Stable Antiferromagnetism of Orthorhombic BiCrO$_3$ under Pressure:

A Theoretical Study

Huan Wang[1,a], Xi Chen[1,b], Xing-Yuan Chen[1,c], Yu-Jun Zhao[1,d]*

[1]Department of Physics, South China University of Technology, Guangzhou 510640, People's Republic of China

[a]email:xinzhuo1215@126.com, [b]email: xichen@scut.edu.cn [c]email:85chenxingyuan@163.com,

[d]email: zhaoyj@scut.edu.cn*

Abstract. The realization of ferromagnetism or ferrimagnetism in BiCrO$_3$ is crucial for its potential application in magnetoelectronic devices. It is known from experiment that the antiferromagnetic monoclinic phase of BiCrO$_3$ transits to orthorhombic as pressure beyond 1GPa. Here, we present a first-principles study of the magnetism of orthorhombic BiCrO$_3$ under pressures up to 80GPa. We find that the energy difference between its ferromagnetic phase and the ground state of G-type anti-ferromagnetic phase becomes greater as the pressure increases, as well as the estimated magnetic transition temperature T_N. This implies the difficulty of transforming BiCrO$_3$ into ferromagnetism by external pressure, and thus other approaches (such as doping magnetic ions) are necessary to explore its potential application in magnetoelectronic devices.

1. Introduction

Multiferroic materials, which exhibit both magnetic order and ferroelectricity in the same phase[1, 2], have attracted renewed fundamental interest not only in condensed mater physics but also for their plausible use in the circuit device industry recently[3, 4]. Owing to the unique property of controlling ferroelectric order by external magnetic field, and vice versa, such systems have enormous potential applications in devices such as multiple-sate memory elements[5], electric(magnetic) field controlling ferromagnetic resonance devices, magnetically modulating piezoelectricity vari-able transducers or electrically modulating piezomagnetism variable transducers[6-9]. Bi-based perovskite structure oxides are particularly promising candidate multiferroic mateials. For instance, ferromagnetic material BiMnO$_3$[10] and antiferromagnetic (AFM) material BiFeO$_3$[11, 12] have been studied extensively in the last decade. In these systems, the ferroelectrity is usually originated from a relative Bi-O displacement induced by the stereochcmical activity of lone pairs on the Bi cations. BiCrO$_3$ was first synthesized in 1968 by using very high pressure firing and was reported to be AFM below 123k with a weak parasitic ferromagnetic moment. Later, first principles calculations confirmed BiCrO$_3$ to be an AFM structure[13]. Belik *et al.* had shown the crystal and magnetic structures of polycrystalline BiCrO$_3$, which was determined by the Rietveld method from neutron diffraction data measured at temperatures from 7 to 490 K. Their experiments indicated that BiCrO$_3$ crystallizes in the orthorhombic system above 420 K (space group *Pnma*; Z=4; a =5.545 Å, b=7.758Å, and c=5.429Å at 490 K) in the GdFeO$_3$-type structure. Below 420 K down to 7 K, a monoclinic structure is stable with *C2/c* symmetry (a=9.464 Å, b=5.479 Å, c=9.585 Å, β=108.56° at 7 K), and an AFM crystal structure with T_N=109K[14]. Hill *et al* also predicted that BiCrO$_3$ may

have antiferroelectric or antiferrodistortive[13] property. The application of BiCrO$_3$ as a possible multiferroic material is also limited due to no collective magnetic moments observed in various phases under normal pressure. Meanwhile, it is well known that high pressure can modify the overlap between the cation and the anion orbitals, as well as the bond angle Cr-O-Cr and bond length Cr-O, which will strongly affect their electronic and magnetic properties. In fact, it is reported experimentally that the structure of BiCrO$_3$ will experience a transition from monoclinic to orthorhombic when pressure is up to 1GPa[15].

