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1 Introduction

Multiferroics are materials that manifest both ferroelectricity and ferromagnetism[1]. Ferroelectricity is a property of a material whereby it shows spontaneous electric dipole moment. Some familiar uses of ferroelectric materials include capacitors and computer memories. Similarly, ferromagnetic materials exhibit spontaneous magnetic dipole moment. Ferromagnets are just the usual magnets used in magnetic tapes and refrigerator magnets. Ferroelectricity derives from the fact that electrons have electric charge while ferromagnetism can be attributed to the fact that electrons possess spin as well. Existence of both charge and spin in electrons opens up exciting possibilities of harnessing ferroelectricity and ferromagnetism in the same material. Hill [1] (now Spaldin) suggests some application of multiferroics which include multistate data storage, in which data is stored in both electric and magnetic polarization or novel memory media, in which writing of ferroelectric data bit allows simultaneous reading of data bit due to the associated magnetic field.

Since multiferroics show both ferroelectric and ferromagnetic properties, we first explain the underlying physics behind these two properties. Then we explain how these two phenomena could be combined. We explore the reasons behind the dearth of multiferroic materials. Then we look at some known multiferroics and study their underlying physics.

2 Ferroelectricity

A ferroelectric material is one that undergoes a phase transition from an ordinary dielectric high-temperature phase to a low-temperature phase with spontaneous polarization[1]. In the high-temperature phase an applied electric field induces an electric polarization in the material that vanishes when the electric field is switched off. As the temperature reaches the transition temperature T_c, the material undergoes a phase transition exhibiting spontaneous dipole electric moment whose direction can be switched by application of an external field. The change in polarization also causes change in shape.

Ferroelectricity was first discovered in Rochelle salt, $KNa(C_4H_4O_6).4H_2O$. However, most ferroelectric materials manifest themselves in the cubic perovskite structured oxides

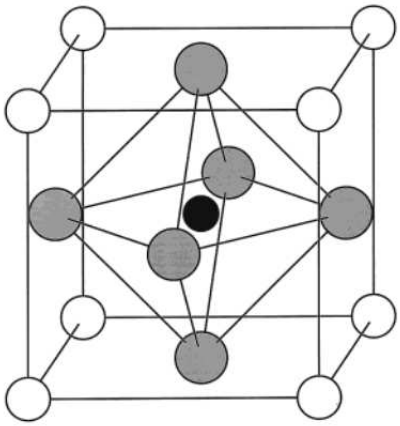

Figure 1: Cubic perovskite structure[1]. The white circles at the corners represent A, grey circles represent O and black circle represents B.

(Fig. 1), ABO_3, where A and B are cations. Below the transition temperature, there is a structural distortion such that the cation B, which is smaller in size compared to A, at the center of an octahedron of oxygen anions shifts slightly away from the center. This creates a electric dipole moment which is solely responsible for the spontaneous polarization.

The underlying reason for the transition from nonferroelectric structure to ferroelectric one is the competition between short-range Coulomb repulsion between atoms and the bonding considerations due to hybridization of orbitals[2]. The short-range repulsion favours nonferroelectric symmetric phase while the stabilizing forces associated with bonding of different atoms may favour ferroelectric phase. At high temperatures, the short-range repulsion dominates. But as the temperature dips below the transition temperature, forces associated with stabilization of polarized bonding dominate.

Cohen [2] has studied two related ferroelectric perovskites $PbTiO_3$ and $BaTiO_3$ to examine the effect of bonding character on polarizability. Both materials have cubic structure as shown in Fig. 1 at high temperatures. Below T_c $PbTiO_3$ is tetragonal while $BaTiO_3$ undergoes series of transition to tetragonal and orthorhombic structure and finally settles at less symmetrical rhombohedral phase. Cohen found that Ti 3d–O 2p hybridization is essential for stabilizing ferroelectric distortion in both compounds. Additionally, Ba-O interaction is ionic in $BaTiO_3$ while Pb-O is bonded by hybridization of Pb 6s and O 2p electrons. This

causes large polarization in $PbTiO_3$ compared to $BaTiO_3$.

