Title	Ab Initio Study of Tetragonal Co-Doped $BiFeO_3$ with Low-Spin and Intermediate-Spin Co
Author(s)	Ricinschi, Dan
Citation	サイバーメディアHPCジャーナル. 2014, 4, p. 37-40
Version Type	VoR
URL	https://doi.org/10.18910/70482
rights	
Note	

Ab Initio Study of Tetragonal Co-Doped BiFeO$_3$ with Low-Spin and Intermediate-Spin Co

Dan Ricinschi

Tokyo Institute of Technology, Interdisciplinary Graduate School of Science and Engineering

1. Introduction

Magnetoelectric multiferroics continue to attract considerable attention in view of applications to non-volatile memories and spintronic devices [1]. Among themr, a lot of research is focused on bismuth ferrite (BiFeO$_3$, BFO), which is one of the few multiferroics with magneto-electric coupling measurable at room temperature. Although BFO has robust ferroelectricity due to its large (even giant) spontaneous polarization [2-3], it is antiferromagnetic (AFM) with a rather weak magnetization. Thus one has to imagine ways to enhance its weak BFO magnetism and magneto-electric coupling. Here we show that doping of BFO with Co with a low-spin (LS) or intermediate-spin (IS) electronic configuration not only dramatically increases its magnetization, but significantly enhances the magneto-electric coupling as well [4].

2. Technical Details of First Principles Calculations

All first-principles calculations have been done using the density functional theory, under the spin-polarized local density approximation including the correction for the strongly correlated 3d electrons of Fe and Co (LDA+U), as implemented in the ABINIT package [5]. For the electronic wavefunctions we used plane-waves truncated at 400 eV, while for all chemical elements we have used projected-augmented wave pseudo-potentials [6]. We have included both valence and semicore states into our calculations, specifically Fe's and Co's 3d and 4s electrons, Bi's 6s and 6p electrons, and O's 2s and 2p electrons. The Brillouin zone integrations were done on a 4x4x4 k-point grid and all structural optimizations were performed until atomic forces are smaller than 2 meV/Å.

3 Results and Discussion

Using 2x2x2 supercells with eight BFO formula units and substituting some of the Fe atoms with Co with HS, LS or IS electron configuration, we have investigated the energetics, structure and magneto-electric properties of 12.5% Co-doped BFO (further refered to as BFCO12). For 50% Co-doped BFO (further refered to as BFCO50), both 2x2x2 and 1x1x2 supercells have been used. In all calculations A-type, C-type and G-type AFM ordering has been implemented (see Fig. 1).

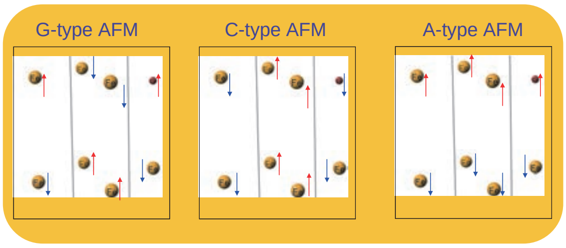

Figure 1: Schematic representation of Fe–Co periodicity inside the 2x2x2 supercells used for calculations of BFCO12 and A-, C-, G-type AFM ordering. The arrows indicate the spin orientation; a Co has replaced a Fe in upper right corner of the supercell only.

The LS-Co electronic configuration has completely occupied d_{xy}, d_{xz} and d_{yz} orbitals with both d_{z2} and d_{x2-y2} empty (i.e., zero magnetic moment overall), whereas IS-Co has singly occupied d_{xy} and d_{x2-y2} orbitals, filled d_{xz} and d_{yz} orbitals and empty d_{z2} orbitals (i.e., a magnetic moment of $2\mu_B$), as seen in Fig. 2. Under these circumstances, BFCO12 (BFCO50) becomes ferromagnetic with a total magnetic moment of $0.625\mu_B$/f.u. ($2.5\mu_B$/f.u.) with LS-Co, and ferrimagnetic with a total magnetic moment of $0.375\mu_B$/f.u. ($1.5\mu_B$/f.u.) with IS-Co, respectively. These values are a significant increase compared to the case of HS-Co, where the total magnetic moment is $0.125\mu_B$/f.u and $0.5\mu_B$/f.u. for BFCO12 and BFCO50, respectively. Hence the magnetization of BFCO would dramatically increase with a change in electronic configuration of Co^{3+} ion from HS to LS or IS.

