Electronic structure of Bi_2CuO_4 with antiferromagnetic spin ordering

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The electronic structure of antiferromagnetic Bi_2CuO_4 is calculated by using generalized gradient approximation considering on-site Coulomb interaction between d-electrons (GGA+U). The GGA+U calculation indicates clearly that the antiferromagnetic phase is the stablest among non-magnetic, ferromagnetic and antiferromagnetic phases. By using U parameter (7.48 eV) and J parameter (0.95 eV), the band gap energy of Bi_2CuO_4 is calculated to be ca. 2.4 eV, which is comparable to the experimental one. The valence band maximum is approximately located at the X-point and the conduction band minimum at the Γ -point. This means that antiferromagnetic Bi_2CuO_4 is an indirect energy gap material. The calculated total density of states of Bi_2CuO_4 well corresponds to the state density experimentally deduced by x-ray photoelectron and electron-energy-loss spectroscopy. Also, it is found from the partial density of states analysis that the top of the valence band is mainly formed by O 2p orbitals, whereas the lower conduction band mainly consists of Cu 3d_{x²-y²} orbitals. The magnetic moment at Cu sites is calculated to be 0.72 μ_B , which is close to experimental values.

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Introduction

Bi_2CuO_4 with a layered oxocuprate (Kusachiite) shows blackish metallic luster.¹⁾ Since the discovery of the high-Tc superconductors, the magnetic and structural properties of Bi_2CuO_4 have been extensively investigated with respect to its non-superconductivity. X-ray and neutron diffraction measurements of Bi_2CuO_4 showed that the CuO_4 square-planar units stack along the c-axis in a staggered way and Bi^{3+} ions occupy spaces between these CuO_4 square-planar units.²⁾ Magnetic and neutron diffraction measurements revealed that Bi_2CuO_4 has three-dimensional (3D) anisotropic antiferromagnetic ordering below the Neel temperature below 42 K.^{2)–4)} In spite of these experimental studies there are few theoretical reports on the electronic and magnetic structures of Bi_2CuO_4 . Recently, Janson et al. investigated the electronic and magnetic structures of Bi_2CuO_4 by using a first-principles energy band calculation and a tight-binding fitting.⁵⁾ Their results well agree with experimental magnetic properties reported in the literature.⁶⁾ However, the electronic structure of Bi_2CuO_4 with AFM spin ordering is not clarified sufficiently. In the present study, we calculate the total energies for the non-magnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) phases and discuss the stability of three phases in Bi_2CuO_4 . As for the most stable phase (AFM), its electronic and magnetic structures of Bi_2CuO_4 are calculated with a full potential linearized augmented plane wave (FLAPW) method based on the density-functional theory (DFT).⁷⁾

Calculation method

It is well-known that the energy band calculations based on a local spin-density approximation (LSDA) or a generalized gradient approximation (GGA) give an incorrect electronic structure of strongly correlated materials such as Bi_2CuO_4 . Alternatively, we employed a generalized gradient approximation considering on-site Coulomb interaction between d-electrons (GGA+U).^{7),8)} The FLAPW calculation was carried out by way of two step scf-cycles, the first step is a GGA calculation and the second step a GGA+U calculation. In the GGA calculation, the exchange and correlation interactions were treated with the potential proposed by Perdew et al.⁹⁾ We used two types of the basis functions; a linear combination of (1) radial functions multiplied by spherical harmonics inside the muffin-tin (MT) region and (2) plane waves in the interstitial region. The MT spheres radii (R_{MT}) of the Bi, Cu and O atoms were respectively 2.0, 1.9 and 1.7 a.u. and approximately 3600 plane waves were adopted. The plane wave cutoff was $R_{\text{MT}} \cdot K_{\text{max}} = 7.0$ and the Brillouin-zone integrations were performed using the modified tetrahedron method within the irreducible wedge (24 k points for $P4/ncc$ and 42 k points for $P4cc$). In the GGA+U calculation, Coulomb (U) and exchange (J) parameters, which are mean values for Coulomb and exchange interactions in the considered shell, were assumed to be 7.48 and 0.95 eV, which are typical values for copper oxides.¹⁰⁾

Results and discussion

The crystal structure of Bi_2CuO_4 is shown in Fig. 1. Arrows in Fig. 2 indicate the orientation of the Cu^{2+} moment below the

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Fig. 1. Crystal structure of Bi_2CuO_4 . Fig. 2. Antiferromagnetic spin structure of Bi_2CuO_4 . Only Cu atoms are presented by circles.

