), there exist two distinct types of oxygen ions that surround the central Ho ion in the HoO₈ unit. The two axial (apical) oxygen ions along the hexagonal c axis (abbreviated as O_A) correspond to the first type while the six oxygen ions located at two different triangular in-planes (abbreviated as O_I) belong to the second type. Notice that O_A and O_I are equivalent to O_P (in-plane oxygen) and

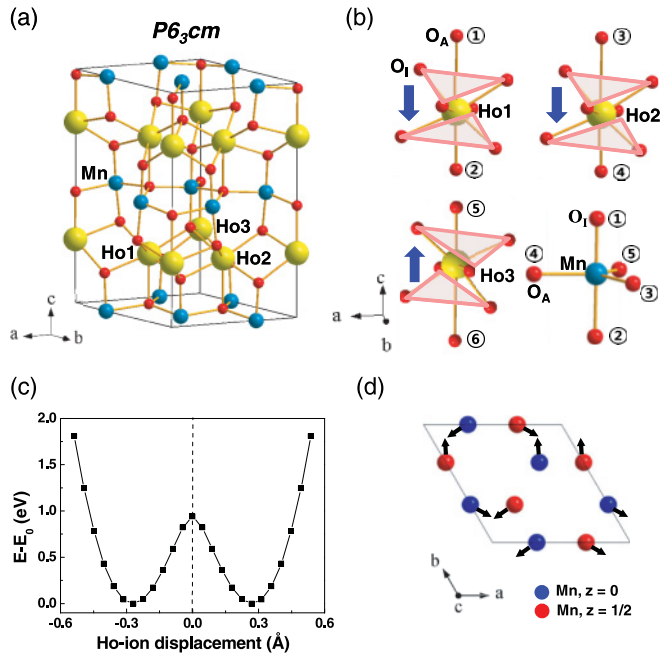


FIG. 1. (Color online) Crystal, off-centering, and spin structures of HoMnO₃ (HMO). (a) Crystal structure of the ferroelectric $P6_3cm$ phase. (b) The three distinct HoO₈ units and the MnO₅ bipyramidal unit in the ferroelectric state. The three blue-colored arrows indicate the direction of the off-centering displacement in each HoO₈ unit. (c) The computed double-well potential plotted as a function of the Ho-ion displacement from the centrosymmetric position. (d) A schematic representation of the noncollinear spin configuration adopted in our DFT calculations. Here 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 red-colored Mn ions represent the directions on the a - b plane at $z = 1/2$.

O_T (on-top oxygen), respectively, in the MnO₅ bipyramidal unit.⁷⁻⁹

The computed local structure and bond lengths reveal that the ferroelectricity in the $P6_3cm$ phase originates mainly from the vertical shift of the Ho ion from the centrosymmetric position.⁷ The three Ho ions in the hexagonal unit cell are located at the same plane in the paraelectric $P6_3/mmc$ state. However, they become distinct upon the transition to the ferroelectric $P6_3cm$ state. More specifically, two Ho ions shift downward along the c axis while the third ion moves upward in the $P6_3cm$ phase, as depicted in Fig. 1(b). As the three local dipoles do not cancel each other, the net ferroelectric polarization occurs along the c axis. On the other hand, the net off-centering distortion in the MnO₅ bipyramidal unit is negligible (Table I), indicating that the MnO₅ unit is not responsible for the hexagonal ferroelectricity.

The computed double-well potential is shown in Fig. 1(c) as a function of the Ho-ion displacement from the centrosymmetric position. This computed result indicates that the energy barrier for the dipole switching along the c axis is 0.940 eV per unit cell. This clearly demonstrates the thermodynamic stability of the ferroelectric $P6_3cm$ phase over the centrosymmetric $P6_3/mmc$ phase. According to our DFT calculations, the equilibrium off-centering displacement of the Ho ion along the c axis is 0.270 Å and is antiparallel

TABLE I. The computed bond-length asymmetry for the three distinct HoO₈ units in the ferroelectric $P6_3cm$ phase and the five nearest-neighbor bond lengths in the MnO₅ bipyramid.