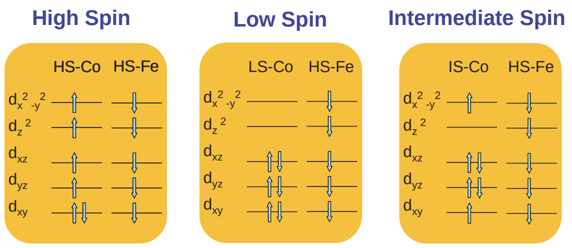

Figure 2: Illustration of HS-Fe, HS-Co, LS-Co and IS-Co electronic configurations of magnetic ions in the BFCO supercells used for calculations.

The calculations have further revealed that, irrespective on Fe/Co ratio and the type of AFM ordering, the calculated total energy of the tetragonal BFCO supercells with LS-Co and IS-Co is always larger than that for HS-Co (Fig. 3). Furthermore, the tetragonal phase with lowest energy has G-type AFM ordering for both the LS-Co and IS-Co, This may reflect the fact that once the Co spin is reduced, the type of AFM ordering in BFCO will be decided by HS-Fe ions, which exhibit G-type AFM ordering in undoped BFO.

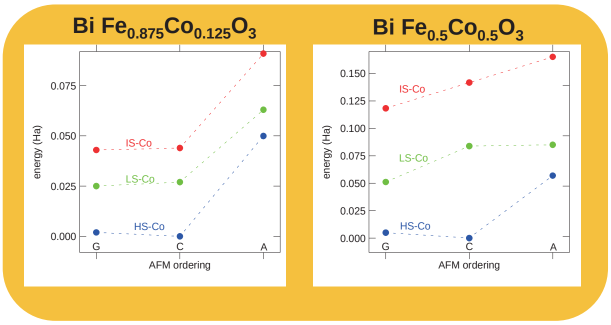

Figure 3: Total energy for tetragonal BFCO12 (left) and BFCO50 (right) with HS-Co, LS-Co and IS-Co and G-type, C-type and A-type AFM ordering.

Examining the tetragonality ratios estimated using the lattice constants resulted from structural relaxation of each tetragonal supercell, we remark in Fig. 4 a significant drop in c/a simultaneously with magnetic moment collapse. The decrease in tetragonality ratio is particularly severe in case of BFCO50, which tends to become pseudo-cubic in case of C-type AFM ordering, as seen in Fig. 4. We also found a significant change in tetragonality ratio (more than 2%) in BFCO with LS-Co and IS-Co caused by changing the type of AFM ordering between G-type, C-type and A-type. The dependence of c/a on the type of AFM ordering is even more pronounced in case of BFCO50 (with a more than 8% variation, as indicated by Fig. 4(b)). Such a significant impact of the type of AFM ordering on the tetragonality ratio (which can be considered to be, to a first approximation, proportional to the spontaneous polarization) in compounds with unconventional electronic configuration of Co adds up to strong magneto-electric coupling. This effect appears to be a consequence of the geometrical frustration associated to the unconventional spin configurations of Co^{3+} (and is thus unlikely to appear in BFCO with HS-Co).

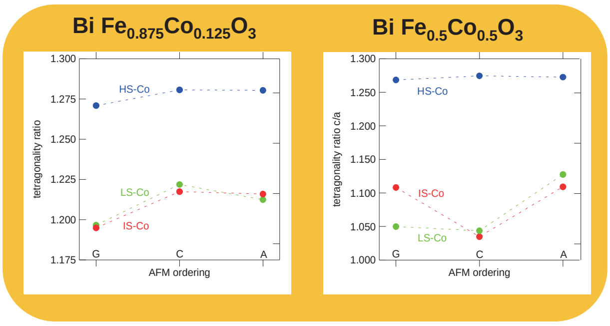

Figure 4: c/a ratio for tetragonal BFCO12 (left) and BFCO50 (right) with HS-Co, LS-Co and IS-Co and G-type, C-type and A-type AFM ordering.

