We present results of local spin density approximation (LSDA) pseudopotential calculations for the ferroelectric and non-ferroelectric perovskite manganites is determined by comparing the calculated properties of yttrium manganite in its ferroelectric hexagonal and non-ferroelectric orthorhombic phases. In addition, orthorhombic YMnO₃ is compared with the prototypical non-ferroelectric manganite, lanthanum manganite. We show that, while the octahedral crystal field splitting of the cubic perovskite structure causes a centro-symmetric Jahn-Teller distortion around the Mn³⁺ ion, the markedly different splitting in hexagonal perovskites creates an electronic configuration consistent with ferroelectric distortion. We explain the nature of the distortion, and show that a local magnetic moment on the Mn³⁺ ion is a requirement for it to occur.

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I. INTRODUCTION

The observation of colossal magnetoresistance (CMR) in (La,Ca)MnO₃ [1] has prompted a flurry of recent research on this material and related perovskite structure manganites [2]. The majority of the recent research has focused on manganites in which the large (A-site) cation is a rare earth from the left hand side of the lanthanide series. The manganites of these large rare earth ions (lanthanum manganite through dysprosium manganite) all crystallize in the cubic perovskite structure (Figure 1), with the same low temperature orthorhombic distortion and A-type antiferromagnetic ordering of the Mn³⁺ ions.

During the recent studies, many rare earth manganites have been found to show strong coupling between their magnetic and structural, or magnetic and electric order parameters. For example, a magnetically induced structural phase transition has been observed in La₀.₈₃Sr₀.₁₇MnO₃ [3] indicating strong coupling between the local magnetic spin moments and the lattice structure. In Nd₀.₅Sr₀.₅MnO₃, strong coupling between the magnetic spin moments
and the electronic charge carriers was demonstrated when an electronic metal-insulator transition was induced by an external magnetic field [4]. Indeed the large change in conductivity with applied magnetic field, which causes colossal magnetoresistance is believed to originate from a similar type of phase transition [3].

The strong coupling between magnetic and electric order parameters is of particular interest in the manganites of yttrium and the smaller (holmium through lutetium) rare earths at the right hand side of the lanthanide series. In these materials, the hexagonal perovskite structure (Figure 2) is the lowest energy structure. However the metastable orthorhombic cubic perovskite phase can be regained by annealing at high pressure [4], or by appropriate choice of synthetic method. The phase transition between the stable hexagonal phase and the metastable orthorhombic phase is reconstructive and first order.

In the hexagonal manganites, as in the cubic manganites, superexchange between adjacent Mn$^{3+}$ ions causes antiferromagnetic ordering. However in addition to the magnetic ordering, the hexagonal manganites also undergo a phase transition to a non-centrosymmetric low temperature state which has ferroelectric ordering. Therefore the hexagonal yttrium and rare-earth manganites belong to the rather small group of materials known as ferroelectromagnets, in which magnetic and ferroelectric ordering occurs simultaneously. Although there are thirteen point groups which permit the occurrence of spontaneous magnetization and spontaneous polarization in the same phase [5], remarkably few ferroelectric materials show any kind (ferro- ferri- antiferro-, etc.) of magnetic ordering. Understanding the fundamental physics that tends to discourage simultaneous ferroelectricity and magnetic ordering is an area of current research activity [8]. And the fact that the ferroelectric hexagonal manganites can be readily transformed to their non-ferroelectric cubic form makes them ideal prototypes for studying this phenomenon.

The goal of the study described in this paper is to explore theoretically the similarities and differences between non-ferroelectric cubic manganites and their ferroelectric hexagonal counterparts. To achieve this goal we evaluate the electronic and magnetic properties of some representative perovskite manganites using a plane wave pseudopotential (PWPP) implementation of density functional theory (DFT) within the local spin density approximation (LSDA). Our choice of theoretical approach is influenced by successful first-principles studies of non-magnetic perovskite ferroelectrics [9,10], and by earlier work which elucidated the origins of the differences between related cubic perovskite manganites [11,12]. We calculate the differences between the electronic properties of cubic and hexagonal YMnO$_3$ to determine the reasons for the lack of ferroelectricity in cubic manganites, and its presence in hexagonal manganites. We also compare our calculated results for cubic YMnO$_3$ with those for the prototypical cubic perovskite manganite, LaMnO$_3$, to establish whether the metastability of the cubic phase of YMnO$_3$ is merely the result of the small size of the yttrium ion, or if electronic factors also play a role.

The remainder of this paper is organized as follows: In Section II we summarize the experimental results for YMnO$_3$ from the literature. In Section III we briefly describe our plane wave pseudopotential implementation of density functional theory and outline the technical details of the calculations used in this work. In Section IV our results for cubic and hexagonal YMnO$_3$ are presented, followed by a comparison of the properties of cubic YMnO$_3$ with those of LaMnO$_3$. Our results are summarized in Section V.
II. SUMMARY OF EXPERIMENTAL RESULTS

The literature on the hexagonal manganites is much more limited than that on the cubic perovskite manganites, and modern work focuses largely on yttrium manganite, YMnO$_3$. Although yttrium is not a rare earth, it forms a stable trivalent cation with a similar ionic radius to those of the smaller rare earth ions. It is favored over the smaller rare earth ions in research studies for two reasons. First, study of magnetic ordering on the Mn$^{3+}$ ions is more straightforward in YMnO$_3$ than in the rare earth manganites since there is no perturbation from the rare earth $f$-electron magnetic moment. In addition, YMnO$_3$ forms both the hexagonal and orthorhombic phases on solution synthesis at ambient pressure \[13\] making it particularly appealing for use in a comparative study.

