

Electronic structure of the antiferromagnetic phase of $\text{Sr}_2\text{Co}_2\text{O}_5$

V. Pardo^{a,b,*}, P.M. Botta^a, D. Baldomir^{a,b}, J. Rivas^a, A. Piñeiro^{a,b}, C. de la Calle^c,
J.A. Alonso^c, J.E. Arias^b

^aDepartamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, E-15782 Campus Sur s/n, Santiago de Compostela, Spain

^bInstituto de Investigaciones Tecnológicas, Universidad de Santiago de Compostela, E-15782, Santiago de Compostela, Spain

^cInstituto de Ciencia de Materiales de Madrid, CSIC, Campus de Cantoblanco, 28049-Madrid, Spain

Abstract

Ab initio calculations analyze the properties of the G-type antiferromagnetic $\text{Sr}_2\text{Co}_2\text{O}_5$ as a high-spin system. The description of the electronic structure is given; all the Co atoms are in a high-spin state with a small unquenched orbital angular momentum. Thermal analysis on a polycrystalline sample shows a magnetic phase transition at high temperatures.

© 2007 Elsevier B.V. All rights reserved.

PACS: 75.25.+z; 71.20.-b; 71.27.+a

Keywords: Cobaltates; Oxygen deficiency; First-principles calculations; Differential scanning calorimetry

Co oxides are becoming increasingly important nowadays due to the great variety of physical properties they present, such as colossal magnetoresistance [1] or superconductivity [2] and the plethora of applications they can be used for. In particular, oxygen deficient perovskites present potential applications as electrodes in solid state fuel cells.

We have carried out density functional theory calculations on the compound $\text{Sr}_2\text{Co}_2\text{O}_5$ within a full-potential, all-electron approach by using the WIEN2k software [3]. Electronic correlations were taken into account by means of the LDA + U approximation [4].

Polycrystalline $\text{Sr}_2\text{Co}_2\text{O}_5$ was synthesized using the citrate technique method described elsewhere for related compounds [5]. X-ray diffraction pattern revealed an orthorhombic crystalline structure with space group $\text{Ibm}2$. The structure can be described as a brownmillerite-type [6] with two inequivalent Co atoms: one of them in an octahedral environment (Co1) and the other in a tetrahedral environment (Co2). Thermal analysis of the powder

sample was carried out by differential scanning calorimetry (DSC). The scans were performed under a nitrogen flow from 150 to 350 °C, using a heating rate of 20 °C/min.

DSC curve (Fig. 1) shows a very clear endothermic peak at 263.5 °C, which can be assigned to the loss of magnetic ordering. This is in good agreement with early neutron diffraction studies reporting a Néel transition in this temperature interval [7].

$\text{Sr}_2\text{Co}_2\text{O}_5$ is a charge-transfer insulator with the O p levels on top of the valence band and the Co d unoccupied bands forming the conduction band. We can see in Fig. 2 that the bands with a higher Co d character lie far below the Fermi energy and the O p levels occupy the bands closer to the Fermi level. However, the conduction band has a large d-character.

We can schematically say that both Co atoms are in a HS state ($t_{2g}^4 e_g^2$ in the case of the octahedral and $e_g^3 t_{2g}^3$ for the tetrahedral Co).

The electronic structure of Co1 (distorted octahedral environment) has the t_{2g} levels split into a lower lying doublet and a singlet due to the tetragonal distortion (elongation along x -axis of the oxygen octahedron) that lifts the d_{yz} level to a higher energy. This can be observed in Fig. 3 by the non-negligible occupation of the spin-down channel of levels d_{xz} and d_{xy} that form the doublet.

*Corresponding author. Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, E-15782 Campus Sur s/n, Santiago de Compostela, Spain. Tel.: +34 981 563 100 x13960; fax: +34 981 520 676.

E-mail address: vpardo@usc.es (V. Pardo).

