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2004 J. Phys.: Condens. Matter 16 S5677

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First-principles study on the electronic structure of bismuth transition-metal oxides

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Received 24 May 2004

Published 19 November 2004

Online at stacks.iop.org/JPhysCM/16/S5677

doi:10.1088/0953-8984/16/48/026

Abstract

The electronic structure, magnetic and electric properties, and lattice stability of multiferroic BiMnO₃ as a typical system in perovskite Bi transition-metal oxides (BiMO₃) are studied from first principles. It is demonstrated theoretically for the first time that the orbital ordering within the Mn e_g orbitals is actually realized in BiMnO₃, being consistent with crystallographic data, and plays a crucial role in the appearance of ferromagnetism. Total-energy calculation shows the ferromagnetic state is indeed stabilized. Electrical polarization of BiMnO₃ is also estimated based on the Berry phase theory. Lattice instability to off-centred displacement, which is driven by strong covalent bonding between Bi 6p and O 2p states, is found to be rather common in the BiMO₃ series.

1. Introduction

Multiferroic materials, where more than one of ferromagnetic, ferroelectric and ferroelastic properties appear simultaneously, have attracted much attention because of their novel phenomena and possible applications to new devices. Among them, perovskite-type bismuth transition-metal oxides (BiMO₃) form a unique material group of particular interest. BiMnO₃ is well known to reveal biferric (ferromagnetic and ferroelectric) properties [1–5]. BiFeO₃ has anti-ferromagnetic and ferroelectric behaviours in the rhombohedral bulk phase. Recently, it has been reported [6] that epitaxial BiFeO₃ thin film shows large room-temperature spontaneous polarization ($>50 \mu\text{C cm}^{-2}$) greatly enhanced from its bulk value of about $6 \mu\text{C cm}^{-2}$.

In this study, we investigate the electronic structure, magnetism and lattice stability of BiMO₃ by particularly focusing on BiMnO₃ as the typical multiferroic system. Although some results of band structure calculations for BiMnO₃ have been presented [7, 8], important information such as the realization of orbital ordering [9–13] investigated in this work has never been reported. For the first time it is confirmed theoretically that, in BiMnO₃, orbital

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ordering does exist with the same structure as proposed experimentally. In BiMnO₃ electrical polarization is calculated and compared with available experiments. We show that lattice instability to the off-centre displacement seen in BiMnO₃ is rather general in perovskite BiMO₃, where hybridization between Bi 6p and O 2p orbitals plays an essential role.

2. Properties and crystal structure of BiMnO₃

At electric Curie temperature $T_E \simeq 770$ K, BiMnO₃ undergoes a structural phase transition from *Pbnm* orthorhombic to non-centrosymmetric *C2* monoclinic structure [2, 4, 5], where insulating resistivity was found and spontaneous electrical polarization may exist. At magnetic Curie temperature $T_M \simeq 105$ K, a further paramagnetic-to-ferromagnetic transition [3, 5] is revealed, while retaining *C2* crystal structure, i.e. ferromagnetism and ferroelectrics may coexist therein. Both ferromagnetic and ferroelectric hysteresis loops for thin films and impure bulk samples have actually been observed [3]. The magnetic moment measured [1] was $3.6 \mu_B$ at 5 T and 5 K although an insulating ferromagnet should have an integer value, $4 \mu_B$ in this case. Interestingly, around T_M where the magnetic fluctuation is strong, the magnetocapacitance effect [5] has been observed recently.

The magnetism of BiMnO₃ is in sharp contrast with that of LaMnO₃. A simple consideration of the nominal ionic valence gives that, in both materials, the Mn 3d state is formally given by the $t_{2g}^3 e_g^1$ configuration (Mn³⁺ 3d⁴) and thus is Jahn–Teller (JT) active. Furthermore, the ionic radii of Bi and La are very close to each other. Despite these resemblances, their magnetic structures are completely different. It is well established for LaMnO₃ that the orbital ordering among the e_g states takes place and stabilizes the A-type antiferromagnetic spin arrangement. By contrast, a different type of orbital order may occur in BiMnO₃, which makes ferromagnetic spin order favourable, and which might have correlation with the off-centred displacement that is not seen in LaMnO₃.

