The origin of ferroelectricity in magnetoelectric YMnO₃

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Understanding the ferroelectricity in magnetic ferroelectric oxides is of both fundamental and technological importance. Here, we identify the nature of the ferroelectric phase transition in the hexagonal manganite, YMnO₃, using a combination of single-crystal X-ray diffraction, thorough structure analysis and first-principles density-functional calculations. The ferroelectric phase is characterized by a buckling of the layered MnO₅ polyhedra, accompanied by displacements of the Y ions, which lead to a net electric polarization. Our calculations show that the mechanism is driven entirely by electrostatic and size effects, rather than the usual changes in chemical bonding associated with ferroelectric phase transitions in perovskite oxides. As a result, the usual indicators of structural instability, such as anomalies in Born effective charges on the active ions, do not hold. In contrast to the chemically stabilized ferroelectrics, this mechanism for ferroelectricity permits the coexistence of magnetism and ferroelectricity, and so suggests an avenue for designing novel magnetic ferroelectrics.

Ferroelectric materials have a spontaneous electric polarization that can be switched by an applied electric field. They are used in a wide range of applications, including data storage and as capacitors, transducers and actuators, as a result of their wide variety of physical and electronic properties. Most technologically important ferroelectrics are perovskite structure oxides, but there is increasing interest in the class of ferroelectric hexagonal manganites as non-volatile memory materials, as gate ferroelectrics in field-effect transistors and because of their coupled magnetic and ferroelectric behaviour. In addition to their technological relevance, the fundamental physics of ferroelectrics is rich and fascinating. In particular, many ferroelectrics undergo a phase transition from a high-temperature, high-symmetry phase that behaves as an ordinary dielectric, to the spontaneously polarized phase at low temperature, and a great deal of research has focused on understanding the nature of, and driving force for, these ferroelectric phase transitions.

In fact, perovskite structure oxides in which the bonding is entirely ionic are always centrosymmetric (and therefore not ferroelectric). This is because the short-range Coulomb repulsions between electron clouds on adjacent ions are minimized for centrosymmetric structures. The existence or absence of a ferroelectric instability is therefore determined by a balance between these short-range repulsions, which favour the non-ferroelectric centrosymmetric structure, and additional bonding considerations, which act to stabilize the ferroelectric phase. Currently two distinctly different chemical mechanisms for stabilizing the distorted structures in ferroelectric oxides have been identified. Both are described as second-order Jahn–Teller effects in the literature, see for example ref. 6. The first is the ligand-field hybridization of a transition metal cation by its surrounding anions. This is the origin of the off-centre displacement of the small cation in the common perovskite ferroelectrics such as BaTiO₃ and Pb(Zr, Ti)O₃. It was first identified theoretically in PbTiO₃, and described as a Ti 3d–O 2p hybridization. Note that this mechanism requires that the d orbitals on the small cation are formally unoccupied, and so precludes the coexistence of ferroelectricity and magnetism. The second mechanism occurs around cations that have an (ns)² valence electron configuration. The tendency of (ns)² ions to lose inversion symmetry is well established, with the conventional explanation invoking a mixing
between the (ns) ground state and a low-lying (ns) (np) excited state, which can only occur if the ionic site does not have inversion symmetry. This stereochemical activity of the lone pair is the driving force for off-centre distortion in the group IV chalcogenides (for example GeTe) and in Bi-based perovskites, such as BiMnO$_3$ and BiFeO$_3$ (refs 12 and 13, respectively). Sometimes both mechanisms occur in the same material, for example in PbTiO$_3$ (recently visualized directly in electron-density maps obtained using X-ray powder diffraction), and Na$_2$La$_2$TiO$_6$ (ref. 15). Until recently, all known magnetic ferroelectrics were thought to need lone-pair activity to introduce the ferroelectricity; TbMnO$_3$ has been shown to have a small ferroelectric polarization that results from magnetoelectric coupling to the incommensurate sinusoidal antiferromagnetic ordering.

In this paper, we present evidence that the ferroelectricity in the hexagonal manganite, YMnO$_3$, arises from a fundamentally different mechanism. Using a combination of single-crystal X-ray diffraction (measured on an Enraf-Nonius CAD-4F diffractometer, using monochromated Mo K$_\alpha$ radiation) and density-functional computations, we confirm that the ferroelectricity in YMnO$_3$ arises from a buckling of the MnO$_5$ polyhedra (analogous to the GaFeO$_3$ rotation observed in many cubic perovskite oxides), combined with the unusual Y coordination and the triangular and layered MnO$_5$ network. In striking contrast to the two established mechanisms described above, there is no re-hybridization or change in chemical bonding between the para- and ferroelectric phases. In addition to being of fundamental interest, this mechanism offers a new route for designing magnetic ferroelectrics that have been historically difficult to achieve, but are appealing for ‘spintronics’ applications.

