Electronic structure and optical properties of $Y_2BaCuO_5$ with antiferromagnetic spin arrangements

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First-principles energy band calculations are performed for $Y_2BaCuO_5$ (YBC211) with ferromagnetic and three types of antiferromagnetic (AFM) spin orderings, namely, A, C, and G. The most stable phase is found to be G AFM ordering (AFM$_G$.YBC211). The calculated magnetic moment at the Cu sites is almost identical to the experimental one reported in the literature. However, the energy bandgap is estimated to be only 0.55 eV. The valence band (VB) maximum locates on the S–Γ line and the conduction band (CB) minimum locates at the Γ point, suggesting that AFM$_G$.YBC211 is an indirect bandgap oxide. From the density-of-states analysis, the VB of AFM$_G$.YBC211 comprises mainly the Cu 3$d$ and O 2$p$ states. The lower CB comprises the Cu 3$d$ states, whereas the upper CB is attributed mainly to the Y 4$d$, Ba 5$d$, and O 2$p$ states. Furthermore, in the dielectric function calculation of AFM$_G$.YBC211, the $e_2$(ω) curves exhibit very strong peaks for the $yy$ and $zz$ components at 0.87 eV, whereas the corresponding peak for the $xx$ component is weak. This difference is attributed to the anisotropy of the momentum matrix elements between the VB and the lower CB.

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1. Introduction

Since the discovery of oxide superconductors with high $T_c$, the relationship between the magnetic properties and crystal structure of $Y_2BaCuO_5$ (YBC211) has attracted much attention regarding its non-superconductivity. YBC211 is as an impurity phase of the superconductor $YBa_2Cu_3O_6$ with high $T_c$, and is green in color. The crystal structure of YBC211 has been identified by powder X-ray diffraction measurements. Michel et al. reported that (i) the YBC211 structure consists of distorted monocapped trigonal prisms (YO$_7$), (ii) the YO$_7$ prisms share a triangular-face Y$_2$O$_{11}$ block, and (iii) the Y$_2$O$_{11}$ blocks form a three-dimensional network which delimit open spaces including Ba and Cu. The magnetic properties have been investigated by neutron powder diffraction, superconducting quantum interference device (SQUID), electron paramagnetic resonance (EPR), and specific heat measurements. As a result, it was found that YBC211 has an antiferromagnetic (AFM) spin ordering configuration with a Néel temperature ($T_N$) in the range of 10–30 K. Also, the electronic structure of YBC211 has been revealed by X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements. From the measurements, it was clarified that the valence band (VB) of YBC211 is formed by the strong interaction between Cu 3$d$ and O 2$p$ orbitals. However, despite of these aforementioned experimental studies, what is most interesting is which of the three AFM spin configurations (A, C, G) is the most appropriate, and what is the detailed electronic structure from the VB to the conduction band (CB). Wunderlich et al. reported an ab initio calculation for non-magnetic (NM) YBC211, but the detailed electronic structure of YBC211 for various spin ordering configurations still remains unknown in the calculation to the best of our knowledge.

Thus, we performed first-principles calculations of YBC211 with NM, ferromagnetic (FM), and three kinds of AFM spin ordering configurations in the present study. Then, for the most stable AFM phase of YBC211, its detailed electronic structure, magnetic moment, and optical properties are calculated with a first-principles energy band calculation based on density functional theory.

2. Calculation method

The electronic structure of YBC211 was calculated using the full-potential linearized augmented plane-wave...
plus local orbital (FLAPW + lo) method based on the generalized gradient approximation (GGA). The FLAPW + lo method is the most accurate first-principles energy band calculation technique. The wave functions were expanded by APW basis functions that comprise plane waves in the interstitial region and linear combinations of radial functions multiplied by spherical harmonics inside the muffin-tin (MT) region. The MT spherical radii ($R_{MT}$) of the Y, Ba, Cu, and O atoms were 2.19, 2.35, 2.03, and 1.75 a.u., respectively. The plane wave cutoff was $R_{MT} \times K_{max} = 7.0$, which gave 3860 plane waves and 284 local orbitals. In the density of states (DOS) calculation, the Brillouin zone (BZ) integration was carried out with modified tetrahedron method on a special mesh of 40-$k$ points for NM and FM phases and of 36-$k$ points for AFM phases.

The optical properties of YBC211 were derived using the complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function was calculated numerically from the momentum matrix elements between the unoccupied and occupied electronic states, while the real part $\varepsilon_1(\omega)$ was estimated based on the complex dielectric function $\varepsilon(\omega)$.

