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Ab initio study of the giant ferroelectric distortion and pressure induced spin-state transition in $BiCoO_3$

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Using configuration-state-constrained electronic structure calculations based on the generalized gradient approximation plus Hubbard U method, we sought the origin of the giant tetragonal ferroelectric distortion in the ambient phase of the potentially multiferroic material $BiCoO_3$ and identified the nature of the pressure induced spin-state transition. Our results show that a strong Bi-O covalency drives the giant ferroelectric distortion, which is further stabilized by an xy-type orbital ordering of the high-spin (HS) Co^{3+} ions. For the orthorhombic phase under 5.8 GPa, we find that a mixed HS and low-spin (LS) state is more stable than both LS and intermediate-spin (IS) states, and that the former well accounts for the available experimental results. Thus, we identify that the pressure induced spin-state transition is via a mixed HS+LS state, and we predict that the HS-to-LS transition would be complete upon a large volume decrease of about 20%.

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I. INTRODUCTION

Multiferroic materials, having coexisting magnetism and ferroelectricity, are of great technological and fundamental importance,[1–3] given the prospect of controlling charges by applying magnetic fields and spins by voltages. $BiCoO_3$ was recently synthesized by a high-pressure (HP) technique,[4] and it has been suggested to be a promising multiferroic material by Uratani *et al.*[5] and by Ravindran *et al.*[6] both through first-principles Berry-phase calculations. $BiCoO_3$ has a giant tetragonal lattice distortion of $c/a = 1.27$ with remarkable off-center atomic displacements (see the inset of Fig. 1), and it is an insulator having C-type antiferromagnetism below 470 K—the antiferromagnetic (AF) ab layers stacking ferromagnetically along the c axis.[4]

It was proposed[5,7,8] that the giant tetragonal distortion originates from lifting of the orbital degeneracy of the high-spin (HS, S=2) Co^{3+} ions and is stabilized by the subsequent xy-type ferro-orbital ordering. Note that orbitally degenerate transition-metal oxides quite often display an orbital ordering (OO) but ferroelectric (FE) materials out of them are rare, as ferroelectricity and magnetism seem, and actually in most cases, to exclude each other.[9,10] Therefore, the proposed mechanism for the giant FE distortion appears not straightforward. Using fixed-spin-moment density-functional calculations, Ravindran *et al.*[6] predicted that there is a giant magnetoelectric coupling in $BiCoO_3$: an external electric field (or a small volume compression of $\sim$5%) can induce a strong magnetic response by changing the magnetic Co^{3+}-HS state in the FE phase into a nonmagnetic low-spin (LS, S=0) state in a paraelectric (PE) phase. A corresponding HS-insulator/LS-metal transition was also suggested.[6,11] In sharp contrast, a very recent HP study[7] showed that $BiCoO_3$ even under 6 GPa with a large volume decrease of 18% is still semiconducting. Note however that controversial spin states, both LS and intermediate-spin (IS, S=1), were suggested for the HP phase.[7]

In the present work, we seek the origin of the giant tetragonal FE distortion in the ambient phase of $BiCoO_3$ and identify the nature of the pressure induced spin-state transition, using two sets of configuration-state-constrained GGA+U (generalized gradient approximation plus Hubbard U) calculations. Our results show that the giant tetragonal distortion is driven by a strong Bi-O covalency (rather than by the aforementioned lifting of orbital degeneracy) and is further stabilized by an xy-type OO of the HS Co^{3+} ions. Moreover, we find that the pressure-induced spin-state transition is via a mixed HS+LS state, which accounts for the available experimental results consistently and disproves a recent prediction of a readily switchable HS-LS transition.

II. COMPUTATIONAL DETAILS

We used the structural data of $BiCoO_3$ measured by the neutron power diffraction.[7] Our calculations were performed using the full-potential augmented plane-wave plus local-orbital code WIEN2k.[12] The muffin-tin sphere radii were chosen to be 2.3, 1.9, and 1.4 bohr for Bi, Co, and O atoms, respectively (1.0 bohr for O when calculating the E-V curves shown in Fig. 6). The cutoff energy of 16 Ryd was set for the plane-wave expansion of interstitial wave functions, and 1200 **k** points in the first Brillouin zone for the ambient structure with one formula unit (f.u.) and 300 **k** points for the HP phase with 4 f.u.