Finally, a peculiar thing about in $PbTiO_3$ and $BaTiO_3$ is that Ti^{4+} is in a d^0 state. It is a recurring theme in most other perovskite ferroelectrics that cation B is in d^0 state.

3 Ferromagnetism

A ferromagnetic material also undergoes similar phase transition like a ferroelectric material. The high-temperature phase above the Curie temperature is devoid of macroscopic magnetic moment. In the low-temperature phase, there is magnetization even in the absence of external magnetic field. In the high-temperature phase the magnetic dipole moments of the atoms are arranged haphazardly such that the total macroscopic moment cancels out. In the low-temperature phase the dipole moments of the atoms arrange themselves in the same direction which causes spontaneous magnetism.

The dipole moment in the atom is caused by the spin of electrons in partially filled orbitals. According to the Curie-Weiss theory[3], exchange energy between electrons causes electrons with parallel spins to have lower energy compared to electrons with antiparallel spins. At high temperatures, the thermal energy is larger than the exchange energy resulting in nonpolarized state. However, below the Curie temperature, the exchange energy becomes dominant and magnetically polarizes the material even in the absence of external magnetic field. This theory explains ferromagnetism in most materials. Unfortunately, this theory does not predict the correct magnetic moment per atom in ferromagnetic metals. This theory also predicts that magnetic moment in each atom is same in both ferromagnetic and paramagnetic case, which experiments show not to be the case.

In the Stoner theory[4], the difference between adjacent band energies play competing role with the exchange energy. Exchange energy favours one band to be occupied electrons with only one type of spin. However, exchange energy might not be enough to transfer electrons of opposing spin to band states of higher energy.

The Fig. 2 shows 3d and 4s up- and down-spin density of states in some first-row transition metals along with the Fermi energy (solid horizontal lines). The 3d and 4s states

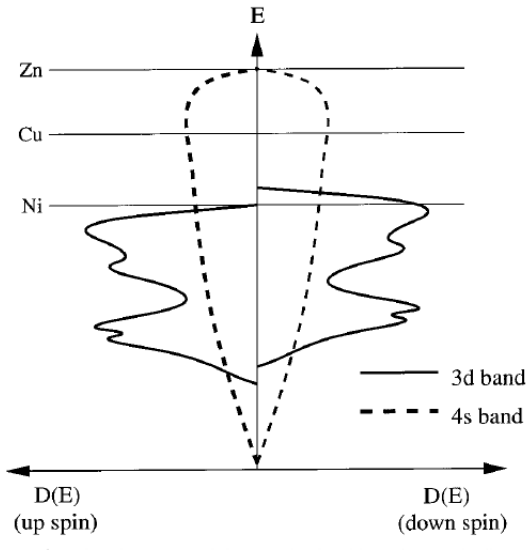

Figure 2: 3d and 4s up- and down-spin densities of states in some transition metals[1]

overlap and hence share valence electrons. But the 3d states have higher density of states compared to the 4s states. So the 3d states contain more electrons. The up and down spin states of 4s band have same energy. However, the exchange energy shifts one spin state of 3d level relative to the other. If the Fermi energy lies within the 3d states, as in Fe, Co and Ni, then there will be more electrons in one spin direction compared to the other. This will result in spontaneous magnetic moment in the ground state. For example, in Ni one 3d subband is filled with filled with 5 electrons and another subband with 4.46 electrons. So the magnetic moment per atom in Ni is $M = 0.54\mu_B$.

4 Multiferroics

The first ferroelectromagnet $Pb(Fe_{2/3}W_{1/3}O_3)$ was discovered by Smolenskii et al. in 1961[5]. By 1982, few dozen multiferroic materials were discovered. Multiferroics can be classified according to four main classes according to structural features as follows.

1. The perovskite structured materials $A(B_1B_2\ldots)O_3$ containing magnetic atoms at B site. These include $BiFeO_3$, $Pb(Fe_{2/3}W_{1/3}O_3)$, $Pb(Fe_{1/2}Nb_{1/2}O_3)$, $Pb(Mn_{1/2}Re_{1/2}O_3)$, etc.