Early (1960s) work on YMnO$_3$ \[13\] established the hexagonal phase to be ferroelectric, with the hexagonal perovskite structure and the $P6_3mc$ space group. The hexagonal perovskite structure consists of ABCACB... stacking of close packed O layers, with the Mn ions occupying 5-fold coordinated sites, and the rare earth atoms in 7-fold coordinated interstices. The ideal high temperature paraelectric structure consists of two formula units per unit cell and is shown in Figure 2. Since this structure does not occur in the perovskite ferrites it has been suggested that the ability of Mn$^{3+}$ to form 5-fold trigonal bipyramids through $dsp^3$ hybrid bonding might be a requirement \[13\]. In addition (not shown in the Figure) at low temperature the MnO$_5$ bipyramids are slightly rotated around the axis passing through the Mn and parallel to one of the triangular base sides. Early reports of a weak parasitic ferromagnetism \[14\] were soon shown to be the result of Mn$_3$O$_4$ impurity contaminating the powdered phase \[13\], and weak ferromagnetism was shown to be absent in single crystal samples \[13\].

Modern studies of hexagonal YMnO$_3$ have established that the ferroelectricity occurs along the $c$ axis (i.e.,[0001]) \[16,17\], with a spontaneous $P \approx 5.5 \mu C/cm^2$ In addition a strong coupling between the ferroelectric and magnetic ordering has been revealed \[18\]. Although the ferroelectric Curie temperature (914K) is quite different from the Néel temperature (80K), anomalies in the dielectric constant and loss tangent near the Néel temperature are indicative of coupling between the ferroelectric and antiferromagnetic orders. The coupling has been attributed to changes in the phonon spectrum associated with the antiferromagnetic transition \[18\]. Raman and infra-red spectroscopy of the high temperature paraelectric and low temperature ferroelectric phases show only weak bands in the ferroelectric phase due to the non-centrosymmetry. This indicates that the structural differences between the ferroelectric and paraelectric phases are very small. Non-linear optical spectroscopy \[19\] shows two types of optical second harmonic spectra of the Mn$^{3+}$ ions in hexagonal YMnO$_3$, one from the non-centrosymmetric ferroelectric ordering of charges, and the other caused by the centrosymmetric antiferromagnetic ordering of spins. Partial overlapping between the electronic transitions results in a nonlinear optical polarization which depends on two order parameters. A generalized Ginzburg-Landau formalism has been developed which shows that the second harmonic generation susceptibility is directly proportional to the bilinear combination of both order parameters \[20\]. Finally, epitaxial thin films of hexagonal YMnO$_3$ have been grown on (111) MgO and (0001) ZnO:Al/(0001) \[16\], and explored for use as non-volatile memory devices. YMnO$_3$ presents some technological advantages over many common ferroelectric perovskites, including lower dielectric constant ($\sim 20$ at room temperature) and non-volatile constituent elements.
In the 1970s, work began on the orthorhombic phase of YMnO$_3$. Susceptibility measurements established that orthorhombic YMnO$_3$ is an antiferromagnet with a Néel temperature of 42K, although significant deviations from Curie-Weiss behavior were seen well above the manganese ordering temperature [6]. A more detailed study [21] concluded that the Mn$^{3+}$ ordering is helical with a propagation wavevector $k = [0,0.0786,0]$ and a helical angle from plane to plane of $14^\circ$. Within each plane the ordering is antiferromagnetic.

There has also been some modern work on the orthorhombic phase of YMnO$_3$. Attempts have been made to find a synthesis which will produce a larger proportion of the metastable orthorhombic phase [22]. In addition the Raman spectrum of orthorhombic YMnO$_3$ has been measured and the Raman active phonon modes determined and compared with those of LaMnO$_3$ [23].

III. COMPUTATIONAL TECHNIQUE

The calculations described in this work were performed using plane wave pseudopotential (PWPP) implementations [24] of density functional theory [25] within the local spin density approximation (LSDA). The accuracy and efficiency of ab initio pseudopotential calculations (compared with all-electron calculations) is now well established for spin-polarized magnetic systems, and the PWPP method has been applied to a wide range of magnetic materials [26].

In this work we use both the optimized pseudopotentials developed by Rappe et al. [27] and the Vanderbilt ultra-soft pseudopotentials [28], to reduce the energy cut-off of the plane wave expansion to around 60 and 35 Ry respectively. For La and Y, we constructed scalar-relativistic pseudopotentials, and for Mn and O non-relativistic pseudopotentials were used with the partial non-linear core correction scheme of Louie et al. [29] applied to the Mn ions. The pseudopotentials were tested for transferability by comparing with all-electron calculations for a range of typical atomic and ionic configurations. The pseudo-eigenvalues and total energies were found to be equivalent to the all-electron values to within a few meVs. All pseudopotentials were converted into the usual Kleinman-Bylander form [30], and the absence of ghost states was confirmed using the ghost theorem of Gonze, Käckell and Scheffler [31]. The pseudopotential construction and the total energy calculations used the Perdew-Zunger parameterization [32] of the Ceperley-Alder exchange correlation potential [33] with the von Barth-Hedin interpolation formula [34].

