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Improper ferroelectricity and multiferroism in $2H$-$BaMnO_3$

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Using first-principles calculations, we study theoretically the stable $2H$ hexagonal structure of $BaMnO_3$. We show that from the stable high-temperature $P6_3/mmc$ structure, the compound should exhibit an improper ferroelectric structural phase transition to a $P6_3cm$ ground state. Combined with its antiferromagnetic properties, $2H$-$BaMnO_3$ is therefore expected to be multiferroic at low temperature. The phase transition mechanism in $BaMnO_3$ appears similar to what was reported in $YMnO_3$ in spite of totally different atomic arrangement, cation sizes, and Mn valence state.

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Multiferroic compounds combining ferroelectric and (anti)ferromagnetic orders present both fundamental and technological interests and have been the topic of intensive research during the last decade.[1–3] The identification of new single-phase multiferroics has been particularly challenging. In this search, a special emphasis was placed on the family of multifunctional ABO_3 compounds within which belong many popular ferroelectric and magnetic materials. Unfortunately, few multiferroic ABO_3 oxides have been identified to date. This scarcity was justified in terms of typical antagonist metal d-state occupancy requirements:[4] On the one hand, ferroelectricity in typical compounds such as $BaTiO_3$ arises from the hybridization between occupied O $2p$ orbitals and empty Ti $3d$ states and requires d^0-ness while, on the other hand, magnetism requires partial d orbitals occupancy, so that ferroelectricity and magnetism often appear to be mutually exclusive.

Exceptions to this rule exist however. In the antiferromagnetic $CaMnO_3$ perovskite, a ferroelelectric instability exists in spite of partial d-state occupancy. In bulk samples, this instability is suppressed by antiferrodistortive oxygen motions but it was predicted theoretically,[5] and recently confirmed experimentally,[6] that $CaMnO_3$ can be made ferroelectric, and *de facto* multiferroic, under appropriate tensile epitaxial strain. In the same spirit, it was proposed that, due to its larger volume, the perovskite form of $BaMnO_3$ should develop a ferroelectric antiferromagnetic ground state.[5,7]

$BaMnO_3$ does not however naturally crystallize in the perovskite structure with corner-sharing oxygen octahedra. Due to its large Goldschmidt tolerance factor, it stabilizes instead in a hexagonal $2H$ structure with face-sharing oxygen octahedra (Fig. 1).[8,9] Increasing pressure decreases the hexagonal character, yielding at high pressure various possible forms including a $4H$ hexagonal structure combining corner- and face-sharing octahedra, which is intermediate between $2H$ and cubic perovskite structures.[9] The stability of the $2H$ structure was confirmed from first-principles calculations[10] but its exact symmetry remains under debate.

From the similarity of spectra with $BaNiO_3$,[11] Hardy originally assigned the $2H$ phase of $BaMnO_3$ at room temperature to the polar $P6_3mc$ space group.[8] Combined Raman and infrared phonon measurements performed by Roy and Budhani[12] are compatible with such a polar character, which is also in line with a recent report of room-temperature ferroelectricity in $2H$-$BaMnO_3$ by Satapathy *et al.*[13]

Nevertheless, Christensen and Ollivier reported that $2H$-$BaMnO_3$ should better belong to the $P6_3/mmc$ space group.[14] We notice that a similar reassignment to $P6_3/mmc$ was also proposed for $BaNiO_3$,[15] which had served as reference material to Hardy. This was also the choice of Cussen and Battle[16] who found no clear evidence to assign the room-temperature structure of $2H$-$BaMnO_3$ to the polar $P6_3mc$ space group but instead chose the nonpolar $P6_3/mmc$ space group. Going further, they highlighted a structural phase transition between room-temperature and 80 K to a polar $P6_3cm$ space group, yielding unit-cell tripling. Moreover, while Christensen and Ollivier[14] did not observe any clear magnetic order above 2.4 K, Cussen and Battle[16] reported an antiferromagnetic ordering below $T_N = 59$ K in the $P6_3cm$ phase, with neighboring spins antiferromagnetically coupled along the polar axis and forming a triangular arrangement perpendicular to it. Although it was not explicitly emphasized, according to this, $BaMnO_3$ should be multiferroic at low temperature in its stable $2H$ polymorph. Nevertheless this has to be taken with caution since Cussen and Battle cannot rule out the possibility of a centrosymmetric $P\bar{3}c1$ space group (subgroup of $P6_3/mcm$) at low temperature.[16] Also, no consensus has been achieved yet regarding the stable structure at room temperature.[13]

In order to get additional insight into the possible ferroelectric nature of $2H$-$BaMnO_3$, we performed first-principles calculations. We show that the high-temperature phase should belong to the $P6_3/mmc$ space group and that the compound should undergo an improper ferroelectric structural phase transition to a $P6_3cm$ phase, through a mechanism similar to what happens in hexagonal $YMnO_3$. Combined with its anti-ferromagnetic properties, this study confirms that $2H$-$BaMnO_3$ should be multiferroic at low temperature.