Fig. 3 reveals that BFCO with A-type AFM ordering always have the highest total energy among the tetragonal structures with various spin configurations for Co^{3+}. Because of this, it would be interesting to identify ways to reduce the total energy of such A-type AFM ordered tetragonal structures. Considering the BFCO supercells with HS-Co, IS-Co and LS-Co, particularly useful would be to somehow lower the total energy simultaneously with a transforming of the A-type AFM ordered structures (which are actually ferromagnetic due to uncompensated magnetic ions at B-site perovskite positions) into ferromagnetic ones. Such a ferrimagnetic-to-ferromagnetic phase transition could be moments of Fe and/or Co ions in the supercell. In the case of a BFCO12 supercell, one could reverse the magnetic moment of the Fe^{3+} ion located oppositely from the Co ion along [111] direction, or along [110] direction, or along [001] direction, or reversing the magnetic moment of the Co^{3+} ion itself, as indicated in Fig. 5.

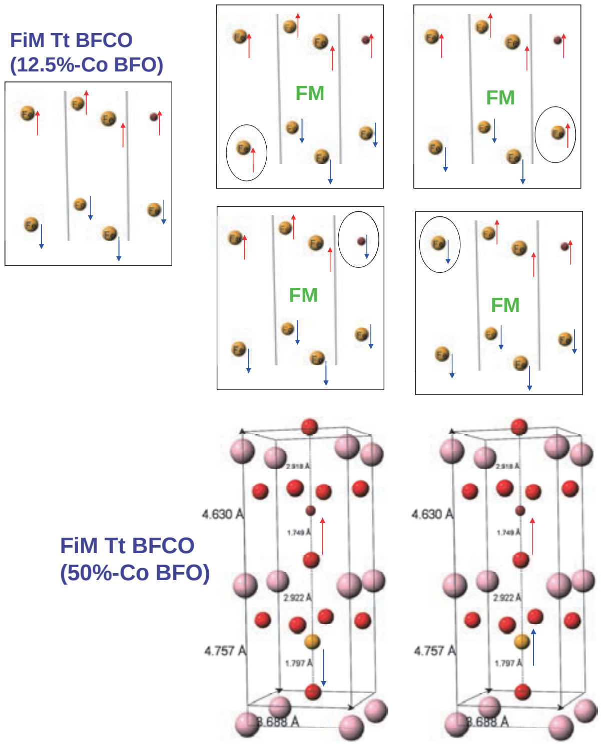

Figure 5: Schematics of triggering a ferromagnetic (FiM) to ferromagnetic (FM) phase transition in BFCO12 (top) and BFCO50 (bottom). The Co ion is placed in upper right corner of the 2x2x2 BFCO12 supercell (top) and in upper perovskite block of BFCO50 1x1x2 supercell (bottom).

The effect of such a ferrimagnetic-to-ferromagnetic phase transition on total energy and tetragonality ratio can be assessed from Fig. 6. We note that one can indeed reduce the total energy of tetragonal BFCO12 with A-type AFM ordering, with lowest energy corresponding to reversing the Fe^{3+} ion which is placed oppositely to Co^{3+} along [001] in case of supercells with LS-Co and IS-Co, and the Co^{3+} ion itself in case of compounds containing HS-Co. Furthermore, upon reversal of the magnetic moment for one of the magnetic ions, the tetragonality ratio changes significantly in case of BFCO with LS-Co and IS-Co and negligibly in case of BFCO with HS-Co, as seen in Fig. 6.

