The ferroelectric transition in YMnO$_3$ from first principles

Craig J. Fennie and Karin M. Rabe
Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854-8019
(Dated: January 7, 2022)

We have studied the structural phase transition of multiferroic YMnO$_3$ from first principles. Using group-theoretical analysis and first-principles density functional calculations of the total energy and phonons, we perform a systematic study of the energy surface around the prototypic phase. We find a single instability at the zone-boundary which couples strongly to the polarization. This coupling is the mechanism that allows multiferroicity in this class of materials. Our results imply that YMnO$_3$ is an improper ferroelectric. We suggest further experiments to clarify this point.

PACS numbers: 77.80.Bh, 61.50.Ks, 63.20.Dj

The hexagonal manganites, ReMnO$_3$ for Re=Ho-Lu and Y, are a class of multiferroic materials that are simultaneously ferroelectric (FE) and antiferromagnetic (AFM). In particular, YMnO$_3$ is FE at room temperature (RT) crystallizing in space group P6$_3$cm (C6v, Z=6). Above $\approx$1270K it has been shown to undergo a transition to paraelectric (PE) P6$_3$/mmc (D$_{3d}$, Z=2).

The sequence of phase transitions from the low-temperature FE to the high temperature PE phase has been the subject of much debate. Based on pyroelectric measurements and lattice constants determined by x-ray diffraction, Ismailzade and Kizbaev argued that YMnO$_3$ undergoes a FE transition from P6$_3$cm (Z=6) to an intermediate nonpolar P6$_3$/mmc (Z=6) at $\approx$930K. In contrast, Lukaszewicz and Karut-Kalicinska were unable to resolve this intermediate nonpolar space group at 1005 K and saw no clear anomalies in the lattice constants at $\approx$930K. Katsufuji et al. confirmed the latter results on the temperature dependence of the lattice constants and resolved the FE space group up to 1000K, the highest temperature they considered. The FE space group immediately below the zone-tripling transition is also supported by the structural refinements of Lonkai et al. on the closely related compounds ReMnO$_3$, for Re = Lu, Tm, Yb. The other hand, Néert et al. recently interpreted their x-ray diffraction measurements to support the observation of the intermediate P6$_3$/mmc (Z=6) between 1020K and 1270K. The presence of some kind of feature at 930K is suggested by small anomalies in resistivity data at $\approx$950K (also observed in HoMnO$_3$). Thus, the nature of the phase right below the 1270 K transition out of the PE phase, a precise characterization of the behavior around 900-1000 K, and the identification of the PE-FE transition in this material, remain subjects of great interest.

It has been established that to coexist with magnetism, the nature of the ferroelectricity cannot be that found in prototypical perovskite FEAs such as BaTiO$_3$. Indeed, first-principles calculations have shown that the usual indicators of a FE instability (e.g. large Born effective charges) are absent in YMnO$_3$. Polarization $P_s$ = 6 $\mu$C/cm$^2$ results from the tilting of the Mn-centered oxygen octahedra and buckling of the Y-O planes, with no significant off-centering of the Mn cations as would be characteristic of a perovskite FE. As such, YMnO$_3$ has been referred to as a “geometric ferroelectric.” In this paper, we combine a group theoretical analysis of the experimental FE structure with first-principles calculations to describe the mechanism by which this “geometric ferroelectricity” originates. Computation of the coupling between a zone-boundary instability and a soft, but stable, zone-center phonon shows that it induces a low temperature $P_s$ $\approx$ 6.5 $\mu$C/cm$^2$ consistent with experiments. Identifying this zone-boundary mode as the primary order parameter (OP), we argue that there is an improper FE transition in YMnO$_3$ at the observed zone-tripling transition, $\approx$ 1270K. We suggest possible origins for the feature that has been observed around 1000K.

First-principles density-functional calculations using projector augmented-wave potentials were performed within the LSDA+U (local spin-density approximation plus Hubbard U) method as implemented in the Vienna ab initio Simulation Package (VASP). The wavefunctions were expanded in plane waves up to a kinetic energy cutoff of 500 eV. Integrals over the Brillouin zone were approximated by sums on a 4 $\times$ 4 $\times$ 2 Γ-centered k-point mesh. Values of on-site Coulomb interaction U = 8eV and exchange parameter J=0.886eV were used for the Mn d-orbital as calculated by Ref. 16. Polarization was calculated using the modern theory of polarization as implemented in VASP. All results presented are within LSDA+U with A-type AFM order. Calculations of phonons, structural energetics, and polarization were also performed within LSDA, and with both frustrated AFM and FM order; the results are essentially unchanged.