Our calculations have been performed within density functional theory (DFT) using the CRYSTAL09 package.[17] We used the B1-WC hybrid functional[18] that was previously found appropriate for the study of multiferroic oxides.[19] Relativistic pseudopotentials and a 3ζ valence basis sets were used for the barium atoms.[20] Small core Hay-Wadt pseudopotentials, associated with 2ζ valence basis sets,[21] were used for the manganese atoms. All-electron 2ζ basis sets, specifically optimized for O^{2-}, were used for the oxygen atoms.[22] The calculations were carried out on a $4 \times 4 \times 8$ k-point grid for the tripled unit cell (30 atoms). The polarization was computed from the displacement of Wannier function centers.[23,24] We

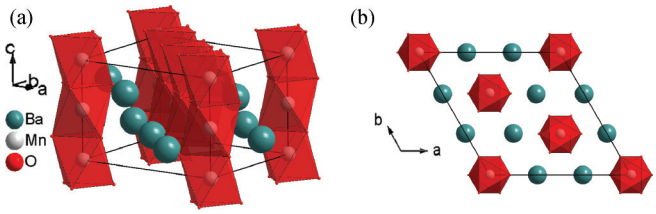

FIG. 1. (Color online) Crystallographic structure of $2H$-$BaMnO_3$ compound at low temperature ($P6_3cm$ space group). (a) Face-sharing MnO_6 octahedra forming chains along the $\vec{c}$ axis. (b) Triangular arrangement of the MnO_6 octahedra in the $(\vec{a},\vec{b})$ plane.

worked within a collinear-spin framework assuming an A-type antiferromagnetic order with spins antiparallel along the $\vec{c}$ direction and aligned in the $(\vec{a},\vec{b})$ plane. Calculations with a ferromagnetic ordering provided similar results. We performed geometry optimization of atomic positions until the root-mean-square values of atomic forces were lower than 5×10^{-5} hartrees bohr^{-1} and until the root-mean-square values of atomic displacements were lower than 5×10^{-5} bohr. For better comparison with the experiment, results reported below have been obtained at fixed experimental lattice parameters as reported by Cussen and Battle at room temperature.[16] Similar results have been obtained adopting the lattice parameters reported at 1.7 K and 80 K. Full structural optimization including lattice parameters was also performed providing qualitatively similar results but yielding a smaller ferroelectric distortion, due to small theoretical errors on the lattice parameters.

First, we performed a structural optimization of $2H$-$BaMnO_3$ starting from a polar $P6_3mc$ configuration as initially proposed by Hardy.[8] Surprisingly, the system relaxed to a more symmetric nonpolar $P6_3/mmc$ configuration, with atomic positions (one degree of freedom, $x_O = 0.1473$) in good agreement with what was reported by Cussen and Battle ($x_O = 0.1495$).[16] This demonstrates theoretically that $2H$-$BaMnO_3$ has no tendency, *a priori*, to become ferroelectric but prefers to adopt a nonpolar $P6_3/mmc$ symmetry as proposed by Christensen and Ollivier. This is in conflict with the recent claim of a room-temperature $P6_3mc$ ferroelectric phase by Satapathy *et al.*[13] However the crystal structure they report corresponds in fact to a $P6_3/mmc$ phase[25] and is therefore inconsistent with the polarization they measure. In order to further confirm our result, we computed the zone-center phonon modes of the relaxed $P6_3/mmc$ phase without identifying any zone-center unstable mode, the lowest polar Γ_2^- mode being at a frequency around 56 cm^{-1}.

In order to test the possibility of a phase transition from the $P6_3/mmc$ structure to a $P6_3cm$ or a $P\bar{3}c1$ phase, we computed the phonons at the zone-boundary point $q = (1/3, 1/3, 0)$. In this case, we identified an unstable mode at $25i$ cm^{-1} of K_3 symmetry. This mode is related to oxygen and manganese motions along the polar axis. Its condensation produces a unit-cell tripling and brings the system into the $P6_3cm$ symmetry. We notice that no unstable mode of K_1 symmetry is identified, ruling out the possibility of a transition to a phase of $P6_3/mcm$ or $P\bar{3}c1$ symmetry.