Neel temperature as reported in the literature.^{4),6)} Cu^{2+} spins are stacked ferromagnetically along the c -axis (ferromagnetic chains) and these chains antiferromagnetically arrange with respect to each other. Bi_2CuO_4 has a $P4/ncc$ and unit-cell parameters: $a = 0.85019$, $c = 0.58196$ nm and Bi atoms occupy Wyck-off positions 8f ($x = 0.58138$), Cu atoms 4c ($z = 0.9210$), and O atoms 16 g ($x = 0.4505$, $y = 0.3580$, $z = 0.9091$), respectively.⁴⁾ The calculations for the NM and the FM phases of Bi_2CuO_4 crystal were implemented regarding the structure that has $P4/ncc$ symmetry. In AFM Bi_2CuO_4 crystal, the space group is changed from $P4/ncc$ to $P4cc$. For $P4cc$ symmetry, Cu atoms are allocated for Wyckoff positions 2a ($z = 0$ (Cu (1))) and 2b ($z = 0.1580$ (Cu (2))), Bi atoms for 8d ($x = 0.3314$, $y = 0.1686$, $z = 0.8290$) and O atoms for 8d ($x = 0.2005$, $y = 0.1080$, $z = 0.4881$ (O (1)) and $x = 0.2995$, $y = 0.3920$, $z = 0.6699$ (O (2))). For simplicity, we changed the local rotation matrix for Cu so that the direction of the side of CuO_4 sheets approximately agrees with x - or y -axis in the crystallographic coordination.

There are three different magnetic interactions between the ferromagnetic chains; NM, FM and AFM phases. By using GGA approach, we calculated the total energies for NM, FM and AFM phases. The total energy differences between AFM and FM phases ($E_{\text{AFM}} - E_{\text{FM}}$) and between AFM and NM phases ($E_{\text{AFM}} - E_{\text{NM}}$) are listed in Table 1. Negative values are seen for both the energy differences, $E_{\text{AFM}} - E_{\text{NM}}$ and $E_{\text{AFM}} - E_{\text{FM}}$, indicating that the

Table 1. Total Energy Differences in eV Unit between NM and AFM Phases ($E_{\text{AFM}} - E_{\text{NM}}$) and between FM and AFM Phases ($E_{\text{AFM}} - E_{\text{FM}}$) of Bi_2CuO_4

Calculation method	Total energy difference (eV)	
GGA	$E_{\text{AFM}} - E_{\text{NM}}$	-0.87
	$E_{\text{AFM}} - E_{\text{FM}}$	-0.42
GGA+U	$E_{\text{AFM}} - E_{\text{FM}}$	-0.38

Fig. 3. Energy band structure of up-spin states for AFM Bi_2CuO_4 along the symmetry lines of the first Brillouin zone.

AFM phase is the most stable among the three ground-state magnetic configurations. The GGA+U calculation does not change the conclusion that AFM spin structure is stable compared with that of FM. These results are well consistent with the experimental results obtained from the neutron power diffraction.^{2)-4),6)}

In Fig. 3, the self-consistent band structure of up-spin states for AFM Bi_2CuO_4 with $P4cc$ structure is plotted along the high symmetry lines of the first Brillouin zone for the primitive tetragonal Bravais lattice. The valence band maximum (VBM) is approximately located at the X-point and the conduction band minimum (CBM) at the Γ -point. This means that AFM Bi_2CuO_4 is an indirect energy gap material. The band gap energy of Bi_2CuO_4 is calculated to be ca. 2.4 eV, which is comparable to the results estimated from x-ray photoelectron (XPS) and electron-energy-loss spectroscopy (EELS) measurements for Bi_2CuO_4 single crystal.¹¹⁾ The increase of the band gap energy is caused by including the on-site Coulomb interaction between d-electrons that enhances the splitting between the filled and empty orbitals in Cu 3d manifold.