Plain GGA [or local-spin-density approximation (LSDA)] calculations[5,6,11,13] seem to qualitatively re-

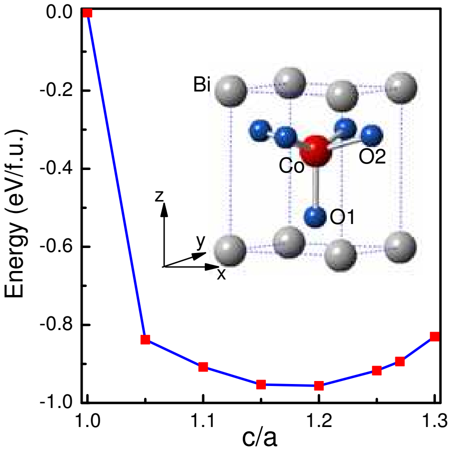

FIG. 1: (Color online) E *vs* c/a curve calculated by GGA+U for the Co^{3+}-LS relaxed structures of $BiCoO_3$ with c/a = 1-1.3 (in a step of 0.05) including 1.27 (expt.). The inset shows a unit cell of the experimental tetragonal structure.

produce the C-type AF and insulating ground state of $BiCoO_3$ in the ambient phase, which was ascribed to the strong Hund-exchange stabilized HS state of the Co^{3+} ions (and thus the AF order and narrow bands) and to the well split-off xy-singlet orbital. However, the band gap of 0.6 eV and the Co^{3+} spin moment of 2.4 μ_B given by the GGA/LSDA calculations are much smaller than the experimental values of 1.7 eV and 3.2 μ_B.[4,14] Moreover, a recent prediction of an insulator-metal transition in $BiCoO_3$ upon a volume decrease of $\sim$5% made by GGA/LSDA calculations[6,11] has already been disproved by a very recent HP study,[7] which shows that $BiCoO_3$ is still semiconducting even under 6 GPa with a large volume decrease of 18%. As seen below, the experimental values of both the band gap and the Co^{3+} spin moment are well reproduced by our GGA+U calculations. Note also that $BiCoO_3$ has an apparent AF order up to 470 K.[4] All these suggest that $BiCoO_3$ should rather be categorized as a Mott insulator, with its band gap determined primarily by Hubbard U, i.e., strong correlation of the Co $3d$ electrons.

To account for the strong electronic correlation,[15] we have carried out GGA+U calculations throughout this paper. In particular, we used the configuration-state-constrained GGA+U method,[16–18] which allows us to access different spin and orbital configuration states of the concern by initializing their corresponding density matrix and then doing self-consistent electronic relaxation.[19] This method is quite useful for study of the spin and orbital physics present in transition-metal oxides.[16–19] All the results shown below are obtained with U=6 eV and Hund exchange J=0.9 eV. We note that our test calculations using other reasonable U values,[13,18,19] U=5 and 7 eV, gave qualitatively the same results.

TABLE I: The total energies of $BiCoO_3$ (in unit of eV/f.u.) relative to the hypothetical cubic-structure LS state calculated by GGA+U: the experimental tetragonal phase assuming an LS state with atomic relaxations (the third row), assuming an HS state in the LS relaxed structure (the fourth row), and assuming the HS state with further atomic relaxations (the fifth (last) row). The optimized atomic z-coordinates are also shown. Note that the structural data of the atomically relaxed HS state are in good agreement with the experiment[7] (see the inset of Fig. 1). See more discussion in the main text.

States	ΔE	z_{Co}, z_{O1}, z_{O2}
Cubic LS	0	
Tetragonal LS-relaxed	–0.90	0.5897, 0.1889, 0.6853
Tetragonal HS at LS-relaxed	–1.47	
Tetragonal HS-relaxed	–1.97	0.5631, 0.1912, 0.7237

III. RESULTS AND DISCUSSION

We first seek the origin of the giant tetragonal distortion by starting with our calculations assuming an ideal cubic structure (space group $Pm\bar{3}m$) having the same volume as the experimental ambient tetragonal structure. Then we changed the c/a ratio of the tetragonal structure (keeping the volume unchanged) in our calculations. All those calculations were carried out by setting a hypothetical LS state of the Co^{3+} ions, and by doing a full electronic and atomic relaxation for the cases of c/a = 1.05-1.3 in a step of 0.05, and for the experimental 1.27 as well. All the solutions are insulating. As the LS Co^{3+} has a closed sub-shell t_{2g}^6 (thus no orbital degeneracy) and is an isotropic ion, we can use this set of LS-constrained GGA+U calculations as a computer experiment to probe mainly the Bi-O covalent effect.