As demonstrated in figure 1, the *C2* structure of BiMnO₃ can be regarded as a highly distorted perovskite [4]. The unit cell is composed of four formula units, containing two Bi, three Mn and six O sites. The fundamental nature of this structure is perceived as follows. First, there is a π rotation symmetry around the *b* axis, ruling out any net polarization except along the *b* axis. Secondly, BiO₃ tetrahedra are tightly formed with shortened bond length, resulting mainly from O displacements. It seems that the electrical polarization, if it exists, is produced by these tetrahedra. Two of them are oriented toward *b*, while the other two are oriented toward $-b$. Hence this structure should be considered basically as *antiferroelectric* and a small difference in local environment between the two Bi sites makes it *ferrielectric*. Finally, each MnO₆ octahedron, which gets warped strongly from the regular one, bears a weak signature of the JT uniaxial elongation. Based on this, a three-dimensional orbital ordering of Mn e_g orbits is proposed [2, 4], as illustrated in figure 1, where ferro-alignment of the occupied e_g orbitals is seen on (111) planes and a set of four sheets (Mn(1), Mn(2), Mn(3) and Mn(2) planes) determines the periodicity of the three-dimensional ordering. Provided this kind of the orbital ordering, the Kanamori–Goodenough rule [9–13] shows that the ferromagnetic state could be favourable [4]. However, the assumed orbital ordering has never been confirmed so far, either experimentally or theoretically. Such confirmation from first principles is the main purpose of the present study.

3. Electronic band structure of BiMnO₃

In order to calculate the electronic structure and related properties, we use the all-electron full-potential linear augmented plane wave (FLAPW) method based on the local spin density approximation (LSDA) and the LSDA + *U* approach [14, 17] in the scalar-relativistic regime.

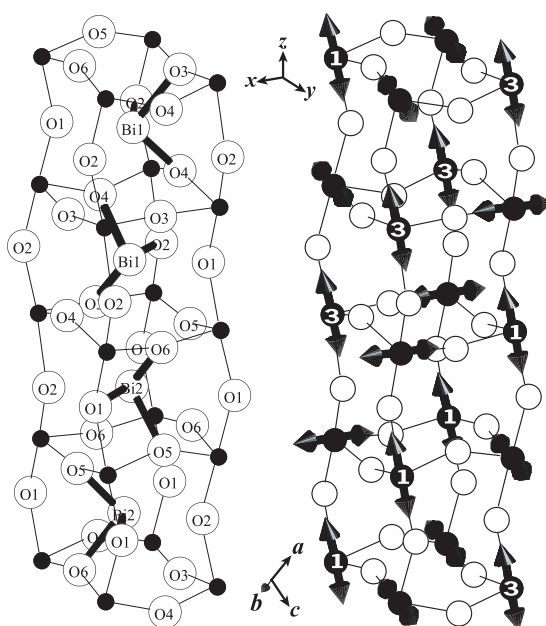


Figure 1. C_2 monoclinic crystal structure of BiMnO_3 (not a unit cell), carving out four contiguous pseudo cubes. The C_2 axes (a , b , and c) are shown together with the principal axes of the pseudo cube. Note $b \parallel$ cubic $[110]$. Left: the filled sphere denotes Mn. Formation of BiO_3 tetrahedra is clearly seen. The site numbering is after [4]. Right: schematic view of the proposed orbital ordering. The occupied Mn e_g orbital is shown by arrows. The filled sphere without a number represents a Mn(2) site.

