Solid State Communications 147 (2008) 130–133

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Electronic and magnetic properties of $YBa_2Fe_3O_8$ from a first-principles study

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ARTICLE INFO

Article history:
Received 5 February 2008
Received in revised form
10 April 2008
Accepted 29 April 2008 by F. Peeters
Available online 15 May 2008

PACS:
71.15.Mb
71.20.-b
71.30.+h
72.80.Ga

Keywords:
A. First-principles calculations
B. Magnetic properties
C. $YBa_2Fe_3O_8$

ABSTRACT

The electronic and magnetic properties of $YBa_2Fe_3O_8$ have been systematically investigated within the framework of density-functional theory using the standard generalized gradient approximation (GGA) as well as the GGA plus Hubbard U(GGA + U) method. The GGA results show that the G-type antiferromagnetic (AFM) state is preferred among the considered magnetic configurations. The striking ionic character is shown for Y and Ba atoms while very strong hybridization is found between Fe 3d and O 2p orbitals. Furthermore, the Fe–O–Fe superexchange interaction should be responsible for the stability of the AFM magnetic structure in this case. In addition, our theoretical calculations reveal that the ground state of $YBa_2Fe_3O_8$ is a strongly correlated charge-transfer insulator with a finite band gap above the Fermi level obtained by the GGA + U scheme, which is in agreement with the experimental observations.

1. Introduction

The substitution of copper by other metal species in high-*Tc* cuprates provides unrivalled possibilities for studying the change of the superconducting properties and the special role of copper in high-*Tc* superconductivity. However, the possibility of observing superconductivity in other compounds with a structure similar to the cuprates is still an open topic. To date, $YBa_2Fe_3O_8$ is the only triple-perovskite analog of superconductor $YBa_2Cu_3O_7$ where copper is fully replaced by another transition metal Fe, while Y and Ba sites are left intact [1–6]. As a typical example, the $YBa_2Fe_3O_8$ system has attracted much attention in recent years. Early structural work has reported that $YBa_2Fe_3O_8$ adopts a tetragonal structure at room temperature, while polarized-neutron-diffraction measurements showed an antiferromagnetic spin configuration [1]. Furthermore, Karen et al. studied the nuclear and magnetic structure of oxidized and reduced $YBa_2Fe_3O_{8+w}$ using neutron powder diffraction. They found that the long-range antiferromagnetic order in $YBa_2Fe_3O_8$ occurs below the magnetic transition temperature T_N of ~660 K and the variation of the oxygen content is too small to affect the magnetic exchange interactions significantly [2]. More recently, the crystal and magnetic structures of stoichiometric $YBa_2Fe_3O_8$ were definitively determined by means of Rietveld refinement of combined high-resolution, high-intensity neutron and synchrotron X-ray diffraction data [6]. Even though the mentioned experimental results for this system have been published, to the best of our knowledge, no systematic theoretical investigations on $YBa_2Fe_3O_8$ have been performed. The theoretical calculations that can provide further details for better understanding this system are highly desirable. Therefore, in this work, we study the electronic and magnetic properties of $YBa_2Fe_3O_8$ using first-principles calculations.

2. Computational details

Our investigations were carried out within the framework of density-functional theory utilizing the full-potential linearized augmented plane wave plus local orbital (FP-LAPW + lo) method [7,8], implemented in the WIEN2k package [9,10]. As is well known, this method separates space into muffin-tin (MT) spheres surrounding the atoms and an interstitial region (IR) between the spheres. The values of the atomic sphere radii (R_{MT}) were chosen as 2.36, 2.50, 1.83 and 1.62 a.u. for Y, Ba, Fe and O atoms, respectively. In order to achieve energy convergence, the wave functions in the interstitial region were expanded in plane

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doi:10.1016/j.ssc.2008.04.042

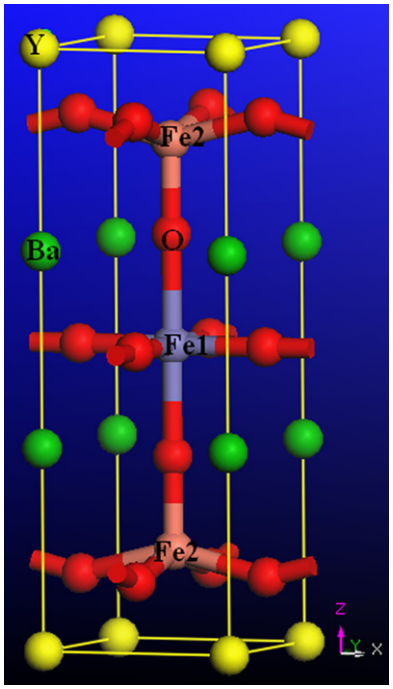

Fig. 1. (Color online) Crystal structure of $YBa_2Fe_3O_8$ with space group $P4/mmm$.

waves with a cut-off $R_{MT}^{min}K_{max} = 7$, where R_{MT}^{min} denotes the smallest atomic sphere radius and K_{max} gives the magnitude of the largest K vector in the plane-wave expansion. The valence wave functions inside the spheres were expanded up to $l_{max} = 10$ while the charge density was Fourier expanded up to $G_{max} = 14$. A large number of 1000 k points was sampled in the total Brillouin zone. Self-consistency was considered to be achieved only when the total-energy difference between succeeding iterations was less than 10^{-5} Ry per formula unit. The present set-up has been checked to ensure sufficient accuracy of the calculations.