The total energies and band structures were calculated using the CASTEP 2.1 [35,36] and PWSCF ultra-soft pseudopotential programs. For cubic perovskites we used a plane wave cut off of 60 Ry, which corresponds to around 3500 plane waves in a cubic unit cell with lattice constant of around 4 Å. A 6x6x6 Monkhorst-Pack [37] grid was used for all calculations for cubic systems. This led to 10 k-points in the irreducible Brillouin Zone for the high symmetry structures, and a correspondingly higher number for the structures with lower symmetry. In calculations for the hexagonal structure, a 5x5x4 Monkhorst-Pack grid was used, resulting in 18 k-points in the irreducible Brillouin Zone for the high symmetry structures. A variable Gaussian broadening between 1 eV and 0.002 eV was applied to the k-point sampling to speed convergence for metallic systems. For density of states (DOS) calculations we calculated first-principles eigenvalues of a large ($\approx 100$ in the irreducible Brillouin zone) k-point set, then interpolated using the interpolation scheme of Monkhorst and Pack [37]. We then applied the Gilat-Raubenheimer method [38] to integrate
over this fine mesh. Finally, for the band structure plots, and for use in the tight-binding analysis, symmetry labels along high-symmetry lines were assigned using projection operators for the corresponding irreducible representations.

IV. RESULTS

A. Calculated Electronic Properties of cubic and hexagonal YMnO$_3$

In this section we compare the electronic properties of YMnO$_3$ in its metastable cubic perovskite structure with those of the stable hexagonal phase. We begin by calculating the electronic structure for the ideal high symmetry structures, without including magnetic effects, then lower the magnetic symmetry to the hypothetical ferromagnetic and observed antiferromagnetic phases. Finally we introduce structural distortions to simulate the effects of the onset of ferroelectricity. This ability to isolate structural and magnetic distortions is unique to computational studies, and allows identification of the essential microscopic interactions which cause the observed macroscopic behavior.

1. High Symmetry Paramagnetic Structures

First we present the calculated electronic structures for YMnO$_3$ in the ideal cubic and hexagonal structures, without spin polarization (we call this the paramagnetic (PM) phase).

a. Cubic  Figure 3 shows the calculated density of states (DOS) for cubic paramagnetic YMnO$_3$. We chose a lattice constant of 3.84 Å which corresponds to the average of the lattice constants in the low temperature orthorhombic unit cell. The plotted energy range is from -8 eV to 4 eV, and the lower lying semi-core states have been omitted for clarity. The Fermi level is set to zero. The broad series of bands between approximately $-2$ and $-7$ eV arises primarily from the oxygen 2$p$ orbitals. Above the oxygen 2$p$ bands, and separated from them by an energy gap, are the Mn 3$d$ bands. The Mn 3$d$ bands are divided into two sub-bands - the lower energy $t_{2g}$ bands, and the higher energy $e_g$ bands - as a result of the crystal field splitting by the octahedral oxygen anions. The Fermi level lies near the top of the Mn 3$d$ $t_{2g}$ bands and is in a region of high density of states. The large DOS at the Fermi level confirms that the cubic PM structure is unstable, and that a lower energy structure could be achieved by allowing spin-polarization and/or structural distortion.

b. Hexagonal  The hexagonal paraelectric structure has three lattice parameters; the usual $a$ and $c$ parameters plus an internal $u$ that gives the distance (in units of $c$) between oxygen and yttrium layers, and is not fixed by the symmetry. In ideal hexagonal structures (without tilting of the oxygen octahedra) the atomic positions in crystal coordinates are: Y at $(0,0,0)$ and $(0,0,\frac{1}{2})$, Mn at $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{4})$ O at $(0,0,\frac{1}{4})$, $(0,0,\frac{3}{4})$, $(\frac{1}{3},\frac{2}{3},u),(\frac{2}{3},\frac{1}{3},1-u)$, $(\frac{2}{3},\frac{1}{3},\frac{1}{2}+u)$ and $(\frac{1}{3},\frac{2}{3},\frac{1}{2}-u)$, with $u$ not fixed by the symmetry. By energy minimization we obtain $a=3.518$ Å, $c=11.29$ Å, and $u=0.084$, in very good agreement with the experimental values $a=3.539$ Å, $c=11.3(4)$ Å, and $u=0.084$. This suggests that the oxygen tilting which we are neglecting in these calculations indeed has little effect on the structural properties. Note however that in the ideal, non-magnetic, high symmetry structures, we find that the hexagonal phase is not energetically stabilized over the cubic phase. This indicates that the low temperature structural distortions
and magnetic polarizations which we investigate in the next section are responsible for the stability of the hexagonal phase.