Here we investigate the BiCrO$_3$ under high pressure by first-principles in order to explore its potential application in novel electronic devices. To our best knowledge, there is no theoretical investigation done on the magnetic property of BiCrO$_3$ under high pressure. In this paper, we construct five types of magnetic configurations: paramagnetic (PM, approximated by non-spin polarization calculations as well employed in first-principles studies), ferromagnetic (FM), G-type AFM, A-type AFM, and C-type AFM, to investigate the possible changes of magnetic ordering of BiCrO$_3$ under various hydrostatic pressures.

2. Computational details

Calculations in this work are preformed by plane wave methods with the interactions between valence electrons and ions represented by the projector augmented wave (PAW) pseudo-potentials as implemented in the Vienna *ab-initio* simulation package (VASP)[16, 17]. We adopt the standard generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof scheme[18]. While the GGA description of transition metal oxides usually leads to a significant underestimation of band gap, it is known that the GGA + U method is especially suitable for treating strong correlated transition-metal systems[19-22]. Here, we also adopt the GGA + U method for a better description of the strongly-correlated BiCrO$_3$. In order to achieve energy convergence, we adopt a 4×3×4 Monkhorst-Pack grid and a high plane wave cutoff of 500eV. The Hubbard U value of 3.0eV for the Cr d orbital is employed, following a work of BiCrO$_3$ based on the artificial rhombohedral *R3c* symmetry[23]. The initial lattice parameters and atomic coordinates for the normal pressure are taken from Ref. 15, and the final structures are fully relaxed in our calculations under various pressures. Radius for Bi, Cr, and O are chosen to be 1.635, 1.323, and 0.820Å for the projected DOS plot, respectively.

3. Results and discussion

First, we calculate the total energy of BiCrO$_3$ in all the five types of magnetic structures in order to investigate the ground state of orthorhombic BiCrO$_3$. The paramagnetic configuration is studied with an approximation of enforcing spin degeneracy for all species. In G-type AFM ordering, each Cr^{3+} ion is surrounded by neighbors of the opposite spin, the A-type AFM phase with AFM interplanar and FM intraplanar coupling, the C-type phase with FM interplanar and AFM intraplanar coupling. The detailed structures are shown in Fig. 1. The total energy differences between various magnetic structures are listed in Table 1. We set the energy of G-type AFM to zero as a reference, since it is always lower than other configurations, irrespective of the GGA and GGA+U calculations. It indicates that magnetic ordering of BiCrO$_3$ following the sequence of G-type AFM < C-type AFM < A-type AFM < FM < PM in the stability. The sequence for the AFM configurations is consistent with the numbers of nearest AFM pairs of Cr, which are 6, 4, 2, for G-type, C-type, and A-type, respectively.
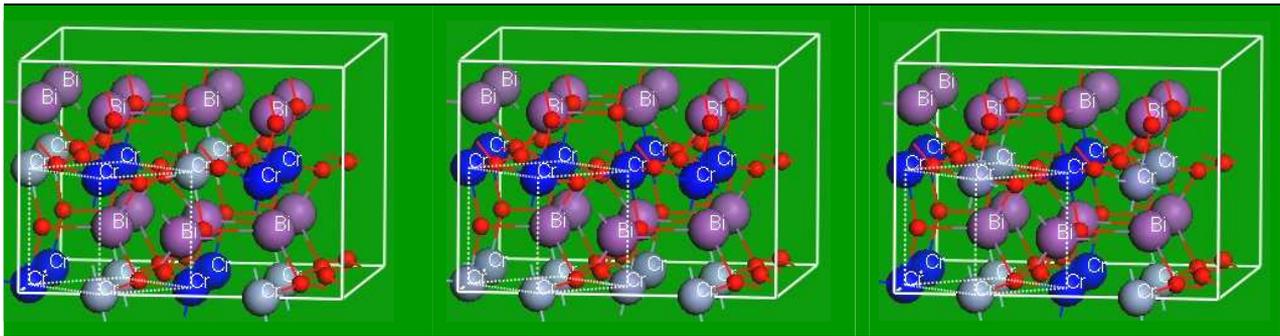
| (a) G-type AFM | (b) A-type AFM | (c) C-type AFM |

Fig. 1(color online)．Crystal structures of G-type, A-type, and C-type AFM BiCrO3. Bi and O ions are denoted by purple and red balls, while spin-up and spin-down Cr ions are represented by blue and gray balls, respectively. The dotted cell is illustrated for a clear view of the magnetic ordering.

