First Principles Study of Multiferroic Magnetoelectric Manganites

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Abstract. Multiferroic magnetoelectrics are materials which are both ferromagnetic and ferroelectric in the same phase. As a result they have a spontaneous magnetization which can be switched by an applied magnetic field, a spontaneous polarization which can be switched by an applied electric field, and often some coupling between the two. Very few exist in nature, or have been synthesized in the laboratory. In this paper we explore the fundamental physics behind the scarcity of ferromagnetic ferroelectric coexistence, and examine the properties of some known magnetically ordered ferroelectric materials. We find that in general the transition metal $d$ electrons, which are essential for magnetism, reduce the tendency for off-center ferroelectric distortion. Consequently, an additional electronic or structural driving force must be present for ferromagnetism and ferroelectricity to occur simultaneously.

INTRODUCTION

The last few years have seen a flurry of activity in the study of magnetic materials, which previously (according to a recent “Physics Today”!) had an image of “musty physics laboratories peopled by old codgers with iron filings under their nails” [1]. Advances in atomic- and nano-scale growth and characterization techniques have led to the production of modern magnetic materials which reveal a range of fascinating phenomena. These phenomena derive from the fact that electrons have spin as well as charge, giving an extra level of complexity to the physics, and an extra degree of freedom in device design. Today, the science and technology of magnetism have undergone a renaissance, driven both by the urge to understand the new physics, and by demand from industry for better materials [2].

This paper explores a somewhat obscure class of magnetic materials known as magnetoelectric multiferroics, which are simultaneously ferroelectric and ferromagnetic (or at least show some kind of magnetic ordering) [3]. Such materials have all the potential applications of both their parent ferroelectric and ferromagnetic materials. In addition, a whole range of new applications can be envisaged, including multiple state memory elements, in which data is stored both in the electric and the magnetic polarizations, or novel memory media which might allow writing of a ferroelectric data bit, and reading of the magnetic field generated by association
Aside from the potential applications, the fundamental physics of multiferroic materials is rich and fascinating.

In this work we focus on the puzzling question of why so few multiferroic magnetoelectrics exist. After briefly reviewing the history and properties of multiferroic materials, we describe the properties of one specific multiferroic material - bismuth manganite - and present the results of our calculations to determine the origin of the multiferroism in this material. Finally we suggest some potential avenues for exploration of new multiferroic materials.

HISTORY OF MAGNETOELECTRIC MULTIFERROICS

The first ferromagnetic ferroelectric material to be discovered [5] was weakly ferromagnetic nickel iodine boracite, Ni$_3$B$_7$O$_{13}$I. This was followed by the synthesis of many more multiferroic boracite compounds, all of which have complex structures with many atoms per formula unit, and more than one formula unit per unit cell. The large number of inter-ionic interactions in the boracites prevented isolation of the essential factors causing multiferroicity, and of the nature of the coupling between the magnetic, electric polarization, and structural order parameters. Nickel iodine boracite can be thought of as the “Rochelle salt” of magnetic ferroelectrics - invaluable for demonstrating proof of concept, but unlikely to find wide applicability, or to contribute to our increased understanding in the field.

The search for other ferromagnetic ferroelectrics began in Russia in the 1950s, with the replacement of some of the $d^0$ B cations in ferroelectric perovskite oxides by magnetic $d^n$ cations [6]. The first synthetic ferromagnetic ferroelectric material, $(1-x)$Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$ - $x$Pb(Mg$_{1/2}$W$_{1/2}$)O$_3$, was produced in the early 1960s using this approach. Here the Mg$^{2+}$ and W$^{6+}$ ions are diamagnetic and cause the ferroelectricity, and the formally $d^5$ Fe$^{3+}$ ion is responsible for the magnetic ordering. Other examples include B-site ordered Pb$_2$(CoW)O$_6$ [7] which is ferroelectric and ferromagnetic, B-site disordered Pb$_2$(FeTa)O$_6$ [7] which is ferroelectric and antiferromagnetic and Pb$_2$(FeTa)O$_6$ [8] and Pb$_2$(FeTa)O$_6$ [9], which are both ferroelectric and antiferromagnetic, with weak ferromagnetism below around 10K. As a result of dilution of the magnetic ions, these materials all have rather low Curie or Néel temperatures. However a number of simple perovskite materials are known to have ferroelectric and magnetic (mostly of the antiferromagnetic type) ordering. These include the manganites of the small rare earths and yttrium, and a few compounds in which Bi is the large cation.