The hexagonal structure adopted by YMnO$_3$ and the manganites of the small rare earths consists of non-connected layers of MnO$_5$ trigonal bipyramids corner-linked by in-plane oxygen ions (O$_p$), with apical oxygen ions (O$_a$) forming close-packed planes separated by a layer of Y$^{3+}$ ions. Schematic views of the crystal structure are given in Fig. 1 and Fig. 2. We emphasize that although this structure has sometimes been described as a hexagonal perovskite structure in the literature, this is in fact a poor choice of phrase, as it is markedly different from the cubic perovskite structure, which features MnO$_6$ octahedra corner-linked to form a three-dimensional (3D) network. Indeed we will show that the 2D layered structure is essential for the formation of the ferroelectric state.

Early work in the 1960s established YMnO$_3$ to be ferroelectric, with space group P$_6_3$cm, and revealed an A-type antiferromagnetic ordering with non-collinear Mn spins oriented in a triangular arrangement. The coexistence of magnetism and ferroelectricity is rare, particularly in materials lacking lone pairs, and recent reports of coupling between the magnetic and ferroelectric ordering in YMnO$_3$ provide compelling motivation for understanding the origin of its ferroelectric behaviour. In the 1970s, the high-temperature crystal structure of YMnO$_3$ was investigated, and a change in symmetry above the ferroelectric ordering temperature was observed. However Raman and infra-red spectroscopy of the high-temperature paraelectric and low-temperature ferroelectric phases showed only weak bands in the ferroelectric phase due to the non-centrosymmetry, indicating that the structural differences between the ferroelectric and paraelectric phases are very small.

Although the studies described above correctly identified YMnO$_3$ to be ferroelectric, a thorough understanding of the crystal structure, including the crystallographic origin of the ferroelectric properties, has not yet been presented. Indeed, the early structure determinations incorrectly concluded that the ferroelectric polarization arises from an off-centre distortion of the Mn ion towards one of the apical oxygen ions. (The two Mn–O$_a$ distances in closely related LuMnO$_3$ have been reported to be 1.84 Å and 1.93 Å, in violation of the ‘d 0-ness’ criterion for transition metal off-centring$^{\text{10}}$). However, the early diffraction experiments did not include the anomalous scattering contributions, which are essential for twinned, non-centred crystals. Instead, our single-crystal X-ray diffraction experiments, using reflections of the entire Ewald sphere, on several hexagonal manganites, correctly analyse such contributions, and show that the Mn ions remain very close to the centre of the oxygen bipyramids.

We find that the main difference between the paraelectric P$_6_3$/mm and ferroelectric P$_6_3$cm structures is that in the paraelectric phase, all ions are constrained to planes, parallel to the apical plane, whereas below the ferroelectric transition temperature, the mirror planes perpendicular to the hexagonal axis are lost. There are two major atomic displacements in the crystal structure from the centrosymmetric P$_6_3$/mm to the ferroelectric P$_6_3$cm. The first change is the buckling of the MnO$_5$ bipyramids, which results in a shorter c axis. Furthermore, due to the buckling, O$_a$ ions are shifted in-plane towards the two longer Y–OP$_p$ bonds. The second change is the vertical shift of the Y ions away from the high-temperature mirror plane, while keeping the distance to O$_p$ constant. Both the bond lengths within the MnO$_5$ bipyramids and the Y–O$_a$ bond lengths within the sixfold coordination remain unchanged.

As a result, one of the two ~2.8 Å Y–O$_a$ bond lengths is reduced to ~2.3 Å, while the other is enlarged to 3.4 Å, leading to a net electric polarization. Recent neutron-powder–diffraction experiments also recognize the asymmetric environment of the Y ions, however they report Mn–O$_a$ bond lengths that suggest off-centring of the Mn ion.

To confirm our experimental results, particularly in light of their conflict with earlier reports, we calculated the minimum energy structure using first-principles density-functional theory. We used our self-interaction-corrected ultrasoft pseudopotential implementation, as standard local-spin-density methods fail to obtain a bandgap for YMnO$_3$ (ref. 34). First, we evaluated the lattice parameters by total energy minimization of the structure within the paraelectric (P$_6_3$/mm) symmetry, assuming A-type antiferromagnetic magnetic ordering. Subsequently, we lifted the inversion symmetry to determine the atomic coordinates of the ferroelectric structure by force minimization. Our calculated atomic positions (Fig. 3) are in excellent agreement with our experimental results, and our calculated ferroelectric polarization (6.2 μC cm$^{-2}$) is close to the measured value (5.5 μC cm$^{-2}$). In particular, we find that off-centring of the Mn ion, as reported previously, is energetically unfavourable.