Atomic relaxation of the $P6_3cm$ phase has been performed, yielding a gain of energy of 21 meV/f.u. with respect to the $P6_3/mmc$ structure. The relaxed atomic positions are reported in Table I and show qualitative agreement with experimental data. $BaMnO_3$ appears in our hybrid functional calculation as an insulator with an electronic band gap of 4.15 eV. As allowed by the polar nature of the $P6_3cm$ space group, this phase also develops a sizable spontaneous polarization $P_s = 0.92$ μC cm^{-2} along the polar axis. Since this polarization can be either up or down (and is so *a priori* switchable), this phase can be labeled as ferroelectric.

TABLE I. Atomic positions (in fractional coordinates) in the $P6_3cm$ structure of $2H$-$BaMnO_3$. Experimental values are those of Cussen and Battle at 1.7 K and 80 K (Ref. 16).

	Theory (present)	Exp.[16] (1.7 K)	Exp.[16] (80 K)
x_{Ba}	0.334	0.339	0.332
z_{Ba}	0.208	0.230	0.238
z_{Mn_1}	0.000	0.000	0.000
z_{Mn_2}	−0.067	−0.048	−0.037
x_{O_1}	0.147	0.149	0.150
z_{O_1}	0.251	0.248	0.250
x_{O_2}	0.667	0.664	0.667
y_{O_2}	0.481	0.482	0.483
z_{O_2}	0.182	0.200	0.212

Interestingly, although the condensation of the K_3 mode breaks inversion symmetry, this mode is nonpolar (i.e., its mode effective charge is zero) and its condensation alone does not induce any significant polarization.[26] Further insight into the mechanism yielding a significant polarization at the phase transition from $P6_3/mmc$ to $P6_3cm$ is therefore needed and can be obtained from a decomposition of the atomic distortion condensed at the transition into symmetry-adapted modes, as achievable with the AMPLIMODES software of the Bilbao crystallographic server.[27,28]

The results of this decomposition are reported in Table II. Both theory and experiment find the structural distortion to be principally dominated by a K_3 character. Then, and although underestimating the experiment, another significant atomic motion observed theoretically has a Γ_2^- character. As further discussed below, it is in fact this additional polar distortion that will produce a sizable polarization. We notice that the appearance of additional Γ_1^+ and K_1 atomic distortions is also possible by symmetry but is not observed in our calculations. This last result contrasts with experimental data that suggest the presence of a sizable K_1 contribution. We notice however that experimental data at 1.7 K and 80 K are not fully compatible in that respect, so that further refined experimental characterization of this phase would likely be very useful to clarify that issue.

TABLE II. Amplitude (in Å) of symmetry-allowed displacements for experimental and theoretical structures (at fixed lattice parameters).

	Γ_1^+	Γ_2^-	K_1	K_3	Total
Exp. (1.7 K)	0.015	0.144	0.154	0.534	0.574
Exp. (80 K)	0.035	0.139	0.035	0.420	0.445
Theory	0.001	0.034	0.005	0.766	0.767

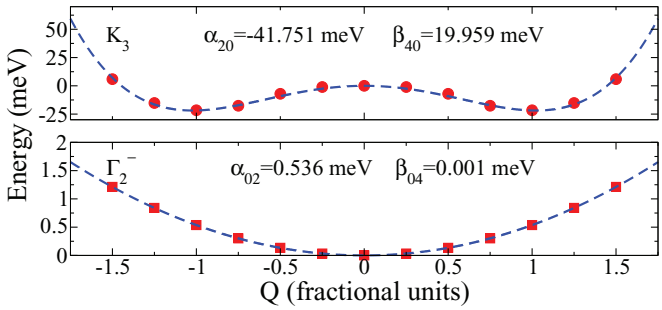

FIG. 2. (Color online) Evolution of the energy (in meV) of $2H$-$BaMnO_3$ in terms of the amplitude $\mathcal{Q}_{K_3}$ and $\mathcal{Q}_{\Gamma_2^-}$ (in fractional units) of the K_3 and Γ_2^- modes. The $P6_3/mmc$ structure was taken as reference.