    The trend of the energy difference between FM, A-type AFM, C-type AFM and G-type AFM for $BiCrO_3$ under various pressure are illustrated in panel (a) of Fig. 2. It is clear that G-type AFM maintains to be the most stable magnetic configuration for $BiCrO_3$ under pressures up to 80 GPa. Moreover, the energy difference between FM and G-type AFM enlarges as the pressure increases. This implies the difficulty of transforming $BiCrO_3$ into ferromagnetism by external pressure. The total and projected DOS of Cr *3d*, Bi *6s* and O *2p* with U=3eV are shown in Fig. 3 for pressures at zero and 80 GPa, where VBM of the two cases are aligned. The majority and minority spins are shown with positive and negative values in the plots, respectively. From the DOS plots, we find that the Cr *3d* levels are strongly hybridized with O *2p*. When the pressure changes from zero to 80GPa, the band gap of $BiCrO_3$ increases by 0.35eV.

Table 1. Total energies of $BiCrO_3$ for various magnetic ordering configurations with respect to that of G-AFM configuration in unit of meV/f.u, corresponding to U values of 0, 1 eV, and 3 eV.

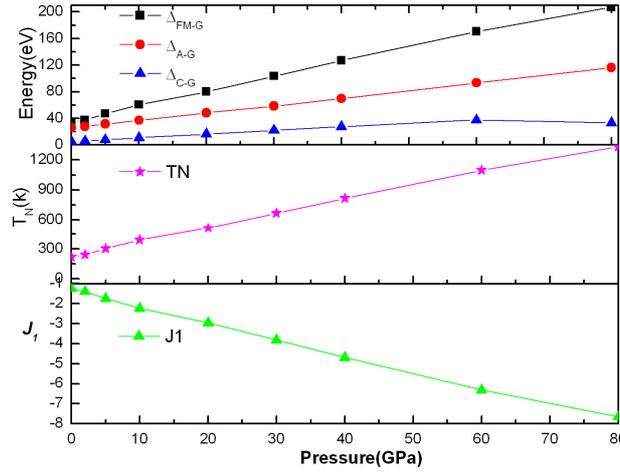|	U=0	U=1 eV	U=3eV
G-AFM	0	0	0
C-AFM	19.4	15.7	10.8
A-AFM	103.7	75.5	45.9
FM	135.4	92.4	49.5
PM	6040.5	8052.4	11171.9

Fig. 2 (color online). (a) The GGA calculated energy difference between the G-type AFM and FM (Δ_{FM-G}), A-type AFM (Δ_{A-G}), C-type AFM (Δ_{C-G}) for BiCrO$_3$ under various pressure, (b) the evaluated exchange constant of the NN, J_1, and (c) the Néel temperature T_N (K) for the G-type AFM from molecular field theory.

Furthermore, it is found that the local magnetic moment of Cr ion decreases from 2.73 μ_B to 2.37μ_B as the pressure increases from zero to 80 GPa. This can be ascribed to the strong hybridization of Cr ion with the O atoms under high pressure. From Table 2, we can find that the bond lengths of Cr-O become shorter remarkably, varing from 2.01 to 1.83Å. The hybridization between Cr and O, therefore, is expected to be stronger as the pressure increases. Meanwhile, the c/a ratio increases from 0.968 to 1.06.

Table 2. Local magnetic moment of Cr, bond lengths of the nearest Cr-O, ratios of c/a and c/b of BiCrO$_3$ under various pressures.