We performed full optimization of the lattice parameters and internal coordinates in the reported FE space group P6$_3$cm. As can be seen in Table II excellent agreement with the experimental RT structure (lattice constants within $\approx$0.5% and bond lengths within $\approx$1% of the experimental values) is obtained.

Group theoretical analysis (e.g. Ref. 15) shows that there are three distinct symmetry-allowed phase transition sequences connecting the high-temperature prototypic phase, P6$_3$/mmc, to the low-temperature FE phase, P6$_3$cm, as shown in Fig. I. There is a clear experimental consensus that the zone-tripling transition occurs...
fore or at the FE transition, thereby excluding P6\textsubscript{3}mc as an intermediate phase and ruling out path (1). In principle, path (2) could account for both the observed zone-tripling transition at 1270K and a possible second transition at \(\approx\)1000K. This transition sequence would be a first-order transition to the non-polar intermediate phase (by the freezing-in of a \(K_1\) phonon), followed by a second-order, proper FE transition to the RT phase (due to a softening of an infrared-active phonon). Path (3) describes a second-order transition out of the prototypic phase, by the freezing-in of a \(K_3\) phonon, directly to the FE space group. Unlike what has been proposed in the literature\(^\text{22}\text{,23}\), Path (3) does not require a second transition to account for FE order (as discussed below)\(^\text{24}\).

Independent of the path\(^\text{21}\), the distortion that relates the prototypic phase to the low temperature FE phase can be decomposed into the symmetry-adapted modes of the prototypic phase as follows: \(\Gamma_2^-\) (zone-center polar mode), \(K_1\) and \(K_3\) (zone-boundary modes at \(q=\frac{2}{3}\),0,0), and \(\Gamma_\text{\textsuperscript{\textbf{+}}}_1\) (the identical representation)\(^\text{22,23}\). This decomposition is shown in Table \(\text{III}\) for the experimental RT structure. The excellent agreement between theory and experiment for the structural transitions one expects a mode that stabilizes an intermediate phase at higher temperatures to be at least comparable in strength (not necessarily the largest) to any other modes appearing in the lower temperature phase. If \(Q_{K_3}\) were the primary structural distortion out of the prototypic phase, it should be retained through the second transition into the low temperature FE phase, which is not the case in YMnO\textsubscript{3}. Thus path (2) tends to be ruled out by the smallness of \(Q_{K_1}\). Finally, we consider the remaining possibility, path (3). The fact that \(Q_{K_3}\) is one to two orders of magnitude larger than \(Q_{\Gamma_2^-}\) and \(Q_{K_1}\) respectively, suggests that \(Q_{K_3}\) is in fact the primary structural distortion out of the prototypic phase (e.g Ref. \(\text{21}\)) and thus that YMnO\textsubscript{3} follows path (3).

First principles (\(T=0\)) investigation of the phonons and the structural energetics around the prototypic phase also shows path (3) to be the most likely scenario. For the structural parameters of the prototypic phase, we used the minimum energy structure within P6\textsubscript{3}mmc: \(a=6.168\)\(\text{A}\), \(c=11.23\)\(\text{A}\) and \(u_{O_{ap}}=0.9166\). This corresponds to a nearly homogeneous compression of the lattice constants by about 1.4% compared with those measured by Lukaszewicz at 1280K, an underestimate typical of LSDA calculations. Phonons at the \(\Gamma\) and \(K\)-point in the Brillouin zone of the prototypic phase were computed by constructing the relevant block of the dynamical matrix from Hellmann-Feynman forces. This allowed us to greatly reduce the number of calculations and provided higher numerical accuracy in the determination of the force-constant eigenvectors. At the \(\Gamma\)-point we find that the three infrared-active \(\Gamma_2^-\) phonons are stable with the lowest frequency \(\Gamma_2^-\) (TO1): \(\omega = 90\) \(\text{cm}^{-1}\). At the \(K\)-point, we computed the three \(K_3\) phonons by a similar approach.