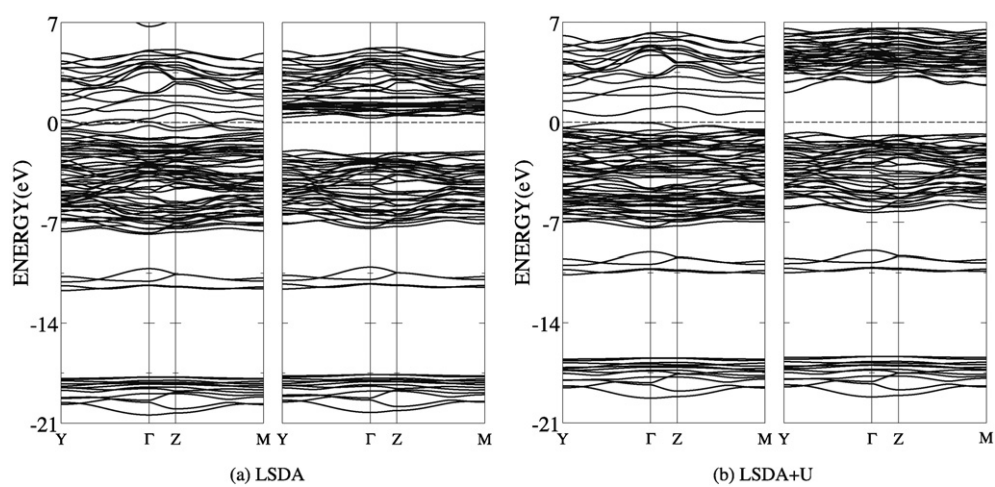


Figure 2. Energy band structure of monoclinic ferromagnetic BiMnO_3 calculated by (a) LSDA and (b) LSDA + U approaches. Zero energy is taken at the Fermi level in (a) and the top of the valence band in (b).

Shown in figure 2(a) is the LSDA band dispersion, using the experimental lattice data determined by neutron diffraction at 20 K [4]. Unfortunately the band gap cannot be obtained for the majority spin state. Instead, a half-metallic electronic structure is achieved with a gap

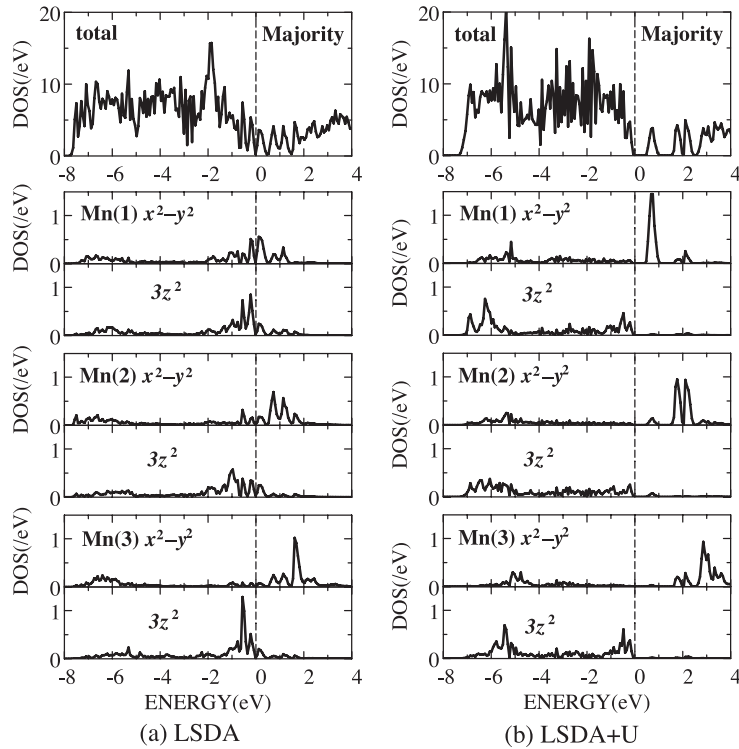


Figure 3. Majority-spin total DOS obtained by (a) LSDA and (b) LSDA + U and their projection onto e_g orbitals of each Mn site. Zero energy is set as the highest occupied level and is depicted by a vertical broken line.

in the minority spin. Those states crossing the Fermi level are dominated by Mn 3d states hybridizing with O 2p states and the failure in having insulating property must be attributed to the well-known shortcoming of LSDA: it generally underestimates band gap and often fails in describing the insulating property for strongly correlated electron systems. One way to cast away this problem is to use the LSDA + U method, where a Hartree–Fock type potential [14] is alternatively adopted to specific states causing trouble, in the current case, Mn 3d states. For the parameter U (equivalently Slater integral F_0), we adopt the typical value of 8 eV for transition metal oxides [15–18]. For F_2 and F_4 , we set 9.132 and 5.7184 eV, respectively, which are from atomic values with appropriate reduction [19] and give $J = 1.06$ eV. The result is shown in figure 2(b). Some of the majority-spin 3d states are pushed down, and we get a small band gap of 0.5 eV. For the minority spin state the band gap is further enhanced.