Pressure(GPa)	Mag(μ_B)	(Cr-O)$_{NN}$(Å)	c/a	c/b
0	2.73	2.01	0.97	0.70
20	2.69	1.94	0.98	0.70
40	2.68	1.89	1.00	0.71
60	2.68	1.86	1.04	0.72
80	2.67	1.83	1.06	0.73

To estimate the Néel temperature of BiCrO$_3$ under various pressure, we have investigated the magnetic interaction constants based on Heisenberg mode[24]:

$$H_{ex} = -\sum_{i,j} J_{ij} S_i S_j , \qquad (1)$$

where the sum is extended over all the Cr ions. $J > 0$ and $J < 0$ are corresponding to FM and AFM coupling, respectively. Here S$_i$=S$_j$=3/2 is adopted for Cr^{3+} ion characterized by a $3d^3$ electronic configuration. Here, we only take the nearest-neighbors (NN) J_1 and the next-nearest-neighbors (NNN) J_2 into account within the second nearest neighbor approximation. In the periodical magnetic structure of BiCrO$_3$, each Cr ion has six NN and twelve NNN spin exchange interactions, in orthorhom-

bic BiCrO$_3$. All six NN and twelve NNN interactions are equivalent. Within the GGA approach, it turns out that J_1 is always negative and its absolute value gets greater with the increasing pressure. This also implies that the NN pair of Cr ions prefers to AFM coupling, which becomes stronger as external pressure increases. Panel (a) of Fig. 2 shows that the magnetic interaction constant increases linearly with respect to the increasing pressure.

Moreover, based on the molecular field theory[24, 25], the Néel temperature T_N could be estimated by：

$$T_N^{G-AFM} = \frac{2S(S+1)}{3k_B} z |J_1|.$$

(2)

Here K_B is the Boltzmann constant. The estimated Néel temperature clearly increases as the pressure increases, as shown in Fig. 2 panel (c). When pressure was zero, the calculated value for T_N=218 k, is twice as large as the experiment measurement of T_N=109 K at ambient environment. It should be mentioned that the molecular field theory generally yields an upper bound of the Néel temperature, as the electronic fluctuations are neglected. In this work, we predicted the tendency of Néel temperature changes when under pressure. The experimentally measured temperature is thus expected to be lower than the predicted one.
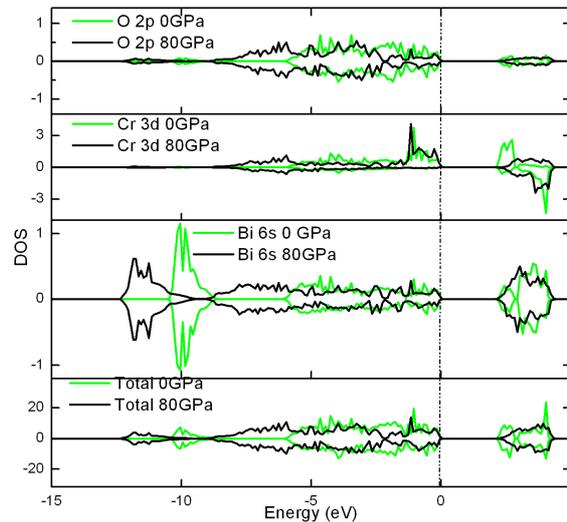

Fig. 3 (color online). GGA+U (U_{eff}= 3eV) calculated TDOS and projected DOS of BiCrO$_3$ in G-type AFM configuration under pressures of zero and 80GPa. The dotted line corresponds to the VBM.

Conclusion

In conclusion, we have investigated the magnetic properties of orthorhombic BiCrO$_3$ under pressure from 0 to 80GPa by first-principles calculations with GGA and GGA+U approaches. Our results indicate that the ground state of orthorhombic BiCrO$_3$ is G-type AFM, which becomes more stable with respect to the FM configuration as the pressure increases. This implies that it is unrealistic to transform BiCrO$_3$ into ferromagnetism by external pressure, and thus, other approaches (such as doping magnetic ions) are suggested[26].

Acknowledgments

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Soft Magnetic Materials

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