In Figure 4 we show the calculated orbital-resolved DOSs for the non-magnetic hexagonal phase at the LSDA minimum energy lattice parameters. For clarity only the DOS on the transverse oxygens is shown since these are most strongly involved in chemical bonding with the Mn ion and will be most important in our later analysis of ferroelectricity. As in the cubic case, the non-magnetic hexagonal phase shows a large DOS at $E_F$, mostly due to the Mn $d$ states located in a narrow region around $E_F$. In sharp contrast with the cubic phase, however, the hexagonal crystal field splits the $d$ states into three groups. The $d_{xy}$ and $d_{x^2−y^2}$ orbitals lie on the (0001) plane and are nearly degenerate (only one of them is shown in the Figure). These orbitals point towards the nearby in-plane oxygens (O$_P$), and so are able to participate in covalent bonding, therefore they form a rather broad band. The $d_{xz}$ and $d_{yz}$ orbitals are also almost degenerate. Their DOSs overlap with those of $d_{xy}$ and $d_{x^2−y^2}$, but are localized in a narrower energy region, since they do not point directly towards oxygens and therefore their bands are not broadened by hybridization. Each orbital of the two doublets is roughly half occupied. Finally, $d_{z^2}$ (shaded gray in the Figure for clarity) is the highest in energy and the least occupied. It points towards the transverse oxygens (O$_T$) which are the closest ligands to the Mn ions and therefore cause the strongest crystal field destabilization. (The distance between the Mn ion and the transverse oxygens along the $c$ axis is 1.875 Å and that between the Mn ion and the in-plane oxygens is 2.03 Å.) However it is important to note that a certain amount of $d_{z^2}$ charge is hybridized with the O$_T$ $p_z$ states located ~ 5 eV below $E_F$.

In the next section we will show that these important differences in the splitting of the Mn $d$ bands resulting from the different Mn coordination in the two structures, which are apparent already in the high symmetry paramagnetic phases, have a profound effect on their subsequent electronic, structural and magnetic properties in the realistic spin-polarized structures.

2. High symmetry structural phases with magnetic polarization

Next we calculate the properties of both cubic and hexagonal phases, still with the ideal structural high symmetry, but this time in the experimentally observed antiferromagnetic ground state. In both cases, allowing spin polarization lowers the total energy, consistent with the Stoner model, and introduces magnetic moments onto the Mn ions.

a. Cubic  In Figure 5 we show the orbital resolved densities of states on single Mn and O ions, in ideal cubic A-type antiferromagnetic YMnO$_3$ at the same lattice constant used for the paramagnetic calculations. The A-type AFM phase consists of ferromagnetically aligned (100) planes of Mn ions coupled antiferromagnetically to each other. Due to the exact AFM symmetry, each atom has a corresponding atom in the cell with anti-aligned spin, so the up and down components of DOS are exchanged. The upper plot shows the up-spin and down-spin Mn $3d$ densities of states above and below the x-axis respectively, and the lower plot shows the up-spin oxygen density of states. The down-spin oxygen density of states is not shown since it is very similar to the up-spin. The oxygen density of states in this region derives almost entirely from the oxygen $2p$ orbitals; there is negligible contribution from the O $2s$ orbitals in
the region shown. The densities of states of the $d_{xy}$, $d_{xz}$ and $d_{yz}$ (not shown) orbitals are very similar. In the absence of the antiferromagnetic ordering these would be identical by symmetry and would form the $t_{2g}$ manifold. Similarly the $d_{z^2}$ and $d_{x^2-y^2}$ bands, from the $e_g$ manifold, are alike. The $t_{2g}$ band is rather narrow for both spin directions, and clearly shows an exchange splitting of around 2 eV. This splitting causes the majority $t_{2g}$ band to be fully occupied while the minority $t_{2g}$ band contains only a small amount of electron density. The $e_g$ band is much broader since the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals are more able to hybridize with their oxygen neighbors. It is roughly half-occupied in the majority case, but completely unoccupied in the minority case. The calculated Mn magnetic moment of around 3 \( \mu_B \), significantly reduced from the Hund’s rule value of 4 \( \mu_B \) expected for a $d^4$ ion, reflects the fact that the exchange splitting is not large enough to produce full spin polarization. It is interesting to note that the region of overlapping energy between the Mn 3$d$ and oxygen 2$p$ states is in fact rather small, with only a small amount of Mn density occurring in the oxygen rich region between around -3 and -9 eV, and vice versa. The similarity between the up- and down- spin oxygen densities of states is a consequence of the small Mn 3$d$ - O 2$p$ overlap.

For comparison, the orbital resolved densities of states in ideal cubic ferromagnetic YMnO$_3$ are shown in Figure 6. The upper plot shows the up-spin and down-spin Mn 3$d$ densities of states above and below the x-axis respectively, and the lower plot shows the up- and down-spin oxygen densities of states. In this case we have plotted only one of the $t_{2g}$ and one of the $e_g$ bands for clarity. The only point that we want to make here is that the densities of states are very similar to those of the antiferromagnetic structure. Therefore as long as spin polarization is allowed, the electronic structure is not very sensitive to the relative polarization of neighboring Mn ions.

b. Hexagonal

The paraelectric hexagonal structure contains two Mn ions per unit cell, allowing studies of FM and AFM spin orientations without employing supercells. We find that the AFM phase is slightly lower in energy than the FM phase, as is the case in experiment. We focus on the AFM phase in what follows although, as we saw already in the cubic case, the spin ordering is not essential for our arguments. The properties that we consider here are determined by the local (i.e. internal to the oxygen cage) spin polarization rather than by long-range magnetic ordering.