As neither Y$^{3+}$ nor Mn$^{3+}$ has a lone pair of electrons, we know that lone-pair stereochemical activity cannot be the driving force for ferroelectricity in YMnO$_3$. Therefore the only possible chemical
mechanism is ligand-field hybridization. However, as the Mn ions remain close to the centre of their oxygen cages (in the computations they move by $\sim 0.01$ Å along the $c$ axis, and remain almost unchanged in-plane), it is highly unlikely that they re-hybridize with the surrounding oxygen anions during the phase transition. And the strong off-centre displacement that occurs between Y and in-plane OP ions, leaves the Y and O ions $\sim 2.3$ Å apart, the distance expected for a fully ionic bond\(^3\) (compare Y$_2$O$_3$ where the average Y–O bond length is 2.27 Å). In this final part of the paper we explore the details of the ferroelectric phase transition.

To investigate chemical activity, two fundamental quantities can be calculated efficiently from first-principles: the (transverse) Born effective charges ($Z^*$) and the orbital-resolved densities of states. The $Z^*$ can be defined as the atomic position derivative of the polarization at zero macroscopic electric field, or the linear-order coefficient between the electric field and the force that the field exerts on an ion at zero displacement. A large $Z^*$ indicates that the force acting on a given ion due to the electric field generated by the atomic displacements is large even if the field is small, thus favouring the tendency towards a polarized ground state. Previous work on ferroelectric perovskite oxides\(^{36-40}\) has

![Figure 2 Three-dimensional schematic view of YMnO$_3$ in the two enantiomorphous polarized states. Arrows indicate the directions of the atomic displacements moving from the centrosymmetric to the ferroelectric structure.](image-url)
part why the polarization of YMnO₃ is smaller than that in typical ferroelectric materials, and explains in terms of the interaction between the Y and O orbitals. The DOS calculated in these materials show close-to-formal Z* values for Mn and O ions, which are consistent with the absence of substantial Mn off-centre displacement with respect to the surrounding oxygen ions. Furthermore, the close-to-formal Z* values for Y and O ions suggest that their relative displacements are very close to the formal charges, which are far larger than (often almost double) the nominal ionic charges.

We calculated the Z* values for YMnO₃ using the Berry phase approach generalized to the case of spin-polarized systems. Our calculated Z* values for both the O and the Mn are very close to the formal ionic charges, whereas Z* for Y is only moderately larger than the nominal Y charge. This is, to our knowledge, the first calculation of close-to-formal Z* values for YMnO₃, which in large part cause the structure to be ferroelectric. The calculation of Z* also allows us to identify the actual mechanism for the large Y–OP displacements that occur in the ferroelectric state. The total deformation can be decomposed into two components, summarized in Table 2. (Note that these are the Fourier-transforms of our calculated ferroelectric displacement vector, rather than formal values.) One, with group theoretical symmetry label K₃, is the tilting of the Mn–O₅ polyhedra, which causes a tripling of the paraelectric unit cell, and by symmetry does not lead to an overall polarization. (Although it creates large local dipole moments, these sum to zero, that is, 2dY₂ + dY₁ = 0, and 2dO₂ + dO₁ = 0, where d is the displacement along the c axis.) The other is the so-called Γ-point component (with symmetry label Γ₁), in which the atomic displacement patterns in each unit cell are identical, and therefore can sum to give a net ferroelectric polarization. The Γ₁ component involves primarily the Y–O₅ displacements and the non-cancelling contribution of the MnO₅ rotational bucklings. Although the ‘local’ dipole moments are large, the moments on O₁ are partially cancelled by their antiparallel ordering to the moments on Y₂. This also contributes to the relatively low polarization. Group theoretical analysis and high-temperature diffraction shows that the transition from the paraelectric P_b2/mmc to the ferroelectric P_b2/mn structure takes place in two steps. (This is consistent with earlier reports of structural phase transition at the ferroelectric Curie temperature, T_c.)

In Fig. 5, we report the calculated energies as a function of the structural distortion for both the total ferroelectric displacement and its Γ-point component. The difference between the two curves is the contribution from the buckling of the oxygen cages. Both curves present the well-known double-well shape around the centrosymmetric point, indicating that both the Γ-point uniaxial Y–O₅ ferroelectric displacements and the K₃ tiltings are independently energetically
favoured with respect to the centrosymmetric structure. The tilting of the Mn–O$_3$ bonds, although not generating a polarization directly, cooperates with the Y–O displacements to contribute a large part of the energy lowering between paraelectric and ferroelectric states. It also enlarges the displacement at which the energy is at a minimum. The total energy lowering is $\sim 60$ meV per formula unit, which corresponds to $T_c \sim 700$ K, consistent with the experimental value. Note that neither distortion is associated with chemical rehybridization, but instead both are stabilized by electrostatic and size effects.