We show in Fig. 1 the calculated total energies as function of the c/a ratios, and one can immediately find that the c/a ratio in the LS equilibrium state is close to 1.2 (about 1.18), already indicating a large tetragonal distortion. The corresponding energy gain, relative to the hypothetical cubic structure (c/a = 1), is 0.96 eV/f.u. For the LS relaxed structure with the experimental c/a = 1.27, the energy gain is 0.90 eV/f.u. We list in Table I (see the third row) the optimized atomic z-coordinates of the LS state with the experimental c/a ratio, and we find that the experimental CoO_5 coordination is well achieved [as seen from the optimized Co-O bondlengths, Co-O1: 1.893 Å×1, 2.832 Å×1 (much larger); Co-O2: 1.919 Å×4] even in the presence of the Co^{3+} LS state without orbital degeneracy. This is also the case for c/a = 1.2 with another optimized Co-O bondlengths, 1.881 Å×1, 2.677 Å×1, and 1.943 Å×4. We plot in Fig. 2(a) a charge density contour of the hypothetical cubic structure in the (100) plane, and in Fig. 2(b) that of the LS relaxed state with the experimental c/a ratio. Fig. 2(a) shows nearly spherical charge densities around both the Bi and O ions, indicative of Bi^{3+}-O^{2-} ionic bonds in the hypothetical cubic structure. In contrast, Fig. 2(b) clearly shows directional Bi-O covalent bonds, which are also indicated the orbitally resolved density of states (see Fig. 3 and the discussion below). All these suggest that the Bi-O covalency drives the giant tetragonal FE distortion and causes remarkable off-center atomic displacements, no matter that the Co^{3+} ions are in this hypothetical LS state or in the real HS state (see below). This is similar to the stereochemical mechanism of the Bi^{3+} $6s^2$ lone-pairs proposed for the highly distorted perovskite manganite $BiMnO_3$.[20]

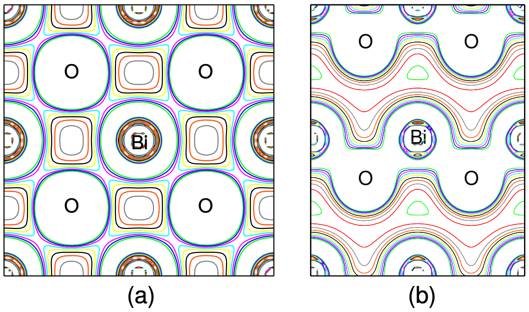

FIG. 2: (Color online) Charge density contour (0.01-0.1 $e/\AA^3$ in a step of 0.01 $e/\AA^3$) of $BiCoO_3$ in the (100) plane of (a) the hypothetical ideal cubic structure and of (b) the LS-relaxed structure with the experimental c/a ratio. The directional Bi-O covalency is apparent in (b).

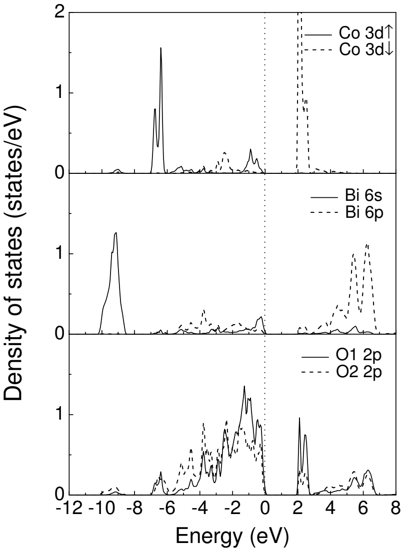

FIG. 3: Partial density of states of $BiCoO_3$ in the C-type AF ground state of the ambient phase.