REQUIREMENTS FOR MAGNETOELECTRIC MULTIFERROICITY

By definition, for a material to be a magnetoelectric multiferroic it must be simultaneously ferromagnetic and ferroelectric. Therefore its allowed physical, structural
and electronic properties are restricted to those which occur both in ferromagnetic and in ferroelectric materials. In this Section we analyze a range of properties and discuss how these limit our choice of potential materials.

**Symmetry.** A primary requirement for the existence of ferroelectricity is a structural distortion from the prototypical high symmetry phase which removes the center of symmetry and allows an electric polarization. There are 31 point groups which allow a spontaneous electric polarization, $\mathbf{P}$, and 31 which allow a spontaneous magnetic polarization, $\mathbf{M}$ [3]. 13 point groups (1, 2, 2', $m$, $m'$, 3, 3$m'$, 4, 4$m'm'$, $m'm2'$, $m'm2'$, 6 and 6$m'm'2'$) are found in both sets, allowing both properties to exist in the same phase. Although this represents a considerable reduction from the total number of possible crystal structures (the total number of Shubnikov point groups is 122), it is not an insignificant number, and many candidate materials which are not in fact ferromagnetic and ferroelectric exist in one of the allowed symmetries. Therefore it is unlikely that symmetry considerations are responsible for the scarcity of ferromagnetic ferroelectric materials.

**Electrical Properties.** By definition, a ferroelectric material must be an insulator (otherwise an applied electric field would inducing an electric current to flow, rather than causing an electrical polarization.) Ferromagnets, although not required to have specific electrical properties, are often metals. For example the driving force for ferromagnetism in the elemental ferromagnets Fe, Co and Ni, and their alloys is the high density of states at the Fermi level, which also of course results in metallicity. Therefore one could assume that the lack of simultaneous occurrence of magnetic and ferroelectric ordering is simply the result of a dearth of magnetic insulators. However if we extend our search to include ferrimagnets or weak ferromagnets (which have canted antiferromagnetic ordering, resulting in a weak magnetic moment in the direction of the canting) this argument no longer holds, since most ferrimagnets or weak ferromagnets are in fact insulators. In addition, there are also very few antiferromagnetic ferroelectrics, even though antiferromagnets are usually insulating materials. Therefore it appears that we cannot blame the lack of magnetically ordered ferroelectrics simply on a shortage of magnetically ordered insulators.

**Chemistry - “$d^0$-ness”**. Most common perovskite oxide ferroelectric materials have a formal charge corresponding to the $d^0$ electron configuration on the B cation. Clearly if there are no $d$ electrons creating localized magnetic moments, then there can be no magnetic ordering of any type, either ferro-, ferri-, or antiferromagnetic. It appears however that, in most cases, as soon as the $d$ shell on the small cation is partially occupied, the tendency for it to make a distortion which removes the center of symmetry is eliminated. This could be the result of a number of effects:

**Size of the small cation.** Are transition metal ions with occupied $d$ shells simply too large to move away from the large space at the center of the oxygen octahedron? The Shannon ionic radii [10] of some common $d^0$ B cations found in ferroelectric perovskite oxides are: Ti$^{4+}$ - 74.5 pm, Nb$^{5+}$ - 78 pm and Zr$^{4+}$ - 86 pm. Some representative $d^0$ cations which are found as the small cations in non-ferroelectric perovskite oxides include Mn$^{3+}$ ($d^4$), Ti$^{3+}$ ($d^1$) and V$^{4+}$ ($d^1$) with radii of 78.5 pm,
81 pm and 72 pm respectively. Therefore typical B site cations with \( d \) electron occupation do not have systematically larger radii than typical \( d^0 \) B site cations. We conclude that the size of the B cation is not the deciding factor in the existence or otherwise of ferroelectricity.