It is important to emphasize that the role of the Mn–O polyhedral rotations in stabilizing the ferroelectric structure is in striking contrast to the situation in the ABO$_3$ cubic perovskites. Such rotations are widely observed in cubic perovskites. For example in LaMnO$_3$, GdFeO$_3$, and YVO$_3$, there is a rotation of the BO$_6$ octahedra, and a shift of the A cations from their pseudocubic sites$^{17,18,46}$. The A cations become asymmetrically coordinated with respect to the oxygen ions and the inversion symmetry with respect to a reference system centred on the A ion is lost. However, as a result of the 3D connectivity, a rotation of the polyhedra around a particular lattice axis forces the corner–linked polyhedra in the two perpendicular directions to rotate in the opposite direction$^{17}$. Therefore the global inversion symmetry is retained. As a consequence, no electric polarization occurs (such materials are sometimes referred to as anti-ferroelectrics). Some materials, such as (Na,Bi)TiO$_3$, do show oxygen cage rotations and ferroelectricity; however, the ferroelectricity—which is driven by the usual off-centring of the Ti$^{4+}$ ion and the lone-pair active Bi$^{3+}$ ion$^{15}$—in this case occurs in spite of the rotations. In YMnO$_3$, instead, due to the layered structure and the triangular symmetry, the rotations break the inversion symmetry and lower the symmetry to that of the ferroelectric phase.

Finally, we point out that our findings are not only relevant to YMnO$_3$. Indeed, it was predicted that a further eight ABO$_3$ compounds from the YMnO$_3$ family will show ferroelectricity$^{47}$, which, if correct, will probably be explained with the same arguments. And ferroelectricity has been predicted to occur in perovskite

Figure 4 Orbital-resolved densities of states of Mn, O and Y ions for paraelectric YMnO$_3$. The overlapping DOSs indicate bonding between the Mn 3d and O 2p states, but there is clearly very little interaction between the Y and O orbitals. The DOS calculated in the ferroelectric phase (not shown) is very similar to that of the paraelectric phase, confirming that there is no significant rehybridization.
unchanged from their values in the centrosymmetric structure) because of large
in the centre of their oxygen polyhedra (that is, the Mn–O bond lengths are nearly
structure. Note that in spite of the relative motions along the
mechanism suggests a new route for designing magnetic ferroelectric
and the triangular and layered MnO₅ network. Furthermore, this
The polarization is a consequence of the unusual Y-site coordination
interactions and oxygen rotations both cooperate to drive the system
Instead, long-range dipole–dipole
materials are two orders of magnitude smaller than that of YMnO₃.
structure NaCaF₃, accompanied by polyhedral CaF₂ rotations⁴⁶
and close-to-formal Z’s (ref. 49). Also, tris-sarcosine calcium chloride,
(\(\text{CH}_3\text{NHCH}_2\text{COOH}\))₃\(\text{CaCl}_2\), is a uniaxial ferroelectric whose order parameter
paraelectric mirror plane. It is reported to have an unusually small
splitting between the longitudinal and optical phonon modes⁴⁶, which
consistent with the non-anomalous Z’s that we obtain for ferroelectrics adopting the mechanism described here. And
rotational ferroelectric soft mode has been reported in some so-called
‘weak ferroelectrics’ such as lithium germanate⁴¹ (Li₂Ge₇O₁₅). We point
out, however, that the spontaneous polarizations in these latter materials are two orders of magnitude smaller than that of YMnO₃.
In summary, our results for structural and electronic properties give
a consistent picture of YMnO₃ as an anomalous ferroelectric oxide, for
which rehybridization and covalency play a minor role (or no role at all)
in the ferroelectric transition. Instead, long-range dipole–dipole
interactions and oxygen rotations both cooperate to drive the system
towards the stable ferroelectric state. Indeed, the huge Y–O₆ off-centre
placements are quite distinct from the small displacements driven by
chemical activity found in conventional ferroelectric perovskites, and
represent a completely different mechanism for ferroelectric distortion.
The polarization is a consequence of the unusual Y-site coordination
and the triangular and layered MnO₅ network. Furthermore, this
mechanism suggests a new route for designing magnetic ferroelectric
bulk or thin-film materials, as it permits the presence of magnetic ions
in the ferroelectric phase.

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Competing financial interests
The authors declare that they have no competing financial interests.