In contrast to the non-spin-polarized phase, in which the $d_{xz}$, $d_{yz}$ and $d_{xy}$, $d_{x^2-y^2}$ doublets were roughly half occupied, here the Stoner exchange produces a \( \sim 2.5 \) eV energy splitting that causes these four orbitals to become almost completely spin polarized (Figure 7). Their total up and down charges are indeed 3.93 and 0.47 electrons, respectively, while the occupation numbers of $d_{xz}^\uparrow$ and $d_{xz}^\downarrow$ orbitals are 0.53 and 0.30 electrons. The resulting magnetic moment on Mn (3.7 \( \mu_B \)) is less than the 4 \( \mu_B \) Hund’s rule value because of the hybridization of $d_{z^2}^d$ with $O_T$ $p_z$ states, and of $d_{xy}$ and $d_{x^2-y^2}$ with $O_P$ $p_x$ and $p_y$ states. However it is larger than the value calculated for the cubic case because of the larger exchange splitting occurring here. A non-negligible magnetic moment, M=0.15 \( \mu_B \), is also present on O$_T$, driven by exchange with the $d_{xy}$ and $d_{x^2-y^2}$ orbitals, whereas the magnetization of O$_P$ is almost vanishing, due to the AFM symmetry (for $u=0$ it would be exactly zero).

The large spin splitting does not manage to open a gap. Indeed there is a tiny DOS at $E_F$, to which $d_{xy}$ and $d_{x^2-y^2}$ orbitals from Mn, and $p_x$ and $p_y$ orbitals from O$_P$ contribute. This means that the bands crossing $E_F$ come completely from orbitals oriented in the $x - y$ plane (the tilting of the oxygen cages in the ferroelectric structure is
probably sufficient to open an energy gap). The mainly planar distribution of the charge density is also evident from the band energies shown in Figure 8, calculated within the $k_z=0$ plane of the Brillouin zone (left panel), and along [0001] (right panel). Only one band crosses $E_F$ at $k_z=0$, and its orbital character is a mix of $d_{xy}^\uparrow$ and $d_{x^2-y^2}^\uparrow$ states from Mn, and $p_x^\uparrow$ and $p_y^\uparrow$ states from O$_P$. The band energies are extremely flat along [0001], as is typical for a strongly layered compound. The system can be described as a poor metal in the $x-y$ plane, and as an insulator perpendicular to it. If we discard the first unoccupied bands coming from in-plane orbitals, we obtain a one-dimensional ‘pseudogap’ of $\sim 2$ eV between occupied O$_T$ $p$ and empty Mn $d_{z^2}$ states, similar to the energy gap present between occupied oxygen states and empty transition metal $d$ states in classic ferroelectric perovskite oxides such as BaTiO$_3$.

3. Effects of ferroelectric distortion on the electronic properties of cubic and hexagonal structures

Finally we investigate the sensitivity of the charge distribution to atomic displacements by moving the Mn and in-plane oxygen atoms in opposite directions along the $c$ and $z$ axes in hexagonal and cubic phases respectively.

The results for the hexagonal structure are shown in Figure 9. Note that since the electric polarization occurs along the $c$ axis, and the bipyramidal tilting does not alter significantly the features of this compound, the paraelectric structure without the addition tilting is a sufficient starting point for the purpose of studying the nature of the ferroelectric displacement. For clarity, only the Mn orbitals most involved in the change of hybridization (i.e. $d_{xz}$ and $d_{z^2}$) are shown. The change of DOS upon distortion is very evident. The Mn $d$ DOS is shifted down by $\sim 2$ eV and is strongly hybridized with the O$_T$ $p$ states that are localized in a $\sim 1$ eV wide energy region. The atomic displacements increase the overlap of $d_{z^2}$ and O$_T$ $p_z$ orbitals, inducing a $pd_\sigma$ hybridization, and the overlap of $d_{xz}$ and $d_{yz}$ with O$_T$ $p_x$ and $p_y$ orbitals, increasing the $pd_\pi$ hybridization. Note that very similar changes in hybridization with ferroelectric displacement are seen in the prototypical ferroelectric BaTiO$_3$ [39]. However in BaTiO$_3$ all the Ti 3$d$ orbitals are formally empty, and so displacement in any direction causes an energy lowering rehybridization as the oxygen ions transfer charge into the empty $d$ orbitals. By contrast, the ferroelectricity in YMnO$_3$ is strongly uniaxial because only the $d_{z^2}$ orbital is empty. Since the majority spin $d_{xz}$ and $d_{yz}$ orbitals are almost completely filled, their changes of hybridizations with oxygen on displacement, although significant, do not contribute to a change in electric polarization.

The markedly different results which we obtain for the cubic structure are shown in Figure 10. Again only those orbitals most affected by the distortion (Mn $d_{z^2}$ and $d_{xz}$ and O$_T$) are shown. The changes in DOS on distortion are much less pronounced and quite different in character from those which we found for the hexagonal phase. The most obvious change is a destabilization of the $d_{xz}$ band which results from the larger crystal field repulsion as the Mn is moved closer to the transverse oxygens along the $z$ axis. Since the $d_{xz}$ orbitals are part of the filled $t_{2g}$ manifold they are unable to lower their energy by rehybridization with the oxygen 2$p$ states, therefore the only contribution to their energetics is the unfavorable crystal field repulsion. Note that a typical Jahn-Teller distortion, in which the oxygens along the $z$ axis move away from the cation, would have the opposite effect. In addition there is a slight broadening and shift down in energy of the $d_{z^2}$ band, which, since it was originally partly unoccupied, is now better able to accept
charge density from the oxygen ligand that it has moved closer to. There is an almost rigid shift of the oxygen 2p bands to lower energy relative to the Fermi energy. This in fact a consequence of the shift of the Fermi level to higher energy due to the destabilization of the Mn 3d bands. The fact that the form of the oxygen bands does not change significantly is an indication that rehybridization is minimal.