Structural distortions. Ferroelectric materials must undergo a phase transition to a low temperature phase that does not have a center of symmetry. This is most often achieved in conventional perovskite ferroelectrics by an off-center displacement of the small (B) cation from the center of the oxygen octahedron. However for cations with certain \( d \) orbital occupancies, the tendency to undergo a Jahn-Teller distortion is strong, and will likely be the dominant structural effect. The Jahn-Teller distorted structure might have a lower driving force for off-center displacement than the otherwise undistorted structure. Examples of this effect are seen in lanthanum manganite, LaMnO\(_3\), in which the Mn\(^{3+}\) ion has \( d^1 \) configuration, and yttrium titanate, YTiO\(_3\), in which the Ti\(^{3+}\) ion is \( d^1 \). Both materials have a d-type Jahn-Teller distortion, in which the elongated axes of the oxygen octahedra are oriented parallel to each other along the crystallographic \( c \) axis [11]. LaMnO\(_3\) is insulating and an A-type antiferromagnet, and YTiO\(_3\) is a strongly correlated ferromagnetic Mott-Hubbard insulator. Neither material is ferroelectric. Note the relevance of the formal charge on the B cation here. In BaTiO\(_3\), the actual occupation of the 3\( d \) electrons is closer to \( d^1 \) than to \( d^0 \) due to donation of charge density from the oxygen ligands [12]. A \( d^1 \) cation should undergo a Jahn-Teller distortion. No Jahn-Teller distortion is observed in BaTiO\(_3\) however, which is consistent with the \( d^0 \) formal charge.

Magnetism versus \( d \) orbital occupancy. It is clear that the existence of \( d \) electrons on the B site cation reduces the tendency of perovskite structure oxides to undergo ferroelectric distortion. However it is not clear whether it is merely the presence of \( d \) electron density, or the influence of the magnetic spin polarization which is the dominant factor in creating this effect. Later we investigate this question by artificially remove the spin polarization in first-principles density functional theory calculations for model materials, and exploring whether they then become ferroelectric.

**Conclusion.** The short answer to the title of the paper is that we don’t know for sure why there are so few magnetic ferroelectrics. We do however have some clues - multiferroism involves a number of subtle competing factors, with \( d \) electron occupancy on the transition metal being a critical variable. In the next Section we present results of our first principles calculations [13] for bismuth manganite, which is ferromagnetic and possibly ferroelectric, with the goal of understanding what makes BiMnO\(_3\) multiferroic.

**BISMUTH MANGANITE**

A large amount of recent research activity has been focused on the rare earth manganites, following the observation of colossal magnetoresistance (CMR) in Ca-
doped LaMnO$_3$ [24]. During these recent studies, many rare earth perovskite manganites have been found to show strong coupling between their magnetic and structural order parameters. For example a magnetically induced structural phase transition has been observed in La$_{0.83}$Sr$_{0.17}$MnO$_3$ [25] indicating strong coupling between the local magnetic spin moments and the lattice structure. In Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, 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 [26]. It is clear that, although the combination of ferromagnetism and ferroelectricity is rare, coupling between electric and magnetic order parameters is not.

All of the rare earth manganites crystallize in the perovskite phase with antiferromagnetic ordering between adjacent Mn$^{3+}$ ions, caused by the super-exchange mechanism [27]. Manganites of the lighter rare earths (LaMnO$_3$ - DyMnO$_3$) have a low temperature orthorhombic distortion and do not show ferroelectricity. In YMnO$_3$, and HoMnO$_3$ through LuMnO$_3$, the orthorhombic phase is not the most stable structure, and instead a hexagonal perovskite structure is formed. The hexagonal manganites are ferroelectric [28]. Bismuth manganite differs markedly from both the orthorhombic and hexagonal rare earth manganites. Although information about BiMnO$_3$ is sparse [29], it is known to be ferromagnetic, with a triclinic structural distortion in its ground state. In addition, preliminary theoretical work has confirmed an early suggestion [29] that BiMnO$_3$ might be ferroelectric [22].