TABLE II: Decomposition of Exp. Ref.\(^\text{2}\) atomic displacements (\(\text{A}\)) into symmetry-adapted modes of prototypic P6\textsubscript{3}mmc. Mode amplitudes, \(Q\), are shown in \(\text{A}\).

| \(\Gamma_2^-\) | \(K_1\) | \(K_3\) |
|---|---|---|
| \([001]\) | \([100]\) | \([010]\) |
| \([001]\) | \([-0.038\) | 0 | 0 | 0.310 |
| \([-0.038\) | 0 | 0 | -0.155 |
| \([-0.005\) | 0.011 | 0 | 0 |
| \([-0.005\) | 0.001 | -0.155 | 0 |
| \([-0.005\) | 0.001 | 0.155 | 0 |
| \(K_3\) | \([-0.054\) | 0 | 0 | -0.307 |
| \([-0.054\) | 0 | 0 | 0.153 |
| \(Q_{exp}\) | 0.16 | 0.03 | 0.93 |
| \(Q_{theory}\) | 0.19 | 0.01 | 1.00 |
method and found one highly unstable mode \( K_3(1) \): \( \omega = i \, 153 \text{ cm}^{-1} \). In contrast, both \( K_1 \) phonons are quite stable with \( K_1(1) \): \( \omega = 264 \text{ cm}^{-1} \) and \( K_1(2) \): \( \omega = 522 \text{ cm}^{-1} \). Since lattice instabilities are known in some cases to be sensitive to volume, we repeated these calculations at the experimental lattice constants; the results are qualitatively unchanged.

The stability of the \( \Gamma_2^- \) and \( K_1 \) modes is additional evidence to rule out paths (1) and (2), respectively. Admittedly, as these are \( T=0 \) calculations there is still a possibility that an intermediate phase could be stabilized by an anomalous entropic contribution to the free energy at finite temperatures, so that, e.g. P6\(_3\)/mcmm would be more stable than P6\(_3\)mcmm for a range of temperatures below 1270K. However, in light of the strength of the \( K_3 \) instability and as we will show, the associated energy scale, the transition out of the PE phase is most naturally driven by the \( K_3 \) mode, corresponding to path (3).

We can understand how the \( K_3(1) \) zone-boundary instability produces a polarization by calculating the energy surface around the prototypic phase as a function of the relevant modes. To simplify the analysis, the fact that all \( \Gamma_2^\pm \) and \( K_1 \) phonons are stable in the prototypic phase and contribute very little to the total structural distortion suggests that the coupling of these modes to \( K_3(1) \) will be small and can be ignored. Within this reduced subspace we expand the energy of the crystal including all symmetry allowed terms to fourth order in \( Q_{\Gamma_2} \) and \( Q_{K_3} \) to obtain:

\[
F(Q_{K_3}, Q_{\Gamma_2^-}) = \alpha_{00} Q_{K_3}^2 + \alpha_{02} Q_{\Gamma_2^-}^2 + \beta_{40} Q_{K_3}^3 + \beta_{04} Q_{\Gamma_2^-}^3 + \beta_{31} Q_{K_3}^3 Q_{\Gamma_2^-} + \beta_{22} Q_{K_3}^2 Q_{\Gamma_2^-}^2
\]

Next we performed a series of first-principles calculations where we freeze-in various amplitudes of \( Q_{K_3} \) and \( Q_{\Gamma_2^-} \) and compute the total energy. The energy expansion, Eq. (1) was then fit using only six data points, yielding excellent agreement with the remaining \( \sim 20 \) data points. As we will show, the model energy fits the calculated data well over the entire energy surface, justifying our truncation of the Taylor expansion to fourth order.