Now, let us look at the occupied and unoccupied Mn 3d state given by the LSDA and LSDA + U calculations in order to clarify what kind of orbital ordering takes place. Figure 3(b) shows the LSDA + U majority-spin density of states (DOS) and its projection onto Mn e_g orbitals. Note that the Mn t_{2g} orbitals (not shown) are fully occupied in the majority-spin bands at all Mn sites. Here the principal axes are rotated in such a way that the local z axis is along the JT elongation at each Mn site. At all Mn sites, the $3z^2$ orbital is occupied, and the unoccupied state is $x^2 - y^2$. This provides the first theoretical confirmation that the expected orbital order is actually realized. The trend of the preferential occupation among the e_g orbitals is also seen even in the LSDA DOS, where no clear band gap was formed, as shown in figure 3(a). According to the Kanamori–Goodenough rule [9–13] with this orbital-ordering structure, the

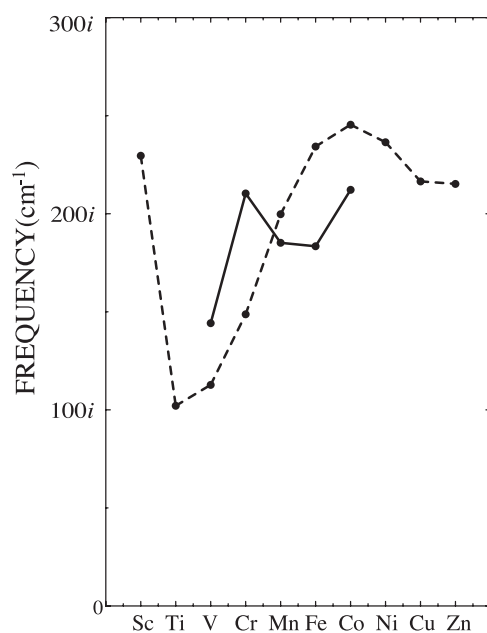


Figure 4. Calculated soft-mode phonon frequencies for BiMO_3 within the frozen phonon approximation. Dots connected with solid and broken lines indicate the results for ferromagnetic and non-magnetic phases, respectively.

superexchange interaction between adjacent Mn ions (six neighbours) is ferromagnetic for four paths and antiferromagnetic for two paths, leading to an inference that the ferromagnetic ground state would be favourable though some magnetic frustration is present [4]. This should be compared with the *ab initio* energetics. For this reason we chose G-type antiferromagnetic structure, in which nearest-neighbouring Mn pairs are all aligned antiferromagnetically. The space group overridden by this magnetic structure is retained as $C2$. Total energy difference between ferromagnetic and antiferromagnetic states, $\Delta E = E_{\text{FM}} - E_{\text{AFM}}$, is -87 and -85 by LSDA and LSDA + U , respectively, in units of meV/fu. Regardless of the method applied, the ferromagnetic state is indeed lower in energy.

4. Spontaneous polarization of BiMnO_3

Once the insulating band gap is formed, the electrical polarization ΔP can be calculated from eigenstates based on the Berry phase technique [20–22]. ΔP is the polarization difference between the experimental ferroelectric $C2$ structure and certain reference structure where net polarization vanishes by symmetry. The point charge model, assuming nominal valences, Bi^{3+} , Mn^{3+} and O^{2-} , gives $2.26 \mu\text{C cm}^{-2}$. This value is far more reduced in the actual LSDA + U calculation, $0.52 \mu\text{C cm}^{-2}$, indicating a considerable screening effect by electrons and covalent-bonding effects as well. Reasonable agreement is obtained between theory and experiment, considering that the bulk sample for the measurement is not single crystal: at 87 K the observed value [3] is $0.13 \mu\text{C cm}^{-2}$ under the electric field of 27 kV cm^{-1} and $0.062 \mu\text{C cm}^{-2}$ as the remnant polarization.