In addition to GGA, we also performed GGA + $U$ calculations by treating on-site Coulomb interaction ($U$) between Cu 3$d$ electrons by mean-field approximation. In the GGA + $U$, the strong correlation between localized 3$d$ electrons was accounted through the screened effective interaction $U_{eff} = U - J$ with Coulomb ($U$) and exchange ($J$) parameters, which are mean values for the Coulomb and exchange interactions in the considered shell. The $U_{eff}$ parameter was changed from 6.12 to 8.84 eV (from 0.45 to 0.65 Ry).

### 3. Results and discussion

**Figure 1** shows the crystal structure of YBC211, which has the space group $Pbnm$ (S.G.62) and lattice parameters $a = 0.7132(2)$ nm, $b = 1.2181(2)$ nm, and $c = 0.5658(2)$ nm. The unit cell contains two types of Y sites (Y1 and Y2) and three types of O sites (O1, O2, and O3). Y1 and Y2 occupy Wyckoff positions 4c, Ba 4c, and Cu 4c, while O1 and O2 occupy Wyckoff position 8d and O3 occupies 4c. In NM and FM calculations, the experimental data were adopted without modifications, while in the AFM-YBC211 calculation the space group was changed from $Pbnm$ to $Pn$ (S.G. 6). The $Pn$ space group has eight types of Y sites (Y1-Y8), four types of Ba sites (Ba1-Ba4) and Cu sites (Cu1-Cu4), and 12 types of O sites (O1-O12) because of the lower symmetry of the AFM-YBC211 structure. For the AFM, we treated three types of AFM ordering configurations, namely A, C, and G, as shown in **Fig. 2**. From the calculated total energies, relative stability of magnetic ordering is discussed. We should note however that Golosovsky et al. proposed collinear AFM ordering with wave vector $[0, 1/2, 1/2]$ from neutron powder diffraction measurements. Such enlarged unit cell is not treated in current studies and will need to investigate in future.

First, we performed first-principles calculations of NM phase with GGA. As shown in the energy bands in **Fig. 3**, this compound was calculated as metal. Four energy bands between $-0.4$ and $0.5$ eV, which are indicated by gray background, are separated from other occupied bands with small energy gaps. The Fermi energy is located in these narrow bands. The origin of these bands was investigated by calculating electronic charge density corresponding to them. We found that the most of densities for these states
Energy bands for NM Y\textsubscript{2}BaCu\textsubscript{2}O\textsubscript{5}. The insets show calculated electron density for states between $-0.4$ and $0.5$ eV, which are indicated by gray background. The Cu and O atoms are indicated by green and dark red spheres. The yellow isosurface is calculated electron density for states between $-1.08$ eV (upper CB). The upper CB comprises mainly Cu 3$d$ and O 2$p$ states, and these strongly hybridize the entire VB. The characteristics of the VB and the VB width are in good agreement with the photoelectron spectroscopic measurement results.

The above results were then used to evaluate the detailed electronic structure and optical properties of the AFM.YBC211 phase with the most stable AFM spin ordering in the GGA calculation. Figures 4 and 5 show the total DOS of AFM.G.YBC211 and the DOS for the constituent atoms (Y, Ba, Cu, and O), respectively. In the present AFM calculation, note that the up-spin and down-spin densities of Cu1 were identical to those of Cu4, with an analogous relationship between Cu2 and Cu3. Figure 5 shows the sum of the up-spin and down-spin states for the constituent atoms (Y, Ba, Cu, and O) of the AFM.G.YBC211 phase for simplicity. The GGA calculation for AFM.G.YBC211 revealed that the VB of the AFM.G.YBC211 phase lies between $-5.12$ and $0$ eV. The VB comprises mainly Cu 3$d$ and O 2$p$ states, and these strongly hybridize the entire VB.