In this Section we study the chemical origins of the differences between BiMnO$_3$ and the protoptypical orthorhombic rare earth manganite, LaMnO$_3$. The goal of our computational work is to identify the factors which promote ferroelectricity in BiMnO$_3$, but over-ride it in the conventional orthorhombic rare earth manganites. In particular, we study the effect of artificially removing the magnetic interactions on the $d$ electrons (by restricting the up- and down- spin charge densities to be identical). This allows us to determine whether it is the magnetism or the $d$ orbital occupation which prevents the ferroelectric instabilities from being unstable in the perovskite manganites.

We investigate the origin of the differences between ferroelectric BiMnO$_3$ and the non-ferroelectric rare earth manganites by comparing the calculated electronic properties of BiMnO$_3$ with those of LaMnO$_3$. We begin by calculating the electronic structure for the high symmetry cubic phases, without including magnetic effects, (the so-called paramagnetic (PM) phase), then lower the magnetic symmetry to the ferromagnetic (FM) phase. Finally we introduce structural distortions in both paramagnetic and ferromagnetic calculations. 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. There are two important questions to answer here. First, why is BiMnO$_3$ ferromagnetic, when the superexchange mechanism causes the other rare earth manganites to be antiferromagnetic. Second, what causes BiMnO$_3$ to be ferroelectric, when the other orthorhombic rare earth manganites do not show a ferroelectric
Cubic Paramagnetic and Ferromagnetic Structures. Figure 1 shows the calculated band structures for cubic paramagnetic LaMnO$_3$ and BiMnO$_3$, along the high symmetry axes of the simple cubic Brillouin Zone. The plotted energy range is from -12 eV to 4 eV, and the lower lying semi-core states have been omitted for clarity. The Fermi level is set to zero in both cases. The broad series of bands between -2 and -7 eV in both materials arises from the oxygen 2p orbitals. Above the oxygen 2p bands, and separated from them by an energy gap, are the Mn 3d bands. The Mn 3d bands are divided into two sub-bands - the lower energy $t_{2g}$ bands, and the higher energy $e_g$ bands - as a result of crystal field splitting by the octahedral oxygen anions. In both cases the Fermi level lies near the top of the Mn 3d $t_{2g}$ bands and is in a region of high density of states. One striking difference between the two band structures is the presence of a band between -10 and -12 eV in the BiMnO$_3$ band structure which does not exist in the LaMnO$_3$ case. This band corresponds to the high lying occupied Bi 6s electrons. In addition, the high energy La 5d electrons have a very different form than the Bi 6p electrons, which occupy a similar energy range.

To quantify the differences between cubic PM BiMnO$_3$ and LaMnO$_3$, we performed tight-binding analyses of the respective band structures. First we fit with only oxygen 2s and 2p and Mn 3d orbitals included in the basis set. We found that this limited basis set reproduced the LaMnO$_3$ bands well, however the behavior of the BiMnO$_3$ bands was less well reproduced, confirming that additional orbital overlaps are essential in producing the observed band structure. We then repeated the fitting procedure for BiMnO$_3$, with Bi 6s and 6p orbitals added to the basis, and found a significant improvement in the quality of the fit to the ab initio bands. The largest of the new parameters were the Bi 6s - O 2p and Bi 6p - O 2p $\sigma$ interactions, with the magnitude of the $\sigma$-bonded Bi 6p - O 2p interaction being approximately 30 % larger than that of the Bi 6s - O 2p. Also significant were the Bi 6p - Bi 6p $\sigma$ interactions.
The results of our calculations in which the high symmetry cubic structure is retained, but the electrons are allowed to spin polarize can be found in Ref. [22]. The most important observation is that the differences between BiMnO$_3$ and LaMnO$_3$ which we observed in the paramagnetic calculations persist into the ferromagnetic phase, the PM to FM transition introducing the same kinds of changes in both materials.