Figure 4 shows the up-spin and down-spin densities of states (DOS) for AFM Bi_2CuO_4 . In the AFM calculation, it should be noted that the up-spin densities for Cu (1) and Cu (2) are identical with the down-spin densities for Cu (2) and Cu (1), respectively. Analogously, there is the same relationship between O (1) and O (2). The valence band can be divided into three

Fig. 4. Density of states of AFM Bi_2CuO_4 obtained from GGA+U calculation. (a) up-spin states, (b) down-spin states.

energy regions ranging approximately from -10.5 to -8.4 eV (part-I), -7.4 to -7.1 eV (part-II) and -6.1 to 0 eV (part-III). Furthermore, the partial DOS which are related to each atomic orbital of Cu(1), Cu(2), Bi, O(1) and O(2) were calculated to carry out a detailed analysis. As shown in Fig. 5, it is found that the small densities in part-I mainly consists of Bi 6s orbitals. In part-II, the narrow densities like atomic states result from Cu (1) $3d_{x^2-y^2}$ orbitals. In part-III region, Cu 3d orbitals are strongly hybridized with O 2p orbitals whereas the contribution of Bi-related orbitals is weak there. On the other hand, the conduction band can be partitioned into the two energy regions below approximately 2.9 eV (part-IV) and above 2.9 eV (part-V). The narrow peak in part-IV almost belongs to Cu (2) $3d_{x^2-y^2}$ orbitals. The conduction band in part-V is mainly built up with the interaction between Bi 6p and O 2p orbitals.

The magnetic moment for each constituent atom of Bi_2CuO_4 was evaluated by the spin magnetization inside each MT sphere

(or LAPW sphere). The magnetic moments calculated by the GGA and GGA+U approaches are listed in Table 2. As seen in Table 2, the GGA calculation for AFM Bi_2CuO_4 leads to the same absolute values of the moments for Cu (1) and Cu (2), i. e., $0.53 \mu_B$, whereas the GGA+U calculation gives $0.72 \mu_B$. An appreciable magnetic moment appears at oxygen sites because of the strong Cu 3d – O 2p hybridization. The theoretical magnetic moment at Cu sites obtained from the GGA approach is smaller than that of the GGA+U approach, because of the underestimation of on-site Coulomb interaction between 3d electrons. The calculated magnetic moment of $0.72 \mu_B$ is approximately identical with experimental ones ($0.85 \pm 0.05 \mu_B$ and $0.7(1) \mu_B$), which were estimated from neutron diffraction measurements.^{4,6)} The agreement between theory and experiment supports a model that Cu^{2+} spins stacking along the c-axis are ordered ferromagnetically and these chains interact antiferromagnetically.

Fig. 5. Up-spin density of states for each atomic orbital of AFM Bi_2CuO_4 obtained from GGA+U calculation.

Table 2. Calculated Magnetic Moment at Cu(1), Cu(2), Bi, O(1), and O(2) Sites Per Atom and Total Magnetic Moment Including Those at Interstitial Sites Per Formula Unit. All Values are Given in μ_B Units

	GGA	GGA+U
Cu(1)	0.528	0.716
Cu(2)	-0.528	-0.716
Bi	0.000	0.000
O(1)	0.069	0.050
O(2)	-0.069	-0.050
Total	0.000	0.000

References

- 1) C. Henmi, *Mineral. Mag.*, **59**, 545–548 (1995).
- 2) J. P. Attfield, *J. Phys., Condens. Matter.*, **1**, 7045–7053 (1989).
- 3) E. W. Ong, G. H. Kwei, R. A. Robinson, B. L. Ramakrishna and R. B. Von Dreele, *Phys. Rev. B*, **42**, 4255–4262 (1990).
- 4) K. Yamada, K. Takada, S. Hosoya, Y. Watanabe, Y. Endo, N. Tomonaga, T. Suzuki, T. Ishigaki, T. Kamiyama, H. Asano and F. Izumi, *J. Phys. Soc. Jpn.*, **60**, 2406–2414 (1991).
- 5) O. Janson, R. O. Kuzian, S. L. Drechsler and H. Rosner, *Phys. Rev. B*, **76**, 115119–115128 (2007).
- 6) B. Roessli, P. Fischer and A. Furrer, *J. Appl. Phys.*, **73**, 6448–6450 (1993).
- 7) P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universitat Wien, Austria), (2001), ISBN 3-9501031-1-2.
- 8) V. I. Anisimov, F. Aryasetiawan and A. I. Lichtenstein, *J. Phys.: Condens. Matter*, **9**, 767–808 (1997).
- 9) J. P. Perdew, S. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865–3868 (1996).
- 10) V. I. Anisimov, J. Zaanen and O. K. Anderson, *Phys. Rev. B*, **44**, 943–954 (1991).
- 11) A. Goldoni, U. D. Pennino, F. Parmigiani, L. Sangaletti and A. Revcolevschi, *Phys. Rev. B*, **50**, 10435–10441 (1994).