B. Comparison of the electronic properties of cubic YMnO$_3$ and LaMnO$_3$

Finally we briefly compare our calculated band structures of YMnO$_3$ in its metastable cubic perovskite structure, with those of the prototypical cubic manganite, LaMnO$_3$. The purpose of this section is to determine whether there are any important differences between the electronic properties of cubic YMnO$_3$ and LaMnO$_3$ which might explain why the cubic phase is stable in LaMnO$_3$ but metastable in YMnO$_3$. (Note that the cubic phase does not support ferroelectricity for either compound, therefore since LaMnO$_3$ does not form in the hexagonal structure it is never ferroelectric.) In fact we will find that the band structures of cubic YMnO$_3$ and LaMnO$_3$ are very similar, and therefore conclude that LaMnO$_3$ only forms in the cubic phase, whereas YMnO$_3$ can be either cubic or hexagonal (and therefore ferroelectric) because the yttrium ion is smaller than the lanthanum ion.

First we report in Table I the relative energies of the paramagnetic (PM), ferromagnetic (FM) and A-type (AFM) phases of cubic YMnO$_3$ and LaMnO$_3$. The relative energies of FM and AFM phases of LaMnO$_3$ are taken from Ref. [12] and those for YMnO$_3$ were calculated in this work. The most important feature for our purposes is that the relative orderings of the states is the same in YMnO$_3$ as in LaMnO$_3$. It is also striking that in both cases the ferromagnetically ordered state is the most stable phase. This has been pointed out previously for LaMnO$_3$ [12], and the relationship between the observed Jahn-Teller distortion and the resulting A-type antiferromagnetic ground state is well understood [41]. Also, in both cases the calculated magnetic moment is about 3.0 $\mu_B$ per Mn for the cubic FM and AFM structures, lower than the spin-only value of 4 $\mu_B$ for the Mn$^{3+}$ ion as discussed earlier. The similarity in magnetic moment indicates similar amounts of spin-polarization and hybridization in both cases.

Figure 11 shows the band structures of cubic PM YMnO$_3$ and LaMnO$_3$ plotted along the high symmetry axes of the simple cubic Brillouin Zone. The Fermi level is set to 0 eV in both cases. The broad O 2p bands between around -2 and -7 eV can be seen clearly in both materials, with the Mn 3d bands above them, separated by an energy gap. In LaMnO$_3$, the Mn 3d bands are largely separated in energy at each k-point from the next highest energy bands, which are the La 5d bands. The highlighted lines in the LaMnO$_3$ band structure plots accentuate the upper and lower Mn 3d bands, which have a similar form to each other and have been seen in other cubic perovskite manganites (see Refs. [11] and [12].) This indicates a ‘universality’ in the manganite structure throughout the cubic perovskite manganite series, which is independent of the identity of the large cation. The same structure for the upper and lower Mn 3d bands can also be identified in the YMnO$_3$ band structure, however the Mn 3d bands are slightly broader than those in LaMnO$_3$ because the smaller lattice constant results in greater Mn 3d - O 2p overlap. The smaller lattice constant, and correspondingly larger crystal field repulsion, is also responsible for the larger $t_{2g}$ - $e_g$ splitting which can be clearly seen at the $\Gamma$ point. In addition the Y 4d bands are lower in energy than the La 5d bands. These factors result
in the lower part of the Y 4d bands intersecting the upper part of the Mn 3d bands in some regions of the Brillouin zone, making the universal structure less well-defined.

To quantify any differences between cubic PM Y\(_{2}\)MnO\(_3\) and LaMnO\(_3\), we performed tight-binding analyses of the \(\Gamma\) to X regions of the respective band structures. Tight-binding parameters were obtained by non-linear-least-squares fitting \([40]\) to the calculated \textit{ab initio} energies at the high symmetry \(\Gamma\) and X points, and at 19 points along the \(\Delta\) axis. The tight-binding parameters thus obtained are given in Table I. In both cases a good (root mean square (RMS) deviation from the \textit{ab initio} energies of 0.20) fit was obtained by including only oxygen 2s and 2p and Mn 3d orbitals in the basis set, since we find no significant covalent bonding between the A cation and either the oxygen 2p or the Mn 3d orbitals. This is consistent with an early proposal by Goodenough \([41]\) that the magnetic properties of the rare earth manganites are determined by the Mn 3d - O 2p hybridization only. The parameters for Y\(_{2}\)MnO\(_3\) are similar to those for LaMnO\(_3\), except for an increase of around 10 % in the Mn 3d - O nearest neighbor overlaps. This is a consequence of the smaller lattice constant in Y\(_{2}\)MnO\(_3\), and results in the slightly broader Mn 3d bands noted above.