Bond length (Å)			
Ho1-O①	3.362	Mn-O①	1.906
Ho2-O②	2.401	Mn-O②	1.902
Ho3-O③	3.360	Mn-O③	2.074
Ho4-O④	2.402	Mn-O④	2.074
Ho5-O⑤	2.291	Mn-O⑤	2.082
Ho6-O⑥	3.471		

to the O_A-ion displacement of 0.320 Å. This indicates that the net off-centering displacement is 0.590 Å along the c axis. The equilibrium polarization evaluated by applying the Berry-phase method^{20,21} is 8.19 $\mu\text{C}/\text{cm}^2$. This value nearly coincides with the previously computed value of 8.0 $\mu\text{C}/\text{cm}^2$.⁶ In our DFT computations, we adopted a noncollinear triangular antiferromagnetic (TAFM) spin configuration [Fig. 1(d)], which had been originally proposed by Katsufuji *et al.*²² Recently this triangular spin configuration was adopted to successfully explain the role of the TAFM spin ordering in stabilizing the ferroelectric $P6_3cm$ phase in hexagonal InMnO₃.⁸

Let us now examine the main issue of the present study, namely, the electronic origin of the hexagonal ferroelectricity. For this purpose, we first compare the computed electron localization function (ELF) of the paraelectric $P6_3/mmc$ phase with that of the $P6_3cm$ phase as the ELF is known to be an informative tool to distinguish different bonding interactions in solids.^{8,23} As shown in Fig. 2(a), the computed ELF value between the Ho ion and the axial O_A is nearly negligible in the $P6_3/mmc$ phase, which demonstrates a dominant ionic bonding character in the Ho-O_A bond. Upon the transition to the ferroelectric $P6_3cm$ phase, the Ho ion moves to an asymmetric position and there occurs a strong covalent-bonding interaction between the Ho ion and one of the two O_A 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 Ho-O_I and Mn-O_I bonds.

To clearly visualize the change in the localized electron density associated with the $P6_3/mmc$ - $P6_3cm$ phase transition, we also present the difference in the electron localization function $[\delta\text{ELF}(\mathbf{r})]$,²⁴ between the ferroelectric and paraelectric states. As presented in Fig. 2(b), the $\delta\text{ELF}(\mathbf{r})$ contour clearly shows asymmetric movements of Ho and O_A ions and a strong asymmetric electron localization along the c axis upon the transition to the ferroelectric $P6_3cm$ phase. All these computed results thus suggest that the asymmetric Ho-O_A bonding interaction is primarily responsible for the paraelectric-to-ferroelectric transition in HMO.

Having demonstrated a strong asymmetric Ho-O_A covalent-bonding interaction associated with the transition to the $P6_3cm$ state, we now address the following important point: What kinds of orbital interactions are involved in the asymmetric Ho³⁺-O_A bonding that is responsible for the c -axis-oriented hexagonal ferroelectricity? To answer this

