Magnetostructural Effect in the Multiferroic BiFeO$_3$-BiMnO$_3$ Checkerboard from First Principles

L. Pálová, P. Chandra and K. M. Rabe

*Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854*

(Dated: June 17, 2009)

Using first principles calculations, we present a magnetostructural effect in the BiFeO$_3$-BiMnO$_3$ nanocheckerboard that is not found in either bulk parent compound or in BiFeO$_3$-BiMnO$_3$ superlattices. We also demonstrate that the atomic-scale checkerboard has a multiferroic ground state with the desired properties of each constituent material: polar and ferrimagnetic due to BiFeO$_3$ and BiMnO$_3$ respectively.

PACS numbers: 75.80.+q,77.80.-e,75.75.+a

There is currently tremendous interest in finding new multiferroic (ferroelectric and ferromagnetic) materials with large magnetoelectric coupling. Advances in the synthesis of artificially structured materials have stimulated efforts to design new multiferroic heterostructures, with first principles methods being an essential tool for the identification and investigation of promising systems. In this Letter, we report the first-principles identification and characterization of an unusual heterostructure, a multiferroic atomic-scale 2D nanocheckerboard$\mid \nabla \Delta \nabla \nabla$ of BiFeO$_3$-BiMnO$_3$, with properties that critically depend on the geometry and are not present in either bulk or layered structures of the constituent materials. In particular, the 2D checkerboard geometry leads to magnetic frustration and to quasi-degenerate magnetic states that can be tuned by an external perturbation that changes the crystal structure, such as an electric field. This results in a novel magnetostructural effect, adding to previous examples of magnetostructural coupling such as bulk and layered manganites, epitaxial EuTiO$_3$ and EuSe/PbSe$_{1-x}$Te$_x$ multilayers$\Delta$.

Our first principles calculations are performed using density functional theory within the local spin-density approximation (LSDA)+U method as implemented in the Vienna Ab-initio Simulation Package VASP-4.6.3$\Delta$$\Delta$.$\Delta$. We test the robustness of our results with two different implementations of the rotationally invariant LSDA+U version, the first as introduced by Liechtenstein$\Delta$ with $U_{Fe} = U_{Mn} = 5eV$, $J_{Fe} = J_{Mn} = 1eV$, and the second due to Dudarev$\Delta$ with $U^{eff}_{Mn} = 5.2eV$, $U^{eff}_{Fe} = 4eV$, where $U^{eff} = U - J$. It has been shown that these $U$ and $J$ values match experimental data in bulk BiFeO$_3$; the value $U^{eff} = 5.2eV$ has been used for previous bulk BiMnO$_3$ ground state calculations$\Delta$. We use projector-augmented wave potentials (PAW)$\Delta$ and treat explicitly 15 valence electrons for Bi ($5d^{10}6s^26p^3$), 14 for Fe ($3p^63d^{10}4s^2$), 13 for Mn ($3p^63d^{5}4s^2$), and 6 for O ($2s^22p^4$). The cutoff energies for the plane wave basis set are 550eV and 800eV in the ionic relaxations and for subsequent self-consistent energy calculations respectively. Gaussian broadening of the partial occupancies for each wavefunction is 0.05eV. A Monkhorst-Pack k-point grid$\Delta$ is generated with density $4 \times 4 \times 4$ for $(\sqrt{2} \times \sqrt{2} \times 1)a_0$ double perovskite and $4 \times 4 \times 2$ for $(\sqrt{2} \times \sqrt{2} \times 2)a_0$ four perovskite cells. Ions are relaxed towards equilibrium positions until the Hellmann-Feynman forces are less than $10^{-3}eV/A$. The spontaneous polarization is calculated by the Berry phase method$\Delta$ with k-point mesh twice as dense as in the energy calculations.

We consider four formula units (perovskite cells), two each with Fe and Mn atoms on the $B$-site, which we repeat periodically in space. For the planar checkerboard, we alternate iron (Fe) and manganese (Mn) atoms at the atomic level to form pillars of the same composition as in Fig. (i). For the layered superlattice, we alternate single unit cell layers along $z$, as in Fig. (ii). In both cases, the supercell is $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 2a_0$.