TABLE II: The relative total energies ΔE (meV/f.u.), Co^{3+} spin moments M (μ_B), and band gap E_g (eV) of $BiCoO_3$ in the 5.8 GPa phase calculated by GGA+U for the LS-relaxed, IS-relaxed, and (HS+LS)-relaxed structures.

States	ΔE	M_{Co}	E_g
(HS+LS)-relaxed	0	3.07, 0.17	0.84
LS-relaxed	91	0	0.95
IS-relaxed	158	2.01	half-metal

Furthermore, we study the effect of the xy-type OO of the HS Co^{3+} ions on the giant tetragonal distortion. Owing to the effective CoO_5 pyramidal coordination already present in the LS relaxed tetragonal structures as described above, the crystal field (particularly the t_{2g}-e_g splitting) is weak and thus less important than the Hund exchange.[21] As a result, an HS state with an OO of the well split-off xy orbital is the ground state and more stable than the hypothetical LS state by 0.57 eV/f.u. for the experimental $c/a = 1.27$ (see the third and fourth rows in Table I) and by 0.59 eV/f.u. for $c/a = 1.2$. In this sense, the xy OO is a consequence of the Bi-O covalency driven tetragonal distortion and the associated CoO_5 pyramidal coordination. Moreover, our calculations doing structural optimization show that an adjustment of the lattice to this xy OO of the HS Co^{3+} ions changes the c/a ratio to 1.28 (as compared to 1.18 for the LS equilibrium state, see Fig. 1). This agrees very well with the experimental $c/a = 1.27$. Correspondingly, the experimental atomic parameters are also well reproduced, see the last row in Table I. Furthermore, we show in Fig. 3 the density of states of $BiCoO_3$ in the C-type AF ground state having the xy OO of the HS Co^{3+} ions. The calculated band gap of 1.98 eV and the Co^{3+} spin moment of 3.01 μ_B are also in good agreement with the experimental values of 1.7 eV and 3.24 μ_B.[4,14] Hybridizations between the Bi $6s6p$ and O $2p$ orbitals are also apparent and evidence again the Bi-O covalency, although the magnitude of their respective density of states is much underestimated within the muffin-tin spheres as those orbitals are spatially quite spread. In a word, all above results allow us to conclude that the giant tetragonal FE distortion of $BiCoO_3$ originates from the Bi-O covalency (rather than from lifting of the orbital degeneracy of the HS Co^{3+} ions[5,7,8]) and is further stabilized by the subsequent xy-type OO.

We now identify the nature of the pressure induced spin-state transition in $BiCoO_3$, using another set of constrained GGA+U calculations for the orthorhombic structure measured at 5.8 GPa, by assuming the LS, IS, and the mixed HS+LS states, respectively, and by doing a full electronic and atomic relaxation for each case.

As seen in Table II, the mixed HS+LS state has the lowest total energy, and the LS (IS) state lies above it by 91 (158) meV/f.u. Those results suggest that either the pure LS or IS state present in the 5.8 GPa phase[7] is not the case. Reversely, if the pure LS state were present in the 5.8 GPa phase, it would give rise to a change of the spin state from the pure HS state in the ambient phase, ΔS=2, being in disagreement with the observed ΔS=1.[7] Moreover, an absence of the IS state is also not surprising, as (1) $BiCoO_3$ in the 5.8 GPa phase is free of a Jahn-Teller distortion (that is expected for the localized IS Co^{3+}); (2) a half-metallic band structure of the IS state (see Fig. 4(a)) disagrees with the measured semiconducting behavior;[7] and (3) up to now a definite example of the insulating IS state appears still lacking, and even in the layered perovskites $LaSrCoO_4$

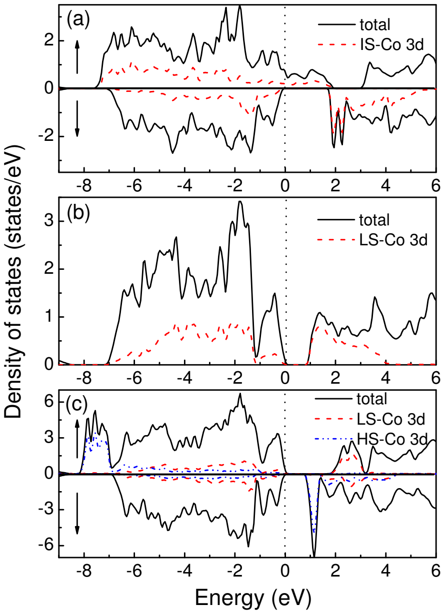

FIG. 4: (Color online) The total and Co $3d$ density of states of $BiCoO_3$ in the 5.8 GPa phase calculated by GGA+U for the relaxed IS (a), LS (b), and mixed HS+LS (c) structures, respectively.