To test the effect of size on the electronic properties, we also calculated the properties of cubic paramagnetic Y\(_{2}\)MnO\(_3\) at the experimental LaMnO\(_3\) lattice constant of 3.95 Å. The resulting band structure of this hypothetical structure (not shown) is qualitatively similar to that of Y\(_{2}\)MnO\(_3\) at the true experimental lattice constant, except for a slight narrowing of the bandwidths as a result of the reduced overlap between the atomic wavefunctions, and a reduced \(t_{2g}\) - \(e_g\) splitting as a result of the lower crystal field repulsion.

We find that introduction of spin polarization causes the same kinds of changes in both compounds, therefore the conclusions drawn from analysis of the paramagnetic band structures continue to be valid. Figure 12 shows the up and down-spin band structures for Y\(_{2}\)MnO\(_3\) and LaMnO\(_3\) along the high symmetry axes of the simple cubic Brillouin Zone. (We chose the ferromagnetic (FM) phases for simplicity in interpreting the band structures; as discussed above, we are interested in the effects of spin polarization rather than the nature of the ordering between magnetic moments.)

First we examine the up- and down-spin LaMnO\(_3\) band structures, and compare with the PM LaMnO\(_3\) band structures to determine the changes which spin polarization causes in a ‘conventional’ manganite. The states which correspond to non-magnetic atoms are unchanged from the paramagnetic state, and are identical for up- and down-spin electrons. For example, the dispersion of the lowest O 2p band is very similar for up- and down-spin, and for the PM phase. Also the La 5d bands, which were above the Mn 3d bands in the PM state are unchanged in form and energy. The characteristic perovskite manganite Mn 3d pattern which we remarked on earlier persists in the FM phase, appearing around 2 eV higher for the down-spin electrons than for the up-spin because of the exchange splitting. The up-spin Mn 3d and O 2p bands are strongly hybridized and there is no gap between them. However, the down-spin Mn 3d are split off from the O 2p bands by a larger gap than in the PM case. As a result, the Mn 3d bands occupy the same energy region as the unoccupied La 5d bands. The Fermi level cuts through the very bottom of the down-spin Mn 3d bands, and the conduction band is occupied almost entirely by up-spin electrons, indicating half-metallic behavior.

Finally we compare the up- and down-spin Y\(_{2}\)MnO\(_3\) band structures. The first notable feature is that the non-magnetic Y 4d bands and O 2p bands are very similar for both up- and down-spin. This is because the exchange
interaction in this hypothetical ferromagnetic Y MnO$_3$ structure does not remove the gap between the majority Mn $d$ bands and the O 2$p$ band. (By contrast, in LaMnO$_3$ the higher O 2$p$ bands overlap with the majority Mn 3$d$ bands and therefore show a polarization dependence). This is again the result of the smaller lattice constant in Y MnO$_3$, which destabilizes the unfavorable FM interactions compared with those in LaMnO$_3$, where the Mn ions are further apart. Both up- and down-spin Mn 3$d$ bands show the characteristic perovskite manganite features (most noticeable in this case along the M-R-X directions) which we noted earlier in our discussions of the PM band structures.

The strong similarities between the calculated properties of cubic Y MnO$_3$ and LaMnO$_3$ that we have presented in this section confirm that the observed differences between the properties of hexagonal and cubic manganites are merely the result of the different sizes of the large cations in the two materials stabilizing different structures, and not due to any additional covalent bonding effects.

V. CONCLUSIONS

In summary, the formal similarity of $d^4$ Mn$^{3+}$ in hexagonal and cubic Y MnO$_3$ does not prevent the two phases from showing quite different properties. In particular, the difference between hexagonal and cubic field symmetry induces a very different charge distribution. In cubic perovskites, the Mn$^{3+}$ ion has partially occupied $e_g$ states. This creates an instability relieved by Jahn-Teller distortion and the ordering of Mn orbitals on the (001) plane. Both Jahn-Teller and orbital ordering tend to favor structural configurations that keep Mn and O aligned on the same plane, and therefore do not result in ferroelectricity. In the hexagonal perovskites, the crystal field produces an ordering of $d$ states that leaves the $d_{z^2}$ orbital mostly unoccupied, and thus able to hybridize with the $p_z$ orbital of the transverse oxygen. This charge environment favorable to electric polarization along the $c$ axis is only realized in condition of spin-polarization, not for the non-magnetic hexagonal phase. Thus, in hexagonal Y MnO$_3$ the spin-polarization is actually the factor which enables the ferroelectricity. Finally, we emphasize that the transition from the AFM to the paramagnetic phase above $T_N=80$ K (i.e. well below the critical temperature of the ferroelectric phase), does not invalidate our picture, since it is the local spin-polarization of Mn$^{3+}$ that matters, independently of the actual presence (or absence) of spin ordering. Note also that there are no fundamental differences between the electronic structures of metastable cubic Y MnO$_3$ and the prototypical stable cubic manganite, LaMnO$_3$. Therefore the metastability of the cubic perovskite phase in Y MnO$_3$ is simply the result of the smaller size of the A cation which is unable to stabilize the cubic phase.

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Figure Captions

FIG. 1. The ideal cubic perovskite structure. The small B cation (in black) is at the center of an octahedron of oxygen anions (in gray). The large A cations (white) occupy the unit cell corners.