2. The hexagonal rare earth maganites $RMnO_3$ with R = Y, Ho, Er, Tm, Yb, Lu, or Sc.

3. The boracite materials of the form $M_3B_7O_{13}X$, where M = Cr, Mn, Fe, Co, Cu, or Ni, and X = Cl, Br, or I. These materials have cubic symmetry $\bar{4}3m$ above T_c and transition to orthorhombic phase $mm2$ below T_c.

4. The compounds of the form $BaMF_4$ with M = Mn, Fe, Co, Ni which have orthorhombic structure in the high temperature phase.

4.1 Some characteristic properties of ferroelectromagnets

Ferroelectromagnets are simultaneously ferroelectric and ferromagnetic. Hence, its physical, structural and electronic properties are constrained to the properties that occur in both ferroelectrics and ferromagnets. In Ref. [1], Spaldin considers following properties to be limiting factors in simultaneous existence of ferroelectricity and ferromagnetism.

1. *Symmetry* We already know that the crystal structure of a material plays an important role in determining whether the material is ferroelectric. When a material undergoes a ferroelectric transition, the structure changes from a high symmetry phase to lower symmetry one without the inversion symmetry. There are 31 point groups that allow spontaneous electric polarization and 31 that allow spontaneous magnetic polarization. In between these two sets of point groups, there are thirteen that belong to both (1, 2, $2'$, m, m', 3, $3m'$, 4, $4m'm'$, $m'm2'$, $m'm'2'$, 6 and $6m'm'$).

2. *Electrical Properties* The ferroelectric materials must be insulators. If not, an electric field will cause an electric current to flow rather than induce electric polarization. Ferromagnets are not required to be metallic but often occur as such. The reason for this is that ferromagnetism is often the result of high density of states at the Fermi energy. This is why elemental Fe, Co and Ni are ferromagnetic.

3. *Chemistry* As we discussed earlier, it turns out that most perovskite structured ferroelectric materials have ions in a d^0 state at the B site. For some reason, a material with an ion having partially filled 3d orbital at the B site loses the tendency to move the

B site cation off center. However, if there are no d electrons creating localized magnetic moments, there can be no magnetic polarization.

5 Why so few multiferroics?

After considering the constraints that entails ferroelectricity and ferromagnetism, we can now appreciate why there are so few multiferroics. First reason for this dearth of multiferroics seems to be the tendency of ferroelectric materials to be insulators and, on the other hand, ferromagnetic materials to be metallic.

Second cause for this scarcity is that the ferromagnetic materials require ions with partially filled d orbitals. However, most ferroelectrics have perovskite structure, and existence of an ion with partially filled d orbital at the B site causes the perovskite structured materials to lose tendency to undergo structural transition to ferroelectric phase.

Let us consider various possibilities that may make the role of d orbital important. First possibility is that ions with partially filled d orbitals are simply too large to move away from the center of the oxygen octahedron. However, the Shanon ionic radii of d^0 cations found in ferroelectric perovskite oxides (Ti^{4+}: 74.5 pm, Nb^{5+}: 78 pm, Zr^{4+}: 86 pm) are comparable to d^n cations found in non-ferroelectric perovskite oxides (Mn^{3+}: 78.5 pm, Ti^{3+}: 81 pm, V^{4+} 72 pm)[6]. So it seems that the size of B site cation is not the main factor on determining whether a material undergoes phase transition to a ferroelectric phase.

To understand the structural instability in perovskites, it is helpful to consider the so called ABX_3 tolerance factor defined by $t = (r_A + r_X)/\sqrt{2}(r_B + r_X)$. Here r_A, r_B and r_X are the Shannon radii of A, B and X ions, respectively. Ideal cubic perovskite structure has $t \approx 1$. However, the case $t > 1$ indicates that B site ion is too small for its site in the ideal cubic structure. This allows materials such as $BaTiO_3$ and $KNbO_3$ to transition to ferroelectric phase[7]. The case $t < 1$ indicates that A site ion is too small for its site in the ideal cubic structure. Examples of ferroelectric with $t < 1$ are $BiMnO_3$ and $BiFeO_3$ (which incidentally also show magnetic ordering).