and $La_{1.5}Sr_{0.5}CoO_4$ both having a strong tetragonal elongation of the $Co^{3+}O_6$ octahedra, the IS state turns out not to be the ground state either,[19] despite an IS state might be intuitively expected.

As such, the mixed HS+LS state is most probably present in the 5.8 GPa phase. An ideal 1:1 configuration of the mixed HS+LS state, with an average S=1, well accounts for the observed change of the spin state.[7] Moreover, a G-type order of the HS and LS Co^{3+} ions (each HS Co ion is surrounded by six LS Co ions, and vice versa), due to a bigger/smaller size of the HS/LS Co^{3+} ions, could help to gain an elastic energy, and the resultant Co-O bondlengths are calculated to be 1.980 (1.930), 1.976 (1.890), and 1.948 (1.906) Å for the HS (LS) Co^{3+} ions along the local xyz axes. Note, however, that a long-range G-type order of the HS and LS Co^{3+} ions is hard to establish, as only single transition-metal species in a single charge state and in the identical octahedral coordinations, i.e., solely Co^{3+} ions are involved. Thus, the average Co-O bondlengths of the mixed and disordered HS+LS state (possibly with a short-range order due to a partial release of the lattice elasticity) are also in good agreement with the experiment.[7] Furthermore, the calculated insulating gap of $BiCoO_3$ is reduced from 1.98 eV in the C-type AF state of the ambient phase to 0.84 eV in the mixed HS+LS state (see Fig. 4(c)), which qualitatively accounts for the decreasing resistivity of $BiCoO_3$ under pressure.[7]

Note that when considering thermal excitation of electrons into the initially empty conduction band and holes left in the valence band for a nominally stoichiometric material, these electron excitations would in a localized picture correspond to HS Co^{2+} states and holes to LS Co^{4+}. They behave like HS Co^{2+} and LS Co^{4+} "impurities" in the matrix of the Co^{3+} ions. As a result, in the ambient phase of $BiCoO_3$ having the HS Co^{3+} matrix, only the HS Co^{2+} "impurities" can transfer their minority-spin t_{2g} electrons to the neighboring HS Co^{3+}, without changing the configuration states (the initial and final states are the same), see Fig. 5(a). However, a hole hopping from the LS Co^{4+} to the HS Co^{3+} is significantly suppressed (see Fig. 5(b)), due to a cost of the Hund exchange energy associated with a large change of the spin states which is referred as to a spin-blockade mechanism.[22] In contrast, in the HP phase having the mixed and disordered HS+LS Co^{3+} matrix, a charge hopping can take place both between the HS Co^{2+} and HS Co^{3+} (Fig. 5(a)) and between the LS Co^{4+} and LS Co^{3+} (Fig. 5(c)). This could also account for the decreasing resistivity of $BiCoO_3$ under pressure.

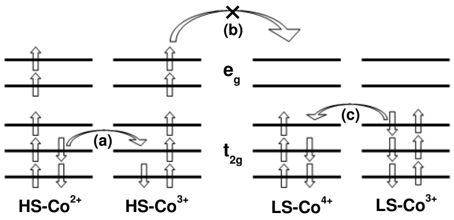

FIG. 5: Electron hopping (a) from an HS Co^{2+} ion to a neighboring HS Co^{3+} and (c) from an LS Co^{3+} to an LS Co^{4+}, but a suppressed electron hopping (b) from an HS Co^{3+} to an LS Co^{4+} due to a spin blockade.