Figure 6 shows the self-consistent up-spin energy band structure of AFM.G.YBC211 in the GGA calculation along the symmetry lines of the first BZ. The energy is measured in electron volts (eV), and the origin of the energy is set arbitrarily as the VB maximum (VBM). $\Gamma$, X, S, R, T, and Z are symmetry points for the BZ of AFM.G.YBC211 and the coordinates are respectively $(0, 0, 0)$, $(0.5, 0, 0)$, $(0.5, 0.5, 0)$, $(0.5, 0.5, 0.5)$, $(0, 0.5, 0.5)$, and $(0, 0, 0.5)$, in units of $g_1^\ast$, $g_2^\ast$ and $g_3^\ast$, where $g_1^\ast$, $g_2^\ast$ and $g_3^\ast$ are the relevant reciprocal-space vectors. The VBM locates on the $\Gamma$-S line and the CB minimum (CBM) locates at the $\Gamma$ point, indicating that AFM.G.YBC211 is an indirect-band-gap material. The band gap is estimated to be only $0.55$ eV, whereas Jose et al. reported an experi-
mental band gap of 2.35 eV. Also confirmed is that the down-spin band structure is identical to the up-spin band structure. The underestimation of the band gap based on the GGA and local density approximation is well known; this results from the self-interaction error and the integer discontinuity in the exchange correlation energy and potential when the number of electrons is changed. We performed additional calculations with GGA + U to correct the self-interaction between Cu 3d electrons. With \( U_{\text{eff}} = 8.16 \text{ eV} \) (0.60 Ry), the band gap was increased to 2.38 eV with the shift of the Cu 3d states to higher energies. This calculated value is almost equal to the band gap value obtained in the experiment. However, the band gap enlarges as \( U_{\text{eff}} \) increases, the magnetic moment at Cu sites was overestimated in the GGA + U calculation compared with the experimental data as summarized in Table 2. In addition, the occupied Cu 3d states separate from main VB of AFM.G.YBC211 as shown in Fig. 7. Such behavior has not been confirmed by the photoelectron spectroscopic measurement. Thus, transition matrix elements from the VB to the CB may not be properly evaluated in GGA + U. We therefore use the GGA calculation for exploring the optical properties of AFM.G.YBC211 in the present study.

Figure 8 shows the real part \( \varepsilon_1(\omega) \) and the imaginary part \( \varepsilon_2(\omega) \) of the dielectric function for the AFM.G.YBC211 phase calculated using the GGA approach. The dielectric tensor has three independent components \( \varepsilon_{xx}, \varepsilon_{yy}, \) and \( \varepsilon_{zz} \) because YBC211 has an orthorhombic crystal system. The real part \( \varepsilon_1(0) \) equals the square of the refractive index. Although the mean refractive index was calculated to be 3.97, a lack of available experimental data means that that value is yet to be verified. Meanwhile, the imaginary
part $\varepsilon_2(\omega)$ of the dielectric function is related to the absorption spectrum due to electronic transitions from the VB to the CB. From comparing their DOS characteristics, the various peaks in $\varepsilon_2(\omega)$ are assigned mainly to transitions from the Cu 3$d$ or O 2$p$ VB states to the Cu 3$d$ CB states. Note here that each peak in $\varepsilon_2(\omega)$ does not correspond to a single interband transition because many direct and indirect transitions contribute to those peaks. An especially distinctive feature in $\varepsilon_2(\omega)$ are the strong peaks of the $yy$ and $zz$ components at 0.87 eV, whereas the corresponding peak for the $xx$ component is weak. This difference is attributed to the anisotropy of the momentum matrix elements between the VB and the lower CB.

To obtain more detailed information, a partial DOS (PDOS) calculation was carried out for the 3$d$ states ($3d_{x^2-y^2}, 3d_{z^2}, 3d_{xy}$, and $3d_{xz}$) of the Cu1–Cu4 atoms. Figure 9 shows the PDOSs of five 3$d$ states summed for Cu1–Cu4 atoms. Among them, the $3d_{z^2}$ component has the largest density in the lower CB, the $3d_{xz}$ densities are weak, and the $3d_{xy}$ states contribute hardly anything; in other words, the Cu 3$d$ states are highly anisotropic in the lower CB. From the selection rule of momentum matrix elements, important contribution arises from $p_z \rightarrow d_{xz}$ for $\varepsilon_{yy}$ and $p_y \rightarrow d_{yz}$ for $\varepsilon_{zz}$. Therefore, it is considered as seen in Fig. 8 that the $yy$ and $zz$ components become larger than that of the $xx$ component upon the transition from the VB to the lower CB.

4. Conclusion

A first-principles energy band calculation was performed for YBC211 with three types of AFM spin orderings, namely A, C, and G, in the framework of the GGA method. The results showed YBC211 with G AFM phase (AFM-G.YBC211) to be the most stable. In the GGA calculation, the calculated magnetic moment at the Cu sites was almost identical to the experimental moment, whereas the band gap was estimated to be only 0.55 eV. From the DOS analysis, the VB of AFM-G.YBC211 comprises mainly the Cu 3$d$ and O 2$p$ states. The lower CB comprises the Cu 3$d$ states, whereas the upper CB comprises mainly the Y 4$d$, Ba 5$d$, and O 2$p$ states. The VBM locates on the $\gamma$-line and the CBM locates at the $\Gamma$ point, suggesting that AFM-G.YBC211 is an indirect-band-gap oxide. In the dielectric function calculation of AFM-G.YBC211, the $\varepsilon_2(\omega)$ curves exhibited very strong peaks for the $yy$ and $zz$ components at 0.87 eV, whereas the corresponding peak for the $xx$ component was weak. This difference is attributed to the anisotropy of the momentum matrix elements between the VB and the lower CB.

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