The interplay between dominant K_3 and Γ_2^- atomic distortions can be better understood from an expansion of the energy around the $P6_3/mmc$ phase in terms of their amplitude $\mathcal{Q}_{K_3}$ and $\mathcal{Q}_{\Gamma_2^-}$:

$$\mathcal{F}(\mathcal{Q}_{K_3},\mathcal{Q}_{\Gamma_2^-}) = \alpha_{20}\mathcal{Q}_{K_3}^2 + \alpha_{02}\mathcal{Q}_{\Gamma_2^-}^2 + \beta_{40}\mathcal{Q}_{K_3}^4 + \beta_{04}\mathcal{Q}_{\Gamma_2^-}^4 + \beta_{31}\mathcal{Q}_{K_3}^3\mathcal{Q}_{\Gamma_2^-} + \beta_{22}\mathcal{Q}_{K_3}^2\mathcal{Q}_{\Gamma_2^-}^2. \quad (1)$$

The coefficients of this energy expansion were determined from DFT calculations on a $\sqrt{3}\vec{a}_{PE} \times \sqrt{3}\vec{b}_{PE} \times \vec{c}_{PE}$ optimized $P6_3/mmc$ supercell with various amplitudes of $\mathcal{Q}_{K_3}$ and $\mathcal{Q}_{\Gamma_2^-}$ condensed. The results are summarized in Fig. 2 and are consistent with what was previously discussed. The Γ_2^- polar mode is stable and associated with a single well while the K_3 mode is unstable and has a typical double-well shape.

The phase transition of $2H$-$BaMnO_3$ from $P6_3/mmc$ to $P6_3cm$ is therefore clearly driven by the unstable K_3 primary mode. Then the sizable polarization arises from the additional condensation of the stable polar Γ_2^- secondary mode which, as further illustrated in Fig. 3, results from a progressive shift of the minimum of the single well, produced by $\mathcal{Q}_{K_3}$ through the $\beta_{31}\mathcal{Q}_{K_3}^3\mathcal{Q}_{\Gamma_2^-}$ coupling term.

This mechanism is similar to what was reported by Fennie and Rabe[29] in $YMnO_3$ and allows us to identify $2H$-$BaMnO_3$ as an *improper* ferroelectric. The evolution of the polarization with $\mathcal{Q}_{K_3}$ is represented in Fig. 4. We first notice that the polarization estimated within the model from the amplitude of $\mathcal{Q}_{\Gamma_2^-}$ assuming constant Born effective charges ($Z^*_{Ba} = +2.10e$, $Z^*_{Mn} = +6.45e$, and $Z^*_{O} = -2.85e$ along the $\vec{c}$ axis in the

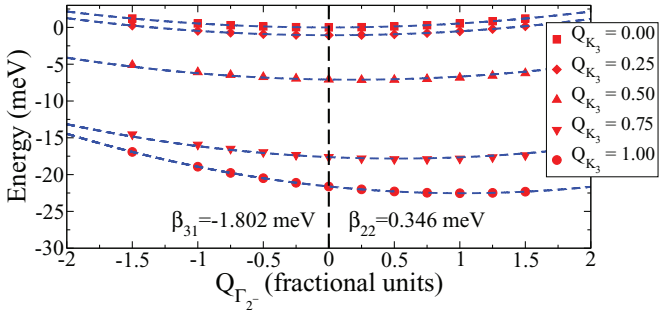

FIG. 3. (Color online) Energy (in meV) as a function of Γ_2^--allowed displacements at fixed $\mathcal{Q}_{K_3}$ (in fractional units).

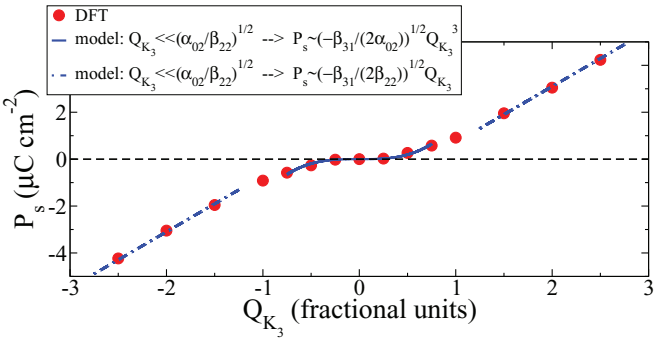

FIG. 4. (Color online) Spontaneous polarization (in μC cm^{-2}) as a function of the primary order parameter $\mathcal{Q}_{K_3}$ (in fractional units).