**Preliminary experimental results for BiMnO$_3$.** The conclusion from our tight-binding analysis, that there is strong hybridization between the O 2$p$ and Bi 6$p$ orbitals, is consistent with recent measurements showing enhancement of charge ordering in Bi-doped CaMnO$_3$ [30]. Cheetham and co-workers observed that the charge-ordered state in Bi$_{0.3}$Ca$_{0.7}$MnO$_3$ persists to a higher temperature than that in La$_{0.3}$Ca$_{0.7}$MnO$_3$. They explained their observations by noting that the electronegativity of Bi enhances Bi-O hybridization and in turn reduces the amount of Mn-O hybridization. This also provides a plausible explanation for the existence of ferromagnetism in BiMnO$_3$. The combination of structural distortion and reduced Mn 3$d$ - O 2$p$ overlap (both driven by bismuth-oxygen covalency) reduces the strength of the antiferromagnetic superexchange interaction, making ferromagnetic coupling more favorable.

**Soft mode ferroelectric distortions.** Finally we calculate the phonon modes in BiMnO$_3$ and LaMnO$_3$ to determine the existence and nature of ferroelectric instabilities. In keeping with the philosophy of this paper, we study the lattice distortions of the high symmetry cubic phases, and compare our results for BiMnO$_3$ with those for LaMnO$_3$. We restrict our discussion to zone center phonons. The force constant matrices for LaMnO$_3$ and BiMnO$_3$ were determined by calculating the Hellmann-Feynman forces resulting from the displacement of each atom in turn 0.1 Å along the z direction of the unit cell. The forces exerted on the Mn ions by the other ions were determined using the acoustic sum rule. We calculated the Mn-Mn force by applying the acoustic sum rule to both the columns and the rows of the resulting matrix. The two values differed by less than around 0.001 eV Å.

| TABLE 1. Eigenvectors and eigenvalues of the dynamical matrix which correspond to the unstable phonon modes in cubic paramagnetic BiMnO$_3$ and LaMnO$_3$. |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                   | BiMnO$_3$         | LaMnO$_3$        |
| $\nu$ (cm$^{-1}$) | Bi    | Mn | Oz  | Ox  | Oy  | Bi    | Mn | Oz  | Ox  | Oy  |
| 98.20i            | -0.43 | 0.09 | 0.16 | 0.62 | 0.62 | -0.59 | 0.22 | 0.21 | 0.53 | 0.53 |

The paramagnetic cubic phases of both LaMnO$_3$ and BiMnO$_3$ each have an unstable zone center phonon mode which results in a ferroelectric distortion. The frequencies and eigenvectors of the mode is given in Table 1, and the displacement pattern is shown in Figure 2 (a). Here the large (Bi or La) cations are moving in opposition to the oxygen cage, resulting in a ferroelectric displacement. The imaginary frequency of this mode is twice as large in BiMnO$_3$ than in LaMnO$_3$, indicating a stronger instability in the Bi compound. It is interesting to note that
the Mn is moving in the same direction as the oxygen ions. This is opposite to the behavior of the Ti ion in BaTiO$_3$ and PbTiO$_3$, but similar to the behavior of Zr in PbZrO$_3$ [31].

**FIGURE 2.** (a) Eigenvector of the unstable ferroelectric $\Gamma$ point phonon mode in BiMnO$_3$. The Mn ion is at the center of the unit cell surrounded by an octahedra of oxygens, with the large cations at the unit cell corners. (b) is a non-ferroelectric mode which is unstable in LaMnO$_3$. Each mode is three-fold degenerate.

In the ferromagnetic phase of BiMnO$_3$, the ferroelectric mode remains strongly unstable, at 82.30 $i$ cm$^{-1}$. However the ferroelectric mode in LaMnO$_3$ is now only slightly unstable, at 21.1$i$ cm$^{-1}$. This weakening of the zone center ferroelectric instability in LaMnO$_3$ is likely indicative of the tendency of the spin-polarized $d^4$ ion to Jahn-Teller distort in the absence of other bonding considerations. Note however that the internal stresses are the same for the paramagnetic and ferromagnetic cubic phases in both materials.