In Fig. 2 we show the total energy (of the 30-atom cell) as a function of the \( Q_{\Gamma_2^-} \) (top) and \( Q_{K_3} \) (bottom) fractional displacements. As expected, the \( \Gamma_2^- \) mode is stable while the double-well potential of the \( K_3 \) mode is apparent. The coupling between the modes can be seen by plotting the energy as a function of \( Q_{\Gamma_2^-} \) at fixed \( Q_{K_3} \) as in Fig. 3. Notice that once \( Q_{K_3} \) becomes non-zero the equilibrium position of \( Q_{\Gamma_2^-} \) (indicated by the arrow) shifts to a positive value and continues to increase with increasing \( Q_{K_3} \). Also as \( Q_{K_3} \) increases, the curvature of the energy increases due to the \( \beta_{22} = 0.155 \text{ eV} \) term which renormalizes the quadratic coefficient of \( Q_{\Gamma_2^-} \). The effect of the \( K_3 \) mode is not to decrease the stability of the \( \Gamma_2^- \) mode, but rather to “push” the \( \Gamma_2^- \) mode to a non-zero equilibrium position, playing a role analogous to that of a field. This “geometric field” is the mechanism for ferroelectricity in the hexagonal manganites. Further, the strong \( \beta_{31} = -0.334 \text{ eV} \) coupling between the \( K_3(1) \) and \( \Gamma_2^- \) (TO1) lattice modes, i.e. phonons, is responsible for the comparatively large value of \( P_s \approx 6 \mu\text{C/cm}^2 \). Indeed, if this coupling were to be turned off, the polarization generated by \( K_3(1) \) (coupling only to the electronic density) is reduced to \( P_s \approx 0.1 \mu\text{C/cm}^2 \). Now let us return to the discussion of the PE-to-FE path. If we now identify \( K_3(1) \) as the primary OP and \( \Gamma_2^- \) (TO1) as a secondary OP, inspection of Fig. 4 reveals interesting crossover behavior of the \( \Gamma_2^- \) mode. Minimizing the free energy over \( Q_{\Gamma_2^-} \) leads to two cases:

**Region 1:** \( Q_{K_3} << \sqrt{\frac{\beta_{22}}{\beta_{31}}} \Rightarrow Q_{\Gamma_2^-} \propto -\frac{\beta_{31}}{2\beta_{22}} Q_{K_3}^3 \)

**Region 2:** \( Q_{K_3} >> \sqrt{\frac{\beta_{22}}{\beta_{31}}} \Rightarrow Q_{\Gamma_2^-} \propto -\frac{\beta_{31}}{2\beta_{22}} Q_{K_3} \)

Since the polarization, \( P_s \), is a first order polar tensor it has the same transformation properties as the symmetry-adapted \( \Gamma_2^- \) mode, i.e. \( P_s \propto Q_{\Gamma_2^-} \). Using the modern theory of polarization we can calculate the polarization as a function of the structural \( \Gamma_2^- \) mode. The physical quantity of interest though is the polarization as a function of the primary OP, \( Q_{K_3} \), which we show in Fig. 4. As the \( K_3 \) structural distortion is initiated, \( P_s \) becomes non-zero but is small due to the \( Q_{K_3}^3 \) dependence until the emergence of a crossover to \( P_s \propto Q_{K_3} \). This leads to an apparent “turn-on” at a finite value of \( Q_{K_3} \). We calcu-
late the total energy (per formula unit) lowering from the PE to FE to be $\mathcal{O}(1000 K)$ (the precise value fortuitously being 1240 K) and the width of this crossover region to be $\mathcal{O}(100 K)$.

In this paper, we have shown that the overwhelming weight of the experimental and theoretical evidence supports path (3), with an improper FE transition out of the high-temperature PE phase at 1270 K. The $K_3(1)$ phonon is strongly unstable and couples to the $\Gamma_2^-$ (TO1) phonon leading to the observed polarization. The unusual dependence of the polarization on the primary order parameter would lead to a broadened pyroelectric peak lower than $T_c$ and could, through coupling to strain, lead to an isostructural, FE-to-FE transition, although this last point is only speculative. This differs from previous models in that YMnO$_3$ is already polar when this isostructural transition occurs. An additional intriguing possibility to explain the apparent lower temperature transition is that, due to the presumably inhomogeneous nature of $K_3$ near $T_c$ (which we have been assuming to be homogeneous), fluctuations suppress the coupling between $K_3(1)$ and $\Gamma_2^-$ (TO1) till some temperature lower than $T_c$, this second transition temperature likely being sample dependent. In this scenario, the path to the FE phase is still along (3), but the P6$_3$cm phase in the intermediate temperature range would be paraelectric in an average sense, as originally suggested by Lukaszewicz and Karut-Kalicinska. Clearly, further theoretical and experimental work is necessary to characterize the lower temperature isostructural transition and the nature of the polarization in the intermediate phase. Finally, it should be appreciated, that regardless of the actual path taken, the softening of the $K_3$ mode sets up a “geometric field” that induces a substantial polarization, thus providing a mechanism to achieve multiferroicity in the hexagonal manganites.