$P6_3/mmc$ phase[30]) properly reproduces the DFT calculation. As discussed by Fennie and Rabe,[29] two independent regimes can be identified: At small $\mathcal{Q}_{K_3}$ amplitude, $\mathcal{Q}_{\Gamma_2^-}$ (and therefore P_s) evolves like $\mathcal{Q}_{K_3}^3$ while at larger amplitude it evolves linearly. Contrary to $YMnO_3$ that has its ground state in the linear regime, $BaMnO_3$ is still in the small-amplitude regime in our calculation.

Although they both crystallize in the same hexagonal $P6_3/mmc$ space group at high temperature, the similarity between $BaMnO_3$ and $YMnO_3$ is astonishing. First, the valence states of the cations are different in both compounds ($+2/+4$ in $BaMnO_3$ versus $+3/+3$ in $YMnO_3$). The cation sizes are also distinct in both compounds yielding a Goldschmidt tolerance factor of 1.097 in $BaMnO_3$ and 0.82 in $YMnO_3$. Consequently, the atomic structure is totally different in both compounds: The Mn atom is surrounded by face-sharing oxygen octahedra in $BaMnO_3$ and corner-sharing oxygen trigonal bipyramids in $YMnO_3$. The atomic motion associated with the unstable K_3 mode is also rather different. In $YMnO_3$, K_3 motions correspond to a tilt of MnO_5 bipyramids accompanied by a shift of Y atoms and O atoms forming the basis of MnO_5 bipyramids along the polar axis. This leads to a more symmetric environment for the Mn atom, reducing its oxidation degree and making the charges of all O atoms similar. In $BaMnO_3$, the K_3 mode is associated only with a shift of Mn and O atoms along the polar axis, increasing the absolute value of the oxidation degree of all atoms. The fact that both compounds exhibit an unstable K_3 mode that can drive improper ferroelectricity appears therefore rather fortuitous.

Finally, we studied the magnetic properties of ground-state $2H$-$BaMnO_3$. In their seminal work, Christensen and Ollivier[14] did not identify any clear magnetic order above 2.4 K but more recently, Cussen and Battle[16] reported an antiferromagnetic ordering below $T_N = 59$ K in the $P6_3cm$ phase: They proposed a configuration comparable to $YMnO_3$ in which neighboring spins are antiferromagnetically aligned along the polar axis and forming a triangular arrangement perpendicular to it.

Although working within a collinear-spin approximation, we estimated the coupling constants J_{ij} between spins at site i and j in the $P6_3cm$ phase through the fit of the Heisenberg effective Hamiltonian limited to nearest-neighbor interactions: $H_{\text{Heisenberg}} = -\sum_{i<j} J_{ij}\vec{S}_i \cdot \vec{S}_j$. $2H$-$BaMnO_3$ presents

two distinct magnetic interactions: one along the polar axis and one perpendicular to it. We found a strong antiferromagnetic coupling $J_c = -32.77$ meV along the polar axis and a much weaker interchain antiferromagnetic coupling $J_{ab} = -0.14$ meV in-plane, comparable to that computed in $YMnO_3$.[31] The estimate of J_{ab} has certainly to be taken with more caution than J_c: In $YMnO_3$, collinear-spin calculations significantly underestimated the magnitude of J_{ab} on a similar triangular arrangement of spins[31] (0.59 meV instead of 2.3–3 meV experimentally). Nevertheless, a strong anisotropy of the magnetic interactions seems to be likely and can be explained from simple geometry arguments. Along the polar axis, there are face-sharing octahedra and the superexchange term between two neighboring Mn atoms goes through three different Mn-O-Mn exchange paths, increasing the overlap between Mn $3d$ and O $2p$ orbitals and the magnetic coupling. On the other hand, Mn-Mn interchain distances are longer and the superexchange term in-plane has to go consecutively through O and Ba atoms (see Fig. 1); the overlap between orbitals will be smaller and the magnetic exchange interactions weaker. So, although it is proposed that both share the same magnetic arrangement, the antiferromagnetic coupling in $2H$-$BaMnO_3$ appears substantially different from that in $YMnO_3$ for which the strongest magnetic interactions are in-plane.

In summary, we propose in this Rapid Communication that $2H$-$BaMnO_3$ is an *improper* ferroelectric. Our calculations moreover confirm its antiferromagnetic character, making it a multiferroic compound amazingly similar to $YMnO_3$, in spite of a radically different atomic arrangement. Improper ferroelectrics have recently generated increasing interest in view of their unusual electrical properties.[32] Not so many ABO_3 improper ferroelectrics have been reported yet and our study illustrates that such behavior can also happen in hexagonal $2H$ compounds. We hope that our theoretical work will motivate the search of new improper ferroelectrics and multiferroics in this class of compounds.

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