We study various collinear spin orderings of the magnetic Fe and Mn atoms, shown for the checkerboard in Fig. (iii). FeFM and FeAFM refer to ferromagnetic and antiferromagnetic ordering respectively for the Fe moments in the relevant structural component (pillar for the checkerboard, layer for the superlattice); similarly MnFM and MnAFM describe the spin ordering of the

Figure 1: (i) BiFeO$_3$-BiMnO$_3$ superlattice with alternation of Fe/Mn planes. (ii) (left) BiFeO$_3$-BiMnO$_3$ checkerboard. Checkerboard ordering of Fe/Mn atoms in the (xy) plane, pillars of the same composition form along the z-direction. (right) Ideal perovskite unit cell. Perovskite cells with Fe/Mn atoms on the B-site repeat according to the checkerboard pattern (ii), or layered geometry (i).
three typically unstable modes of the cubic perovskite
mixed chains. While FM designates the case with FM order along the
order along the mixed Fe-Mn chains in the AFM order along the mixed chains; similarly, FeFMMnAFM: AFM order along Fe/Mn pillars, but FM order in horizontal planes.

Figure 2: From top left to bottom right: (i) G-AFM: rocksalt type antiferromagnetic (AFM) order, (ii) C-FIM: AFM order in horizontal planes, ferromagnetic (FM) order along Fe/Mn pillars, (iii) FM order, (iv) FeAFMMnFM: AFM order along Fe/Mn pillars, FM order along Mn pillars, (v) FeFMMnAFM: FM order along Fe pillars, AFM order along Mn pillars, (vi) FeAFMMnAFM: AFM order along Fe/Mn pillars, but FM order in horizontal planes.

Figure 3: Structural energetics of bulk BiFeO$_3$. Energy difference per perovskite cell (f.u.) for different magnetic orderings (see Fig. 2) and structural distortions: (1) Pm3m: no distortion - ideal perovskite, (2) Γ$^+_4(z)$: polar distortion along z axis, (3) $M^+_2(z)$: oxygen octahedra tilts about z axis, (4) $R^+_4(y)$: oxygen octahedra tilts about y axis, (5) $R^+_4(y)$ and Γ$^+_4(y)$ ($RT(y)$): linear combination of (4) and (2) along y axis, relaxes back to polar Γ$^+_4(y)$ with zero tilting angle, (6) $R^+_4([111])$ ($R^+_4(d)$): oxygen octahedra tilts about [111] axis, (7) $R^+_4([111])$ and Γ$^+_4([111])$ ($RT(d)$): linear combination of (6) and (2) along [111] ($d$), where $d$ refers to the cube diagonal direction.

In the checkerboard, this notation fully specifies the states considered. For the superlattice, the remaining ambiguity is resolved as follows: FeAFMMnAFM magnetic order designates AFM order along Fe and Mn planes with FM order along the mixed Fe-Mn chains in the z direction, while G-AFM designates the case with AFM order along the mixed chains; similarly, FeAFMM-FM designates FM order along Fe and Mn planes with AFM order along the mixed Fe-Mn chains in the z direction, while FM designates the case with FM order along the mixed chains.

In searching for the ground state crystal structure for each spin ordering, we consider structures generated by three typically unstable modes of the cubic perovskite structure as the zone center polar mode Γ$^+_4$, the $M^+_2$ oxygen octahedron rotations (all rotations about a given axis in phase) and $R^+_4$ rotations (sense of rotations alternates along the rotation axis). We freeze in selected modes and combinations of modes and optimize atomic displacements and lattice parameters in the resulting space groups.