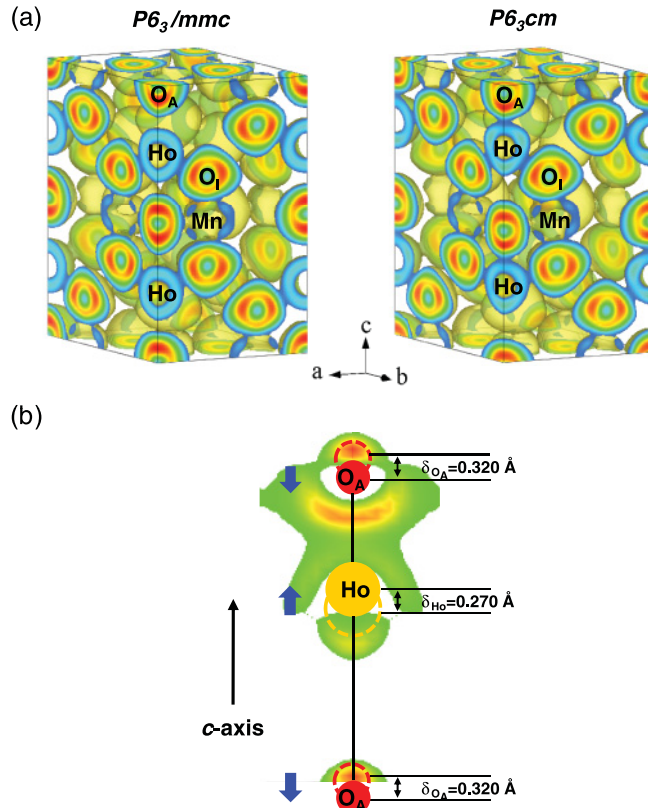


FIG. 2. (Color online) (a) A comparison of the three-dimensional ELF contour of the paraelectric $P6_3/mmc$ phase (left) with that of the ferroelectric $P6_3cm$ phase (right). The isosurface level is equal to $0.06 e/\text{\AA}^3$. (b) The difference in the computed ELF between the ferroelectric $P6_3cm$ state and the paraelectric $P6_3/mmc$ state in HMO. The $\delta\text{ELF}(\mathbf{r})$ contour on $(110)_h$ is presented in this figure.

question, we have considered four distinct possibilities of the $\text{Ho}^{3+}\text{-O}_A$ bonding interaction. As schematically shown in Fig. 3, they are (i) empty $6p_z(\text{Ho})\text{-}2p_z(\text{O}_A)$ interaction, (ii) empty $6p_x(\text{Ho})$ [or $6p_y(\text{Ho})\text{-}2p_z(\text{O}_A)$] interaction, (iii) empty $5d_{z^2}(\text{Ho})\text{-}2p_z(\text{O}_A)$ interaction, and (iv) empty $6s(\text{Ho})\text{-}2p_z(\text{O}_A)$ interaction. Among these four, let us examine $p\text{-}p(\sigma)$ -type interactions first. As schematically presented in Fig. 3(a), the $6p_z(\text{Ho})\text{-}2p_z(\text{O}_A)$ σ -bonding interaction leads to a symmetric covalent bonding (i.e., a symmetric electron-density contour) along the c axis. The $6p_x(\text{Ho})\text{-}2p_z(\text{O}_A)$ interaction [equivalently, $6p_y(\text{Ho})\text{-}2p_z(\text{O}_A)$], on the other hand, does not lead to any bonding interaction (zero-orbital overlapping), as schematically shown in Fig. 3(b).

Contrary to $p\text{-}p(\sigma)$ -type interactions, $d\text{-}p(\sigma)$ or $s\text{-}p(\sigma)$ interaction is able to produce an asymmetric covalent bond. As schematically depicted in Fig. 3(c), the $5d_{z^2}(\text{Ho})\text{-}2p_z(\text{O}_A)$ interaction does induce asymmetric covalent bonding along the c axis of $P6_3cm$. In this way, the central Ho atom is now able to make an asymmetric covalent bond with one of the two neighboring O_A ions (not simultaneously with two neighboring O_A ions), which results in a spontaneous breaking of the centrosymmetric state [Fig. 3(c)]. Similarly, the $6s(\text{Ho})\text{-}2p_z(\text{O}_A)$ interaction also leads to asymmetric covalent bonding along the c axis of $P6_3cm$, as schematically shown in Fig. 3(d).

