Available online at www.sciencedirect.com
ScienceDirect
Physica C 460–462 (2007) 458–459
PHYSICA C
www.elsevier.com/locate/physc

Electronic structure and magnetic properties of Bi_2CuO_4

Oleg Janson [a,b,*], Helge Rosner [a]

[a] Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany
[b] St. Petersburg State University, 199034 St. Petersburg, Russia

Available online 20 April 2007

Abstract

Bi_2CuO_4 is a spin 1/2 model compound with ferromagnetically (FM) ordered chains that are antiferromagnetically (AFM) arranged with respect to each other. To investigate the microscopic origin of this unusual magnetic structure, we performed DFT calculations to evaluate the relevant orbitals and couplings. Total energy calculations yield a magnetic ground state in agreement with the experimental data. Based on a tight-binding fit we estimated the leading exchange integrals. The main coupling arises between the chains, while the in-chain interaction is relatively small. The FM arrangement of chains is due to strong AFM exchange of neighbouring CuO_4 units of the different chains.

PACS: 74.72.Hs; 75.30.Et

Keywords: Electronic structure; Low dimensional cuprates

1. Introduction

Low dimensional spin 1/2 systems have attracted growing interest during the last decade due to the large variety of possible ground states. Especially systems with chains or chain-like sub-units have been in the focus of interest, exhibiting exotic states like the spin-Peierls state in $CuGeO_3$ [1] or the spin spiral in $LiCu_2O_2$ [2] and $NaCu_2O_2$ [3]. To describe the magnetic behavior of a series of different systems consistently based on their observed crystal structure using magnetic Hamiltonians like the Heisenberg model, the knowledge of the relevant exchange interactions is crucial. Here, we approach this goal in a theoretical study for the system Bi_2CuO_4. Below 45 K [4], this system exhibits an antiferromagnetic (AFM) arrangement of ferromagnetically (FM) ordered chains.

2. Method

A DFT-based full potential local-orbital code (FPLO 5.00-18) [5] was applied for the scalar relativistic calculations within the local density approximation (LDA), using the Perdew–Wang exchange-correlation potential [6]. As valence basis states we used Bi (4f, 5s, 5p, 5d)/(6s, 6p, 6d), Cu (3s, 3p)/(4s, 4p, 3d) and O (2s, 2p, 3d) (notation: *semi-core states/valence states*). All lower lying states were treated as core states. A k mesh of 490 points (60 irreducible points) was used for the calculations. Strong on-site correlations were taken into account in L(S)DA + U method [7]. To calculate the magnetic anisotropy, the spin orbit coupling was treated solving the full Dirac equation. The tight-binding model for the antibonding Cu–O bands, leading to a 4×4 matrix was solved analytically and fitted to the LDA band structure at high symmetry points.

3. Results and discussion

The calculated total and partial electronic densities of states for the valence band of Bi_2CuO_4 are shown in

* Corresponding author. Address: Max Planck Institute for Chemical Physics of Solids, 01187 Dresden, Germany.
E-mail address: oleg.janson@cpfs.mpg.de (O. Janson).

0921-4534/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.physc.2007.03.430

Fig. 1. Typical for undoped cuprates, the valence band is dominated by Cu 3d and O 2p states with a small admixture of Bi. At the Fermi level, we find a well isolated complex of four narrow bands (see Fig. 2) according to four Cu sites per unit cell. Due to the underestimation of the strong Coulomb correlations at the Cu 3d orbitals by the LDA, the obtained metallic behavior is in contrast to the experimentally observed insulating ground state. We include the missing correlations by a subsequent mapping of the antibonding LDA bands (see Fig. 2) to a Heisenberg model $\widehat{H} = \sum_{\langle i,j \rangle} J_i, j \vec{S}_i \vec{S}_j$, using a TB fit to evaluate the hopping integrals t_i and the relation $J_i = 4t^2/U_{\text{eff}}$ to calculate the AFM part of the exchange. The leading transfer integrals, resulting in an excellent fit of the LDA bands, are shown in Fig. 3. We find three main contributions from $t_{1u}^{AB} = 74$ meV, $t_{2d}^{AB} = 40$ meV, $t_{1d}^{AB} = 36$ meV, all of them being inter-chain couplings. All other t's are considerably smaller (less than 20 meV). Assuming a standard value for the correlation $U_{\text{eff}} = 4$ eV for our effective one-band model, this results in the following exchange parameters: $J_{1u}^{AB} = 5.5$ meV, $J_{2d}^{AB} = 1.6$ meV, $J_{1d}^{AB} = 1.3$ meV. Comparing total energies for different spin directions, we find a small easy axis anisotropy.