As for the exchange-correlation potential, we adopted the standard generalized gradient approximation (GGA) using the PBE scheme [11]. In addition, to describe properly the strong electron correlation associated with the Fe 3d states, a so-called GGA + U method [12–14] was used which combines the GGA approach with the Hubbard model that is especially suited for treating strongly correlated transition metal systems. In the present work, we took the experimental lattice parameters as reported in Ref. [6].

3. Results and discussion

3.1. Crystal and magnetic structures

$YBa_2Fe_3O_8$ has a tetragonal crystal structure with space group $P4/mmm$ [1], in which Fe ions are positioned in one octahedral and two square-pyramidal environments per unit cell, denoted as Fe1 and Fe2, respectively, shown in Fig. 1. The polarized neutron diffraction data unambiguously prove that $YBa_2Fe_3O_8$ is an antiferromagnet below the magnetic transition temperature T_N of ∼660 K [2,15]. The magnetic structure is of the Wollan–Koehler [16] G-type, characterized by antiferromagnetic interactions both in each FeO_2 plane and along the c direction.

In order to explore the electronic and magnetic properties in the ground state, we compare the total energy of $YBa_2Fe_3O_8$ in different magnetic configurations. Calculations are performed for an artificial nonmagnetic (NM) configuration by enforcing spin degeneracy for all species, as well as ferromagnetic (FM), and G-type antiferromagnetic (AFM) configurations. We found that the G-type AFM phase in total energy is significantly more favorable

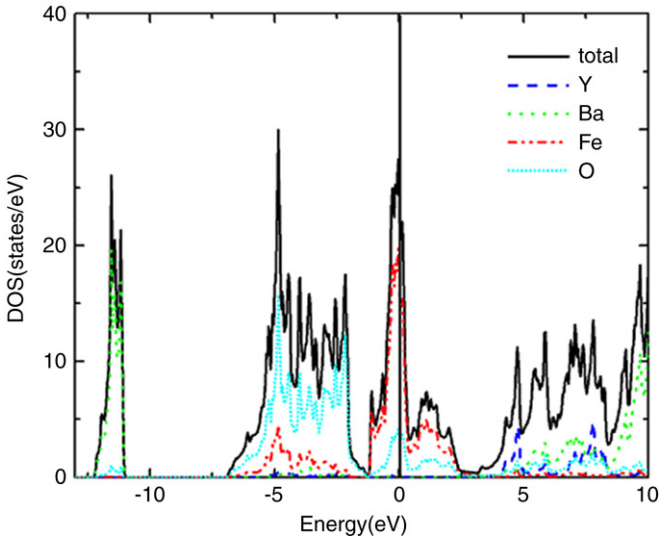

Fig. 2. (Color online) Total and partial DOS for nonmagnetic $YBa_2Fe_3O_8$ calculated by the GGA method, Fermi energy is set to zero. The high density of states at the Fermi level indicates that this is an unstable phase.

than the other two magnetic configurations irrespective of the choice of approximation as GGA or GGA + U, which is consistent with the experimental observations [6].

3.2. Electronic properties of NM structure

Non-spin-polarized calculations using the GGA method are presented in order to estimate spin effects on the equilibrium structure. Fig. 2 shows the total and partial density of states (DOS) of $YBa_2Fe_3O_8$ without spin polarization in the NM configuration. This phase, which is experimentally inaccessible, provides a useful reference for understanding the spin-polarized electronic structures. A sharp peak at −11.5 eV corresponds to the Ba p states, while Y d states are centered at about 4 eV above the Fermi energy. It should be noted that the broad bands between −2 and −6 eV are mainly composed of O 2p and Fe 3d states, which indicates the occurrence of Fe 3d hybridized with the O 2p orbitals. Generally speaking, the hybridization between the transition-metal ions and the surrounding oxygen ligands typically leads to superexchange interactions in magnetic perovskites. Obviously, the DOS of Fe 3d states at the Fermi level is very high. The large DOS at the Fermi level suggests that this phase should be unstable by the usual Stoner argument [17] and spin-polarized calculations will yield an extra contribution to the stability of $YBa_2Fe_3O_8$.

3.3. Electronic properties of FM structure

In this part, we present the electronic properties of $YBa_2Fe_3O_8$ in the FM configuration by means of the GGA approach. Fig. 3 displays the total and site-decomposed DOS of Y, Ba, Fe1, Fe2, and O atoms for $YBa_2Fe_3O_8$ in the FM structure. Obviously, the electronic structure of the FM state is found to be metallic with a number of bands crossing the Fermi level. It is seen that the states of Y and Ba sites in Fig. 3(b) stay relatively far from the Fermi energy level, which indicates that the Y and Ba atoms have a striking ionic character in the FM structure. Most of the Fe1 and Fe2 3d bands are found in the energy range from −7 to 4 eV, covering almost the same range below the Fermi level with the oxygen 2p states. This implies that there must be strong hybridizations between Fe1, Fe2 3d and O 2p states. Moreover, it is noted that Fe1 and Fe2 atoms in $YBa_2Fe_3O_8$ adopt different topologies of DOS profiles shown in Fig. 3(c). This is due to the fact that the Fe1 site associates with