First, to investigate the effect of B-site cation geometry on the magnetic ordering, we present results in Table 1 for the magnetic ordering energies when the structures are held fixed to the ideal perovskite reference structure. In the layered superlattice and both bulk parent systems, the difference in energy between magnetic ground state (FeAFMMnFM in the superlattice, G-AFM in bulk BiFeO$_3$ and FM in bulk BiMnO$_3$) and the first alternative state is 0.11 – 0.12 eV/f.u.; this difference corresponds to a relatively large energy and we do not expect a transition to a different magnetic state. The highest energy magnetic states are more than 0.26 eV/f.u. apart. On the other hand in the checkerboard, all magnetic states are found quasi-degenerate and are confined within the energetical window of 0.12 eV/f.u., that is, all are lower than the lowest states in the layered superlattice and bulk parent compounds. Indeed, the closest magnetic state to the FeAFMMnFM ground state is now only 0.022 eV/f.u. higher, making it much more plausible for a magnetic transition to occur.

Next we study the energetics of the structural distortion and its effect on the spin order. Before discussing results for the BiFeO$_3$ BiMnO$_3$ checkerboard, we look at the structural energetics of the two bulk constituent materials, BiFeO$_3$ and BiMnO$_3$. We plot energies for various magnetic orderings in seven types of structural distortions of bulk BiFeO$_3$ in Fig. 3. Our calculation verifies the R3c ground state of BiFeO$_3$: counter-rotations of the oxygen octahedra ($R^+_4$) and polar ionic distortions ($Γ^+_4$) along the [111] axis are most energetically favorable. The ground state structure has G-type AFM order and spontaneous polarization 90 µC/cm$^2$ along [111] axis. For all structural distortions considered, the lowest energy magnetic ordering is G-AFM.

We study the structural energetics of bulk BiMnO$_3$ in a similar way; the plotted energies for various structural distortions and magnetic orderings are presented in Fig. 4. We find the lowest energy structure with R3c symmetry, the same as the ground state of BiFeO$_3$. The lowest energy structure has a half-metallic character and is...
ferromagnetic. This structure is not the monoclinic centrosymmetric ground state \(C2/c\) of bulk BiMnO\(_3\), which has a larger unit cell than that considered here\(^{20}\). However our calculation shows that it lies close to the ground state (only 43 meV/f.u. above the GS). For all structural distortions considered, the lowest energy magnetic ordering is FM.

In the layered BiFeO\(_3\)-BiMnO\(_3\) superlattice, we calculate magnetic energies for the rocksalt type G-AFM and FeAFMMnFM layered magnetic states in two structural distortions. For \(R_4^+(y)\&R_4^-(y)\), we find \(\Delta E = -0.504eV/f.u.\) for G-AFM and \(\Delta E = -0.553eV/f.u.\) for FeAFMMnFM with respect to the FeAFMMnFM magnetic state in the ideal perovskite cell (see Table I). For \(R_4^+([111])\&R_4^-([111])\), we find \(\Delta E = -0.752eV/f.u.\) for G-AFM and \(\Delta E = -0.761eV/f.u.\) for FeAFMMnFM. For both structural distortions considered, the lowest energy magnetic ordering is FeAFMMnFM.

Let us now look at the results for the structural energetics of the BiFeO\(_3\)-BiMnO\(_3\) checkerboard. In Fig. 4, we present the energies for four different types of structural distortions. These types of distortions show the lowest energies among a larger set of structures that we explored. Notice that the variation of the structural energy is much larger than that of the magnetic energy of the checkerboard.

Not surprisingly, the \(R_4^+([111])\) and \(R_4^-([111])\) (R3c) type of structural distortion is energetically the most favorable; it is the BiFeO\(_3\) ground state and the BiMnO\(_3\) lowest energy structural distortion. The R3c symmetry is now broken due to pillar cation ordering and the space group of the checkerboard ground state becomes \(P1\); we use the notation c-R3c, where c designates “checkerboard”, as a reminder of the origin of the distortions. As shown in the inset of Fig. 5, the two lowest magnetic states G-AFM and FeAFMMnFM, are only 2meV/f.u.