5. Lattice instability in BiMO_3

The lattice instability to off-centre displacement is examined for the hypothetical cubic phase of BiMO_3 ($M = \text{Sc}$ through Zn) with the lattice constant of $a = 4 \text{ \AA}$. A stable

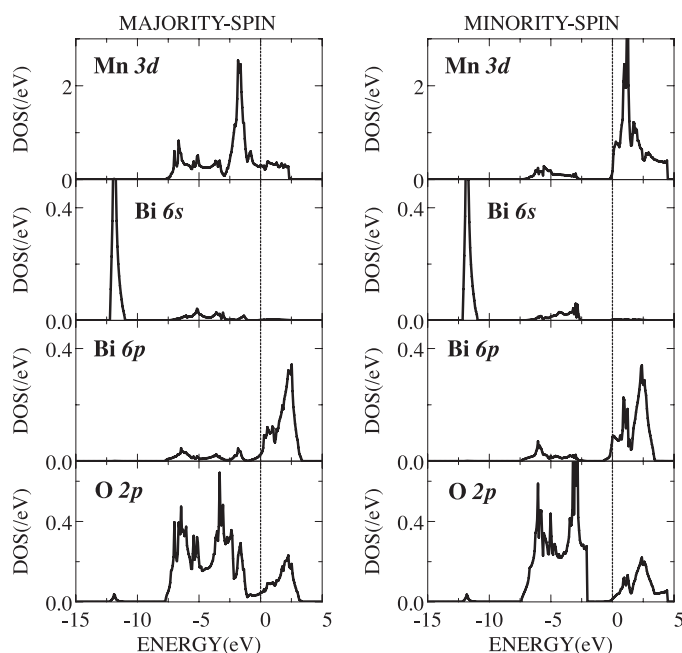


Figure 5. LSDA DOS of cubic ferromagnetic BiMnO₃ projected onto Mn 3d, Bi 6s, 6p and O 2p states. The Fermi level is denoted by the vertical dotted line.

ferromagnetic solution is obtained in BiMO₃ with $M = \text{V, Cr, Mn, Fe and Co}$. For all the cases studied, regardless of the magnetic ordering, we find one zone-centre soft mode, in which the Bi ion and the MO₆ octahedron show opposite displacements, resulting in breakdown of centrosymmetry. Figure 4 shows the soft-mode phonon frequencies calculated for non-magnetic and ferromagnetic BiMO₃ by the frozen phonon approximation. In addition to the off-centre soft mode, we find in some cases another soft mode which keeps the centrosymmetry [7] and is irrelevant in the present investigation.

The lattice instability to the off-centre displacement can be understood quite simply from the characteristic electronic structure inherent in BiMO₃. The noticeable feature in figure 5, where the majority-spin LSDA DOS of cubic ferromagnetic BiMnO₃ is shown, is strong hybridization between Bi 6p and O 2p states, that is not seen for LaMnO₃. Consequently, some portion of Bi 6p states is occupied with the building bonding state with O 2p orbitals. In the cubic structure, Bi has 12 coordinates with O. Allowing off-centre displacement like the present soft mode, the number of coordinates will be decreased. However, with closer bond length achieved for selected Bi–O bonds, the splitting between bonding and antibonding states will become larger and we will have energy gain. This is the driving force for the off-centre displacement commonly seen in BiMO₃. Since [23] it has been widely believed that the Bi 6s lone pair plays an essential role in the off-centre displacement. Our result indicates that the Bi 6s states can hardly play any positive role, at least in BiMO₃, since they are fully occupied with the strong peak located at very deep binding energy and no energy gain associated with the off-centre displacement is expected from them [24].

6. Summary

From the first-principles calculation using the highly precise FLAPW method, we have shown for BiMnO₃ that the Mn 3d states experience orbital ordering, which is consistent with the JT

distortion and stabilizes the ferromagnetic spin ordering. The electrical polarization calculated by LSDA+ U and the Berry phase theory is in reasonable agreement with experiments available. The lattice instability to the off-centred displacement is common in the BiMO₃ series and is due to the strong covalent bonding between Bi 6p and O 2p states. Further first-principles investigation of the electronic properties in BiMO₃ is strongly desired for future materials and device design.

Acknowledgments

This work is supported in part by a Grant-in-Aid for Scientific Research on Priority Area A and COE Research (No. 13CE2002) of the Ministry of Education, Culture, Sports, Science and Technology of Japan. The computation in this work has been partly performed using the facilities of the Supercomputer Center, at ISSP, University of Tokyo, and at IMR, Tohoku University.

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