Useful discussions with S-W. Cheong, D.R. Hamann, G. Néért, T. Palstra, A. Sushkov, and D.H. Vanderbilt are acknowledged. This work was supported by NSF-NIRT Grant No. DMR-0103354.

1. S.C. Abrahams, Acta Cryst. B 57, 485 (2001).
2. B.B. VanAken, A. Meetsma, and T.T.M. Palstra, Acta Cryst. C 57, 230 (2001).
3. K. Lukaszewicz and J. Karut-Kalicinska, Ferroelectrics 7, 81 (1974).
4. G. Néért, Y. Ren, H.T. Stokes, and T.M. Palstra, cond-mat/0106298.
5. I.G. Ismailzade and S.A. Kizhaev, Sov. Phys. Solid State 7, 236 (1965).
6. T. Katsufuji, M. Masaki, A. Machida, M. Moritomo, K. Kato, E. Nishibori, M. Takata, M. Sakata, K. Ohoyama, K. Kitazawa, and H. Takagi, Phys. Rev. B 66, 134343 (2002).
7. Th. Lonkai, D.G. Tomuta, U. Amann, J. Ihringer, R.W.A. Hendrikx, D.M. Többens, and J.A. Mydosh, Phys. Rev. B 69, 134108 (2004).
8. T. Katsufuji, S. Mori, M. Masaki, Y. Moritomo, N. Yamamoto, and H. Takagi, Phys. Rev. B 64, 104419 (2001).
9. From $\partial \ln \rho$ and thermal hysteresis, private communication, S.M. Ye and S-W. Cheong.
10. N.A. Hill, J. Phys. Chem. B, 104, 6694 (2000).
11. B.B. VanAken, T.T.M. Palstra, A. Filippetti, and N.A. Spaldin, Nature Materials 3, 164 (2004).
12. C. Ederer and N.A. Spaldin, Nature Materials 3, 849 (2004).
13. V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B 44, 943 (1991).
14. G. Kresse and J. Hafner, Phys. Rev. B 47, R558 (1993); G. Kresse and J. Furthmüller, ibid. 54, 11169 (1996).
15. P.E. Blöchl, Phys. Rev. B 50, 17953 (1994); G. Kresse and D. Joubert, ibid. 59, 1758 (1999).
16. J.E. Medvedeva, V.I. Anisimov, M.A. Korotin, O.N. Mryasov, and A.J. Freeman, J. Phys.: Condens. Matter 12, 4947 (2000).
17. R.D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, R1651 (1993).
18. H.T. Stokes and D. M. Hatch (2002). ISOTROPY http://stokes.byu.edu/isotropy.html
19. Bilbao Crystall. Server: http://www.cryst.ehu.es
20. H.T. Stokes and D. M. Hatch, Phase Transitions 34, 53 (1991).
21. J.M. Pérez-Mato, M. Aroyo, A. García, P. Blaha, K. Schwarz, J. Schweier, and K. Parlinski, Phys. Rev. B 70, 214111 (2004).
22. J.M. Pérez-Mato, J.L. Mañes, M.J. Tello, and F.J. Zúñiga, J. Phys. C: Solid State Phys. 14, 1121 (1981).
23. J.L. Mañes, M.J. Tello, and J.M. Pérez-Mato, Phys. Rev. B 26, 250 (1982).
24. We normalize to the 30-atom cell. For experimental structure, $Q_{\Gamma^+} = 0$ by construction (see e.g. H.T. Stokes, C. Sadoate, D. M. Hatch, L.L. Boyer, and M.J. Mehli, Phys. Rev. B 65, 064105 (2002.).) From our first-principles calculations, $Q_{\Gamma^+} = 0.033$.
25. M.T. Dove, Structure and Dynamics (Oxford University Press, Oxford, 2003).
26. Using DFT-SIC method, the first-principles study of Ref. [11] found the total $\Gamma$ structural distortion, i.e. $\Gamma_2^+$ +
Γ_1^+ independently unstable. It should be emphasized, the essential physics of the geometrical field is the coupling between the Γ_2^- and K_3 modes and does not depend on the stability of the Γ_2^- mode.

27 C.J. Fennie and K.M. Rabe, unpublished.
28 D.R. Hamann, private communication.