Our above results show that even in the 5.8 GPa phase of $BiCoO_3$ with a large volume decrease of 18%, the HS-to-LS transition is not yet complete, and the system is most probably in the mixed HS+LS insulating state, but not in the pure-LS metallic state which was predicted by the previous GGA/LSDA calculations for $BiCoO_3$ upon a volume decrease of $\geq$5%.[6,11] As we discussed above, $BiCoO_3$ is rather a Mott insulator, and thus the previous GGA/LSDA results are somewhat questionable: particularly the predicted metallic solution was already disproved by a very recent experiment.[7] Recent fixed-spin-moment calculations even predicted that $BiCoO_3$ could have a giant magnetoelectric coupling with a readily switchable HS-LS transition associated with an electric field driven FE-PE transition.[6] We note that the prediction may simply be an artifact of the fixed-spin-moment calculations, as (1) LSDA or GGA (it was mentioned as a density-functional method in Ref[6]) is not well suitable to describe this Mott insulator; (2) most probably those calculations were carried out in a wrong ferromagnetic metallic state; and (3) their metallic solutions blurred the distinction between the different spin and orbital multiplets of the concern and thus suppressed significantly their level splittings and particularly the HS/LS splitting: the fixed-spin-moment calculations showed that for

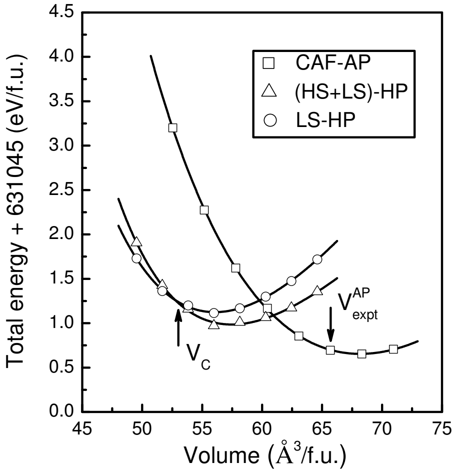

FIG. 6: E-V curves calculated by GGA+U for the C-type AF state of $BiCoO_3$ in the ambient phase, and for the mixed HS+LS state and the LS state under high pressures. The lattice volume of the ambient phase is slightly overestimated within 3%, and the critical volume for a complete transition into the LS state is estimated to be about 53 Å^3/f.u.

the ambient structure, the energy preference of the HS state over the LS state is less than 0.15 eV/f.u. (see Fig. 2 in Ref[6]), whereas the corresponding value we calculated is more than 0.5 eV/f.u. Therefore, the previous prediction of the HS-to-LS transition in $BiCoO_3$ with a small volume decrease of ∼5% was overly optimistic.[6] Instead, we find now that there is no readily switchable HS-LS transition is $BiCoO_3$.

As Bi^{3+} has a very similar ionic size as La^{3+}, it is reasonable to assume that when the local Co-O bondlengths of $BiCoO_3$ in the HP PE phase become identical to those of $LaCoO_3$ in the LS state at low temperature (1.925 Å at 5 K),[23] a complete transition into the LS state would be achieved in $BiCoO_3$. This, together with the structural data of the 5.8 GPa phase,[7] allows us to estimate the critical volume to be about 52.8 Å^3/f.u. (corresponding to a volume decrease of about 20%). Then, by extrapolating the eye-guided line of the V-P data points in the range of 2-6 GPa (see Fig. 1(b) in Ref[7]), we may estimate the critical pressure to be about 8 GPa. It is important to note that the estimated critical volume is indeed well reproduced by our detailed calculations of the E-V curves (see Fig. 6, $V_c \approx 53$ Å^3/f.u.), which also nicely reproduce the equilibrium volume of the ambient phase within 3% and clearly indicate the HS-to-LS transition via the mixed HS+LS state. This prediction of a complete transition into the LS state awaits a further HP study.

IV. CONCLUSION

To conclude, using configuration-state-constrained GGA+U calculations, we demonstrate that the giant tetragonal ferroelectric distortion of $BiCoO_3$ is driven by the strong Bi-O covalency (rather than by lifting of the orbital degeneracy of the HS Co^{3+} ions) and is further stabilized by a subsequent xy-type OO. Moreover, our results show that the pressure induced HS-to-LS transition is via a mixed HS+LS state, and that the transition would be complete upon a large volume decrease of about 20% (under about 8 GPa). The mixed HS+LS state well accounts for the available experimental results.[7]

V. ACKNOWLEDGMENTS

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