### Table I: Calculated magnetic energies in an ideal perovskite setting with lattice constant \(a_0 = 3.893\AA\) for various magnetic states in the checkerboard, layered superlattice, and bulk BiFeO\(_3\) and BiMnO\(_3\). Value of \(U = 5eV\) and \(J = 1eV\) is used.

| Structure          | \(\Delta E\) [eV/f.u.] | Structure          | \(\Delta E\) [eV/f.u.] | Structure          | \(\Delta E\) [eV/f.u.] |
|--------------------|------------------------|--------------------|------------------------|--------------------|------------------------|
| \(\text{FeAFMMnFM}\) | 0.000                  | \(\text{FeAFMMnFM}\) | 0.000                  | \(\text{BiFeO}_3\) |                         |
| FM                 | 0.022                  | FM                 | 0.111                  | FM                 | 0.360                  |
| \(\text{C-AFM}\)  | 0.076                  | \(\text{FeAFMMnFM}\) | 0.136                  | \(\text{C-AFM}\)  | 0.115                  |
| \(\text{FeAFMMnFM}\) | 0.135                  | \(\text{A-AFM}\)  | 0.223                  | \(\text{A-AFM}\)  | 0.000                  |
| \(\text{G-AFM}\)  | 0.181                  | \(\text{G-AFM}\)  | 0.000                  | \(\text{G-AFM}\)  | 0.293                  |
| \(\text{FeFMMnFM}\) | 0.260                  | \(\text{G-AFM}\)  | 0.494                  | \(\text{FeAFMMnFM}\) |                         |

Figure 4: Structural energetics of bulk BiMnO\(_3\). Energy difference per perovskite cell (f.u.) for various structural distortions (see Fig. 3) and magnetic orderings (see Fig. 2); \(P4/mmm\) corresponds to a tetragonally distorted perovskite cell with ideally positioned atoms and \(M\Gamma(z)\) is a linear combination of rotational \(M_\ell^+ (z)\) and polar \(\Gamma_\ell^+ (z)\) modes.

Figure 5: Structural energetics of BiFeO\(_3\)-BiMnO\(_3\) checkerboard. Energy difference per perovskite cell (f.u.) for different magnetic orderings (see Fig. 2) and structural distortions: (1) \(P4/mmm\), (2) \(\Gamma_4^+(z)\), (3) \(R_4^+(y)\) and \(\Gamma_4^-(y)\), (4) \(R_4^+([111])\) and \(\Gamma_4^-([111])\) \((R_4^+, \Gamma_4^-(d))\). Inset: zoomed view of the magnetic energies of c-R3c (4) distortion.
apart. The ground state of the checkerboard has the FeAFMMnFM magnetic order, where Fe spins are ordered antiferromagnetically (AFM) along the Fe pillars, Mn spins are ordered ferromagnetically (FM) along the Mn pillars, reflecting “AFM” and “FM” nature of the parent BiFeO$_3$ and BiMnO$_3$ compounds respectively. A total magnetic moment 3.7µ$_B$ per Fe-Mn pair results from manganese chains. The FeAFMMnFM ground state is insulating with energy gap 0.88eV, and we calculate a value of the polarization 62µC/cm$^2$ pointing in the [0.85, 0.85, 1] direction. The ground state of the checkerboard is multiferroic, being ferroelectric and ferrimagnetic.

In particular we want to relate and contrast the properties of the BiFeO$_3$-BiMnO$_3$ checkerboard to those of its two bulk constituent materials; we recall that BiFeO$_3$ is polar and antiferromagnetic, while BiMnO$_3$ is non-polar and ferromagnetic, and we have found that the checkerboard assumes the desired ferromagnetic-ferroelectric properties of each leading to a multiferroic ground-state whose magnetic behavior is structurally sensitive. We attribute this behavior to the development of a quasi-degenerate manifold of magnetic states in the checkerboard, in contrast to the gapped states in the layered superlattice and in the bulk; this can be understood in terms of frustration of the cations inherent in the checkerboard geometry. Since bulk BiFeO$_3$ is known to be G-AFM, and bulk BiMnO$_3$ FM, the Fe-Fe and Mn-Mn interactions tend to be AFM and FM-like respectively. In the layered superlattice, each Fe(Mn) atom has four Fe(Mn) and only two Mn(Fe) nearest neighbours, so that the Fe/Mn layers prefer to be AFM/FM, leading to minor frustration between the minority of mixed Fe-Mn bonds. The FeAFMMnFM layered ground state is much more preferable and lower in energy than any other magnetic state. In the checkerboard there are more frustrated bonds per each cation, and therefore more weight is given to the mixed Fe-Mn bonds and various magnetic states compete energetically.