It is clear from our analysis, that the presence of ferroelectricity in BiMnO$_3$, and absence of ferroelectricity in LaMnO$_3$, can be explained by the different zone center lattice instabilities. Although a definitive prediction requires calculation of the phonon dispersion throughout the entire Brillouin Zone, it is likely that the weakly unstable zone center phonon in LaMnO$_3$ will be overshadowed by a stronger instability elsewhere in the Brillouin zone, reproducing theoretically the experimentally observed Jahn-Teller distortion. Similarly, the very unstable ferroelectric mode at the zone center in BiMnO$_3$ is likely to dominate over possible unstable modes at other frequencies, confirming theoretically the suggested existence of ferroelectricity in BiMnO$_3$. This mode is driven by Bi-O covalency, and creates a Bi-O electric dipole moment, in contrast to the conventional perovskite oxide ferroelectrics, in which B cation - oxygen covalency is the principal driving force for the ferroelectric distortion. Thus we conclude that the $d$ electron occupation, and particularly the $d$ electron magnetism, on the manganese ion in BiMnO$_3$ continues to inhibit displacement of the B cation. It is only because of the unusual behavior of the A cation that ferroelectricity can occur at all.
SUMMARY AND FUTURE WORK

In summary, we have presented an overview of the field of multiferroic magnetoelectric materials, and a detailed study of one specific magnetically ordered ferroelectric. In the course of our discussion, a ferroelectric “$d^0$” rule has emerged; that is that a ferroelectric displacement of the B cation in perovskite oxides is inhibited if the formal charge does not correspond to a $d^0$ electron configuration. We have seen that this $d^0$ rule can be broken, giving the potential for simultaneous magnetic and ferroelectric ordering, if details of chemistry or structure create an asymmetric potential with a double potential well 

\[ \textit{in spite of the} \ d \ \textit{occupation of the magnetic cation}. \]

In BiMnO$_3$ (and also possibly in BiFeO$_3$) the asymmetry is created by the Bi-O hybridization. In the antiferromagnetic ferroelectric manganeseites of Y and the small rare earth elements, the double potential well is likely created by the five-fold oxygen coordination. And in the classic example of nickel iodine boracite, Ni$_3$B$_7$O$_{13}$I, the anisotropic iodine-oxygen octahedron is believed to cause an electrostatic double potential well along the I-Ni-I axis.

The fundamental theoretical question of if (and why) $d^0$-ness is so strongly favored remains to be answered rigorously, and will undoubtedly contribute significantly to future understanding of both ordinary ferroelectrics and of multiferroic materials. However the existence of a Jahn-Teller distortion seems to be particularly unfavorable, therefore we propose that non-Jahn Teller ions are more likely candidates for magnetic ferroelectric ions.

There has been little modern experimental work on magnetic ferroelectrics, and the synthesis of single crystals of known or candidate multiferroic materials will be essential in elucidating the nature of the interactions involved. We hope that this paper will stimulate experimental work on some of the less well studied, but potentially interesting candidate multiferroic materials. In particular, this paper has focused exclusively on oxide ferroelectrics, however non-oxide based ferroelectrics should also be considered as candidates for multiferroism. In ferroelectrics such as NaCaF$_3$ [32], the driving force for ferroelectricity is Coulomb, rather than covalency. This might allow circumvention of the $d^0$-ness requirement, provided that suitable stable structures can be found.

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2. see for example Physics Today, April 1995, and references therein.
13. The calculations described in this work were performed using a plane wave pseudopotential (PWPP) implementation [14] of density functional theory (DFT) [15] within the local spin density approximation (LSDA). We use the conjugate gradient program CASTEP 2.1 [16] which we have extended to study spin-polarized systems, and calculate the exchange correlation using the Perdew-Zunger parameterization [17] of the Ceperley-Alder potential [18] with the von Barth-Hedin interpolation formula [19]. The optimized pseudopotentials developed by Rappe et al. [20], combined with the the partial non-linear core correction scheme of Louie et al. [21], give us an energy cut-off in the plane wave expansion of around 60 Ry. Further details, including construction of the pseudopotentials, can be found in Refs. [22] and [23].
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