To conclude, ferroelectricity and ferromagnetism involve competing factors such as

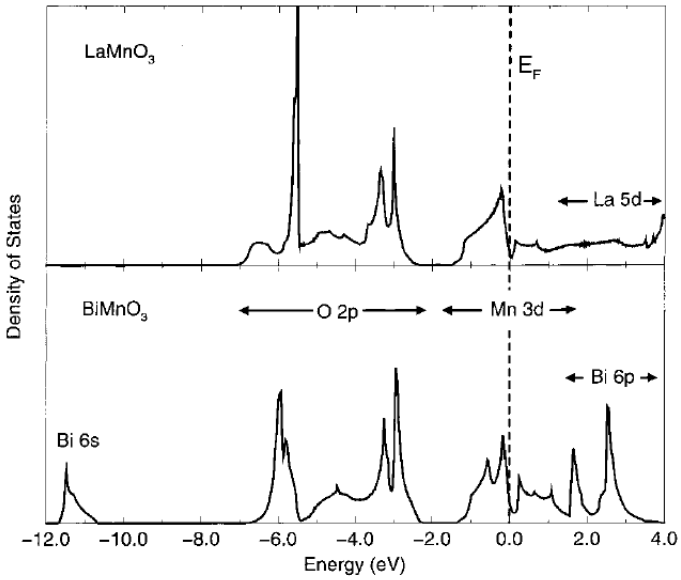

Figure 3: Density of states for cubic paramagnetic $LaMnO_3$ and $BiMnO_3$[1].

electrical conductivity and d-electron occupancy. This is the main reason for the dearth of multiferroics. However, as we have seen in the case of $BiMnO_3$, existence of one property does not preclude occurrence of the other.

6 Multiferroic $BiMnO_3$

In this section we explore the reasons behind existence of both ferroelectricity and ferromagnetism in $BiMnO_3$ as studied by Spaldin in Ref. [1]. We compare it with $LaMnO_3$ which is nonferroelectric and insulating antiferromagnet to learn the factors that are important in making $BiMnO_3$ a multiferroic.

Both $BiMnO_3$ and $LaMnO_3$ have cubic symmetry in high temperature paramagnetic phase. Calculated density of states and band structure along high symmetry lines are shown in Figs. 3 and 4. In both sets of figures, Fermi energy is set to zero. We see that there is high density of states (DOS) at the Fermi level caused by Mn 3d bands. The large DOS at Fermi level suggests that this cubic paramagnetic phase is unstable and a lower energy structure could be achieved by allowing spin polarization or structural destruction.

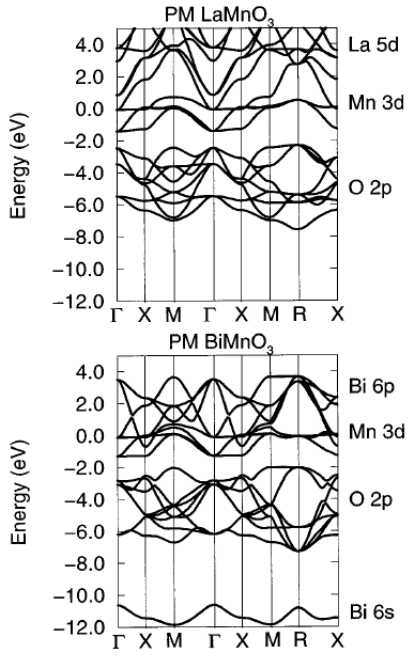

Figure 4: Band structure of $LaMnO_3$ and $BiMnO_3$ along high symmetry lines[1].