We study the sensitivity of the closely spaced magnetic levels in the checkerboard to a structural distortion. As we tune the system from the checkerboard c-I4cm ground state to c-I4cm state with $R_{1}^{+}(y)$&$L_{1}^{-}(y)$ distortions, either the FeAFMMnFM (filled diamond) or the G-AFM (open circle) lowest state is favored. Switching between these two magnetic states occurs as we tune the system to other structural distortions (see Fig. 4). It is the competition between these two magnetic types that allows switching between nonzero and zero magnetization; the magnetostructural effect leads to the possibility of a structurally-driven magnetic transition in the checkerboard. This could be realized, for example, by imposing epitaxial strain constraints.

In summary, we present a magnetostructural effect in the atomic-scale checkerboard BiFeO$_3$-BiMnO$_3$, which is not present in either bulk or in layered structures of these two materials. Furthermore, unlike its parent compounds, the checkerboard has a multiferroic ground state with a nonzero magnetization and polarization; this is a new example of a nanocomposite with properties that can be designed. We note that this behavior is due to the magnetic frustration in this system inherent to the checkerboard geometry; as a result the magnetic states are quasi-degenerate and can be tuned by small perturbations including strain. We remark that our first principles calculations do not include spin-orbit coupling which is known to lead to weak ferromagnetism in bulk BiFeO$_3$. We expect that such corrections will not change our results fundamentally, but this is certainly worth pursuing in future work. We would also plan to investigate similar checkerboards on longer length-scales to make more direct contact with the possibility of future experiments.

We thank V. R. Cooper, M. Dawber, C.-J. Eklund, C. Fennie, A. Malashevitc, M. Marsman and D. Vanderbilt for helpful discussions. This work was supported in part by NSF MRSEC DMR-0820404, NSF NIRT-ECS-0608842 and by the US Army Research Office through MURI-DAAD 19-01-1-0517.

---

1. H. Zheng et al., Science 303, 661 (2004).
2. S. Yeo et al., Appl. Phys. Lett. 89, 233120 (2006); C. L. Zhang et al., Appl. Phys. Lett. 90, 133123 (2007); C. L. Zhang et al., Appl. Phys. Lett. 91, 233110 (2007).
3. B. S. Guiton and P. K. Davies, Nature Mater. 6, 586 (2007).
4. J. L. MacManus-Driscoll et al., Nature Mater. 7, 314 (2008).
5. D. P. Kozlenko et al., J. Magn. Mag. Mat. 258-259, 290 (2003).
6. T. Murata et al., J. Magn. Mag. Mat. 310, 1555 (2007).
7. C. J. Fennie and K. M. Rabe, Phys. Rev. Lett. 97, 267602 (2006).
8. R. T. Lechner et al., Phys. Rev. Lett. 94, 157201 (2005).
9. G. Kresse and J. Hafner, Phys. Rev. B 47, R558 (1993); G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
10. A. I. Liechtenstein et al., Phys. Rev. B 52, R5467 (1995).
11. S. L. Dudarev et al., Phys. Rev. B 57, 1505 (1998).
12. J. B. Neaton et al., Phys. Rev. B 71, 014113 (2005).
13. P. Baettig et al., J. Am. Chem. Soc. 129, 9854 (2007).
14. P. E. Blochl, Phys. Rev. B 50, 17953 (1994).
15. G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
16. H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
17. R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).
18. H. T. Stokes et al., Acta Cryst. B 55, 934 (2002).
19. C. Michel et al., Solid State Commun. 7, 701 (1969).
20. A. A. Belik et al., J. Am. Chem. Soc. 128, 706 (2006); A. A. Belik et al., J. Am. Chem. Soc. 129, 971 (2007).
21. L. Pálová, P. Chandra and K. M. Rabe, in preparation.
22. C. Ederer and N. A. Spaldin, Phys. Rev. B 71, 060401(R) (2005).