Alternatively, the main exchange interactions have been calculated using the difference in total energy for various spin arrangements. Independent of the choice of U_d ($4\text{ eV} < U_d < 8\text{ eV}$) we obtain the experimentally observed ground state. For a standard value of $U_d = 6.5$ eV, we find consistently with the TB approach $J_{1u}^{AB} + J_{2d}^{AB} = 5.1$ meV and $J_{1d}^{AB} = 0.9$ meV. (From the possible spin arrangements

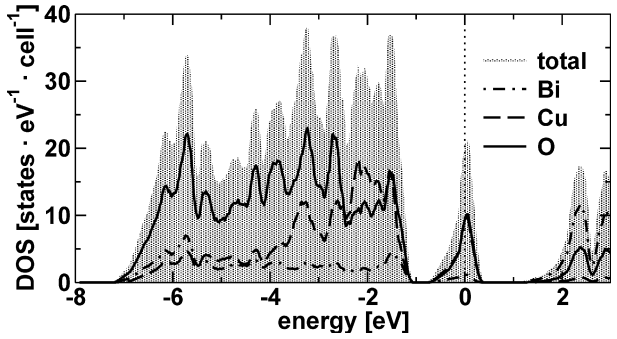

Fig. 1. Total and partial density of states of Bi_2CuO_4.

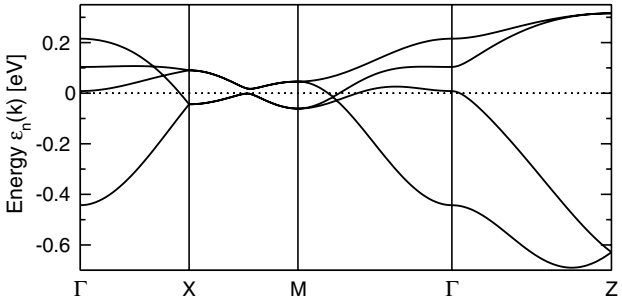

Fig. 2. The band structure of Bi_2CuO_4 (the bands at the Fermi level are shown).

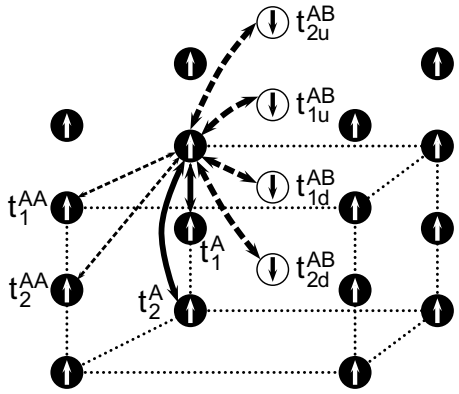

Fig. 3. Main hopping integrals derived from the tight-binding model.

inside a unit cell, only the sum $J_{1u}^{AB} + J_{2d}^{AB}$ can be calculated). The difference between both procedures originates most likely from the uncertainty in the choice of U and small FM contributions that are neglected in the TB approach. Nevertheless, our results are in good agreement with experimental observations from neutron scattering [8] reporting $J_{1u}^{AB} + J_{2d}^{AB} = 5.7$ eV, $J_{1d}^{AB} = 1.7$ meV and Raman spectroscopy [9] obtaining $J_{1u}^{AB} = 0.4$ eV, $J_{2d}^{AB} = 4.6$ eV, $J_{1d}^{AB} = 1.3$ meV (here, J_{1u}^{AB} and J_{2d}^{AB} are indistinguishable and have been assigned by intuitive assumption).

In conclusion, from both theory and experiment, Bi_2CuO_4 has to be described as a compound with 3D coupling where a large AFM inter-chain coupling leads to an FM arrangement along the chains, although the weaker in-chain coupling is AFM, too.

References

[1] M. Hase et al., Phys. Rev. Lett. 70 (1993) 3651.
[2] A.A. Gippius et al., Phys. Rev. B 70 (2004) 020406.
[3] S.-L. Drechsler et al., Europhys. Lett. 73 (2006) 83.
[4] R. Troć, J. Phys.: Condens Matter 2 (1990) 6989.
[5] K. Koepernik, H. Eschrig, Phys. Rev. B 59 (1999) 1743.
[6] J.P. Perdew, Y. Wang, Phys. Rev. B. 45 (1992) 13244.
[7] H. Eschrig et al., J. Sol. Stat. Chem. 176 (2003) 482.
[8] B. Roessli et al., J. Appl. Phys. 73 (1993) 6448.
[9] M.J. Konstantinović et al., Phys. Rev. B 54 (1996) 68.