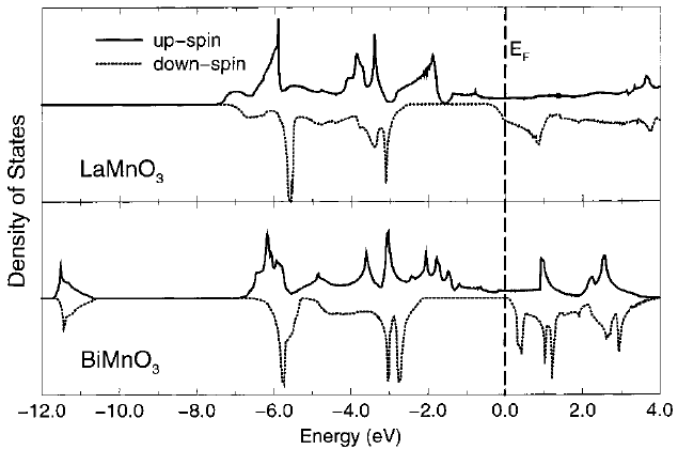

Figure 5: Density of states for cubic paramagnetic $LaMnO_3$ and $BiMnO_3$[1].

Table 1: Eigenvectors and eigenvalues of the dynamical matrix that correspond to the unstable phonon modes in cubic paramagnetic $BiMnO_3$ and $LaMnO_3$.

Material	ν (cm^{-1})	Bi	Mn	Oz	Ox	Oy
$BiMnO_3$	$72.39i$	0.0	0.0	0.0	$-1/\sqrt{2}$	$1/\sqrt{2}$
$BiMnO_3$	$98.20i$	-0.43	0.09	0.16	0.62	0.62
$LaMnO_3$	$49.04i$	0.0	0.0	0.0	$-1/\sqrt{2}$	$1/\sqrt{2}$
$LaMnO_3$	$44.69i$	-0.59	0.22	0.21	0.53	0.53

Figure 5 shows DOS of cubic $LaMnO_3$ and $BiMnO_3$ with spin polarized electrons. In $LaMnO_3$ the majority spin DOS is still very high suggesting that this ferromagnetic structure is unstable. This is consistent with the experimental result that shows $LaMnO_3$ is antiferromagnetic below the transition temperature[8]. The majority spin DOS at the Fermi level of $BiMnO_3$ is smaller compared to $LaMnO_3$, suggesting that ferromagnetic phase of $BiMnO_3$ is more stable compared to that of $LaMnO_3$.

After considering the ferromagnetic part, we now study why $BaMnO_3$ is ferroelectric while $LaMnO_3$ is not. To do so, we look at the phonon frequency at Γ. Existence of imaginary phonon modes will point to an unstable structure. Table 1 shows eigenvalues and eigenvectors of unstable modes of paramagnetic cubic $BaMnO_3$ and $LaMnO_3$. We notice that magnitude of unstable phonon frequencies in $BiMnO_3$ is greater than that of $LiMnO_3$, indicating stronger instability in $BiMnO_3$. The mode in which Bi or La moves in opposite direction to O represents the ferroelectric mode. When the same calculation is done with spin polarized electrons, the ferroelectric mode of $BiMnO_3$ remains strongly unstable with frequency of $82.30i$ cm^{-1}. However, now the ferroelectric mode in $LaMnO_3$ is considerably less unstable with frequency of $21.1i$.

This suggests that presence of ferroelectricity in $BiMnO_3$ and absence of it in $LaMnO_3$ is due to lattice instabilities at the A site.

7 Conclusion

Multiferroics are materials that show spontaneous electric and magnetic polarization. The scarcity of multiferroics can be explained by the fact that factors determining ferroelectricity and ferromagnetism compete with each other. Ferroelectrics are insulators while ferromagnets are mostly metallic. Perovskite structured ferromagnets require an ion with partially filled d orbitals at B site while ferroelectrics require an ion with empty d orbital. However, in some materials these competing factors can be balanced such that it shows both electric and magnetic properties. One such material is $BiMnO_3$. In this case, ferroelectricity is caused due to the structural distortion at the A site (as opposed to the B site in most ferroelectrics) while ferromagnetism is caused by presence of partially filled 3d state of Mn.

References

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