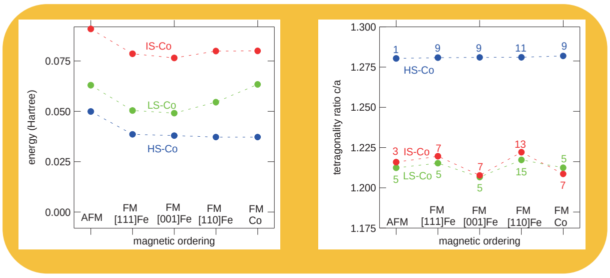

Figure 6: Total energy (left) and c/a (right) calculated for ferrimagnetic-to-ferromagnetic phase transitions triggered in tetragonal BFCO12 with A-type AFM ordering and HS-Co, LS-Co and IS-Co by reversing the magnetic moment of one of the magnetic ions. Numbers inside right figure indicate the magnetic moment for that case.

On the other hand, Fig. 7 reveals that the calculated total energy of the tetragonal BFCO50 with A-type AFM ordering reduces upon reversing the magnetic moment of the Fe^{3+} ion only in the case of IS-Co spin configuration (it stays constant in case of LS-Co and even increases when Co^{3+} is in HS state). Thus, in BFCO50, only in case of IS-Co does a ferrimagnetic-to-ferromagnetic phase transition result in a more stable state than the original tetragonal structure with A-type AFM ordering. As seen in Fig. 7 this phase transformation occurs simultaneously with a significant drop in c/a, again proving that BFCO with IS-Co is expected to have robust magneto-electric coupling.

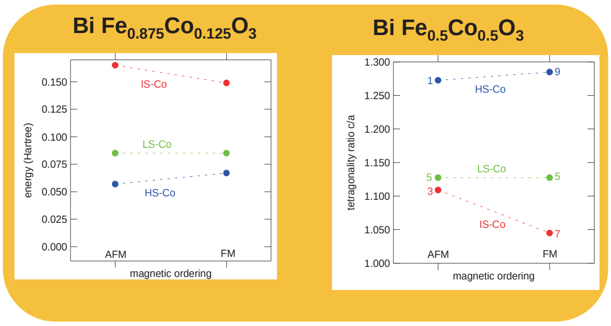

Figure 7: Total energy (left) and c/a (right) calculated for ferrimagnetic-to-ferromagnetic phase transitions triggered in tetragonal BFCO50 with A-type AFM ordering and HS-Co, LS-Co and IS-Co by reversing the magnetic moment of Fe.

5. Conclusion

Our *ab initio* calculations suggest that BFO-based multiferroics with unconventional spin configurations of magnetic ions should be helpful in achieving robust magneto-electric coupling for materials at room temperature. The present results suggest that tetragonal Co-doped BFCO with low-spin and intermediate-spin electronic configuration of Co allow to achieve robust coupling between the spontaneous polarization (assumed here proportional to c/a ratio) and magnetization of such compounds on one hand, and the type of AFM ordering on other hand. Furthermore, we have found an intriguing possibility to enhance the magnetization of tetragonal BFCO compounds with intermediate-spin Co, while remaining coupled to their ferroelectricity, by inducing a ferrimagnetic-to-ferromagnetic phase transition.

Acknowledgements

This research was supported by the Grant-in-Aid for Scientific Research (C) 24560007 provided by the Japanese Ministry of Education, Sports, Culture, Science and Technology. All first-principles calculations have been done using the high performance computing system (PC cluster) of the Cybermedia Center, Osaka University.

References

1) N. A. Spaldin and M. Fiebig: Science 309 391 (2005).

2) K. Y. Yun, D. Ricinschi, T. Kanashima, M. Noda and M. Okuyama: Jpn. J. Appl. Phys. 43 L647 (2004).

3) D. Ricinschi, K. Y. Yun and M. Okuyama: J. Phys. Condens. Matter 18 L97 (2006).

4) D. Ricinschi: Jpn. J. Appl. Phys. 52 09KB01 (2013).

5) X. Gonze et al. Computer Phys. Comm. 180 2582-2615 (2009).

6) M. Torrent, F. Jollet, F. Bottin, G. Zerah, and X. Gonze: Comput. Mat. Science 42 337 (2008).