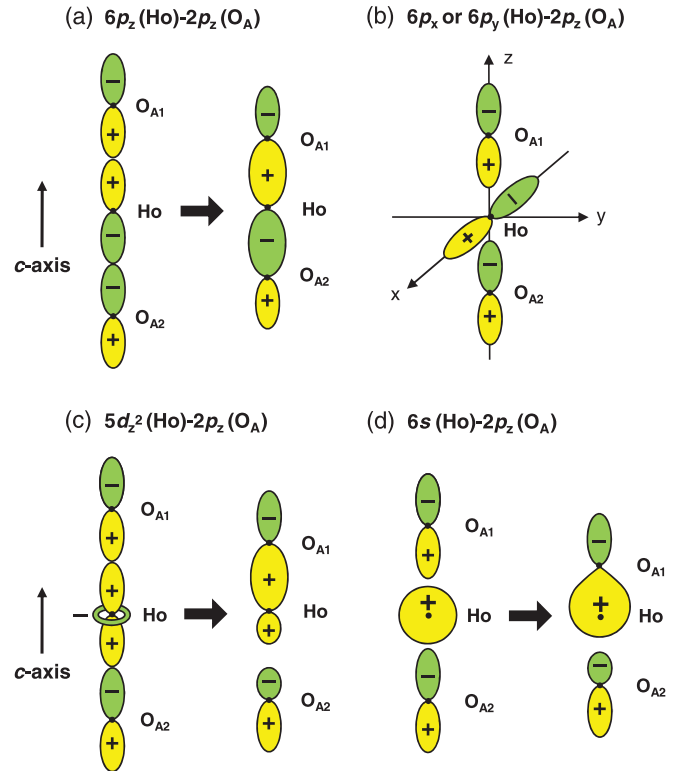


FIG. 3. (Color online) Schematic diagrams of the four distinct possibilities of the $\text{Ho}\text{-O}_A$ orbital interactions in HMO: (a) $6p_z(\text{Ho})\text{-}2p_z(\text{O}_A)$, (b) $6p_x(\text{Ho})$ or $6p_y(\text{Ho})\text{-}2p_z(\text{O}_A)$, (c) $5d_{z^2}(\text{Ho})\text{-}2p_z(\text{O}_A)$, and (d) $6s(\text{Ho})\text{-}2p_z(\text{O}_A)$ orbital interactions.

Accordingly, our next question to be clarified is as follows: Between $5d_{z^2}(\text{Ho})\text{-}2p_z(\text{O}_A)$ and $6s(\text{Ho})\text{-}2p_z(\text{O}_A)$ hybridizations, which one is truly responsible for the manifestation of the hexagonal ferroelectricity? To answer this question, we have carefully examined partial density of states (PDOS) for several atomic orbitals relevant to the asymmetric covalent-bonding interaction. As shown in Fig. 4, there is little tendency of

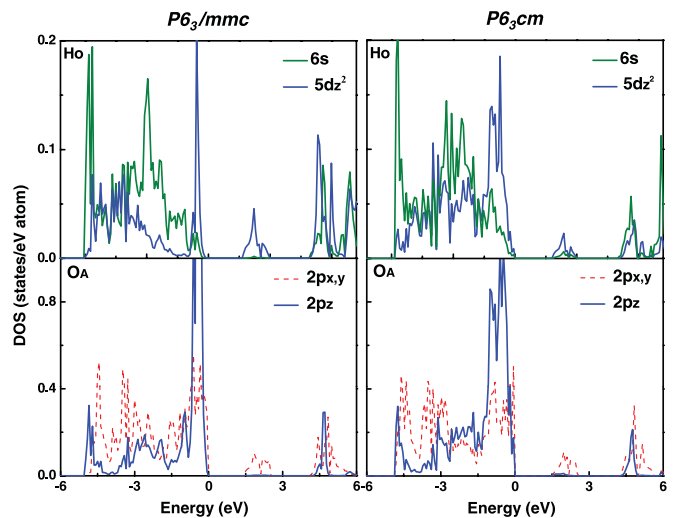


FIG. 4. (Color online) A comparison of the orbital-resolved partial density of states for $5d_{z^2}(\text{Ho})$, $6s(\text{Ho})$, $2p_{x,y}(\text{O}_A)$, and $2p_z(\text{O}_A)$ orbitals of the paraelectric $P6_3/mmc$ phase with those of the ferroelectric $P6_3cm$ phase.

the orbital hybridization between $6s(\text{Ho})$ and $2p_z(\text{O}_A)$ for both paraelectric ($P6_3/mmc$) and ferroelectric ($P6_3cm$) states. Contrary to this, there is a strong overlapping of the $\text{Ho } 5d_{z^2}$ -orbital PDOS with the $\text{O}_A 2p_z$ -orbital PDOS (for the energy range between -1.2 and 0 eV below the valence-band top). This overlapping is remarkably enhanced upon the transition to the ferroelectric $P6_3cm$ state.

In conclusion, the $\text{Ho } 5d_{z^2}$ - $\text{O}_A 2p_z$ orbital overlapping is symmetry allowed only for one neighboring Ho-O_A bond because of the antisymmetric nature of the $2p_z$ orbital wave

function along the z direction. This asymmetric $\text{Ho } 5d_{z^2}$ - $\text{O}_A 2p_z$ hybridization consequently leads to an off-centering ferroelectric distortion along the c axis.

This work was financially supported by the WCU (World Class University) program funded by the Ministry of Education, Science and Technology of Korea (Grant No. R31-2008-000-10059-0). Computational resources provided by KISTI Supercomputing Centre (Project No. KSC-2011-C1-03) of Korea are gratefully acknowledged.

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