FIG. 2. The ideal hexagonal perovskite structure. The small B cation (in black) is five-fold coordinated by oxygen anions (in gray). The dashed lines indicate the oxygen pentahedra. The large A cations (white) occupy seven-fold coordinated sites.

FIG. 3. Calculated density of states for cubic paramagnetic YMnO$_3$.

FIG. 4. Orbital resolved densities of states for Mn and transverse oxygen in the paraelectric non-magnetic phase of hexagonal YMnO$_3$. Only one DOS for each of the nearly degenerate pairs of orbitals ($d_{xy}, d_{x^2-y^2}$) and ($d_{xz}, d_{yz}$) is shown.

FIG. 5. Orbital resolved densities of states on single Mn and O atoms in cubic antiferromagnetic YMnO$_3$.

FIG. 6. Orbital resolved density of states in cubic ferromagnetic YMnO$_3$.

FIG. 7. Orbital resolved DOS of a single Mn ion (top panel), in-plane oxygen O$_P$ (middle), and transverse oxygen O$_T$ (bottom) in the paraelectric AFM phase of hexagonal YMnO$_3$. $p^u$ and $p^d$ indicate up and down components of O p DOS, respectively.

FIG. 8. Band energies of paraelectric AFM hexagonal YMnO$_3$. $Q=\pi/a (0,2/3,1/2,0)$, $P=\pi/a (1,1/3,1/2,0)=\Gamma$.

FIG. 9. Orbital-resolved DOS for single Mn and O in hexagonal AFM YMnO$_3$. The upper panel is for the paraelectric structure, the lower for the structure with Mn and O displaced along the c axis, in the fashion of a ferroelectric distortion.

FIG. 10. Orbital-resolved DOS for single Mn and O in cubic A-type AFM YMnO$_3$. The upper panel is for the paraelectric structure, the lower for the structure with Mn and O displaced along the z axis, in the fashion of a ferroelectric distortion.

FIG. 11. Calculated band structures for cubic paramagnetic LaMnO$_3$ and YMnO$_3$ along the high symmetry axes of the Brillouin Zone. The highlighted lines in the band structure plots accentuate the upper and lower Mn 3$d$ bands, which have a similar form to each other and to those of other perovskite manganites.

FIG. 12. Up- and down-spin band structures for cubic LaMnO$_3$ and YMnO$_3$ along the high symmetry axes of the Brillouin Zone.
TABLE I. Tight-binding parameters (in eV) for cubic LaMnO$_3$ and YMnO$_3$ obtained by non-linear-least-squares fitting to the ab initio eigenvalues along $\Gamma$ to X. E indicates an orbital energy, and $V$ an inter-atomic transfer integral. All transfer integrals are between nearest neighbors, except those with the subscript '2' which are between next nearest neighbors. Only the parameters listed in the table were allowed to be non-zero in the fitting procedure.

|                | LaMnO$_3$                  | YMnO$_3$                  |
|----------------|----------------------------|----------------------------|
| $E_{O2s}$      | -17.836376                 | -17.9649                   |
| $E_{O2p}$      | -4.514022                  | -4.7382                    |
| $E_{Mn3d}$     | -1.191285                  | -1.4097                    |
| $V_{O2s-O2s}$  | -0.243683                  | -0.2461                    |
| $V(O_{2p}-O_{2p})_\sigma$ | 0.620568 | -0.7167                   |
| $V(O_{2p}-O_{2p})_\pi$ | -0.063466 | -0.1069                   |
| $[V(O_{2p}-O_{2p})_\sigma]_2$ | 0.182635 | 0.1688                     |
| $[V(O_{2p}-O_{2p})_\pi]_2$ | 0.082951 | 0.0620                     |
| $V_{O2s-Mn3d}$ | -1.735814                  | -1.9711                    |
| $V(O_{2p}-Mn_{3d})_\sigma$ | -1.838490 | -2.0601                    |
| $V(O_{2p}-Mn_{3d})_\pi$ | 0.878961 | 1.0837                     |
| $V(Mn_{3d}-Mn_{3d})_\delta$ | 0.066346 | 0.0488                     |

TABLE II. Relative energies of different magnetic phases in cubic paramagnetic YMnO$_3$ and LaMnO$_3$.

|                | YMnO$_3$                  | LaMnO$_3$                  |
|----------------|----------------------------|----------------------------|
| FM             | 0                          | 0                          |
| A-AFM          | +140 meV                   | +110 meV                   |
| PM             | +0.70 eV                   | +1.16 eV                   |
Density of States

Manganese

- \( d_{z^2} \)
- \( d_{xy} \)
- \( d_{xz} \)

Oxygen p

Energy (eV)
Density of States

Manganese

- $\text{d}_{xy}$
- $\text{d}_{xz}$
- $\text{d}_{x^2-y^2}$
- $\text{d}_{z^2}$

Oxygen

Energy (eV)
Manganese

Density of States

Energy (eV)
Oxygen $p$-orbitals

Manganese $d_{xz}$, $d_{z^2}$

Density of States

Energy (eV)
Energy (eV)

FM LaMnO$_3$ minority

FM YMnO$_3$ minority

FM LaMnO$_3$ majority

FM YMnO$_3$ majority