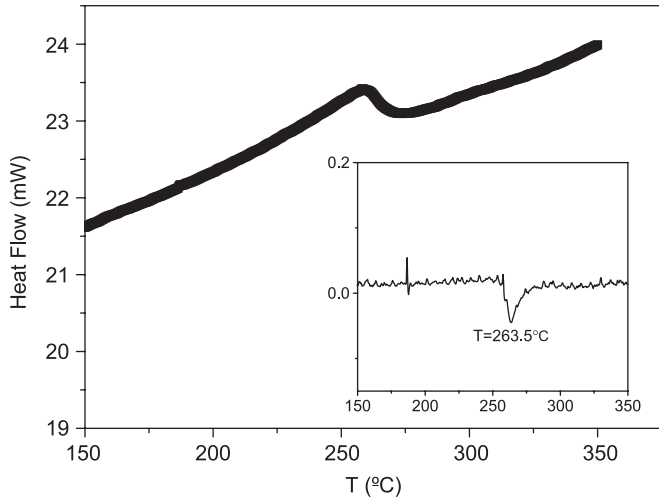


Fig. 1. Differential scanning calorimetry of the synthesized $\text{Sr}_2\text{Co}_2\text{O}_5$. The inset shows the first derivative of the DSC curve.

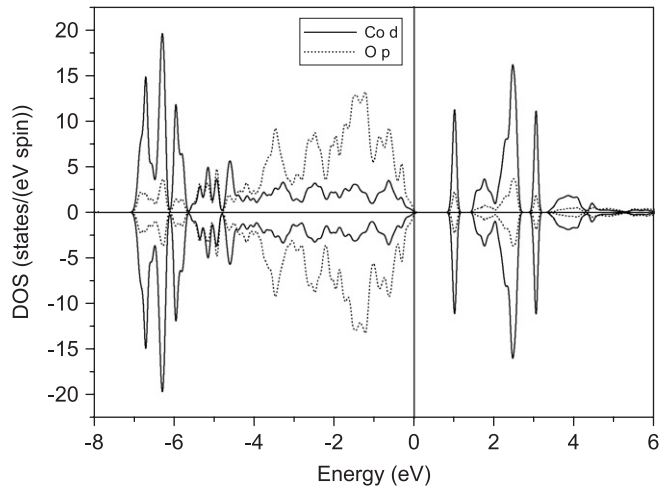


Fig. 2. Partial d DOS plots for all the Co d and O p levels in the unit cell. A charge-transfer insulator character can be observed. Upper (lower) panels correspond to spin-up (down) levels.

The tetrahedral environment of Co2 is largely distorted. The e_g doublet is split, being the $d_{x^2-y^2}$ orbital lowest and, hence, slightly more occupied than the $d_{3z^2-r^2}$ as can be seen in Fig. 4. Analyzing the spin-up channel (in this case the minority channel, since Co2 shown in Fig. 4 is antiferromagnetically (AF) coupled to Co1 in Fig. 3), one can see there is some occupancy of the t_{2g} bands as well due to the small crystal field splitting: the e_g and t_{2g} bands largely overlap, being their bottoms separated by only 0.2 eV.

This partial occupation of the minority levels leads to a small but non-negligible orbital angular momentum (OAM) parallel to the spin moment. The OAM of the tetrahedral Co is twice that of the octahedral one (0.3 and $0.15\mu_B$, respectively). This is due to the smaller crystal field splitting observed in Co2.

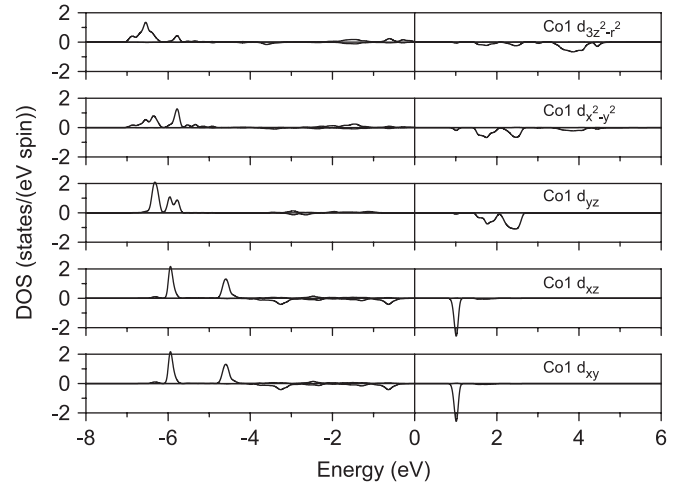


Fig. 3. Partial d DOS plots for Co1, in a distorted octahedral symmetry. A HS state can be observed. Upper (lower) panels correspond to spin-up (down) levels.

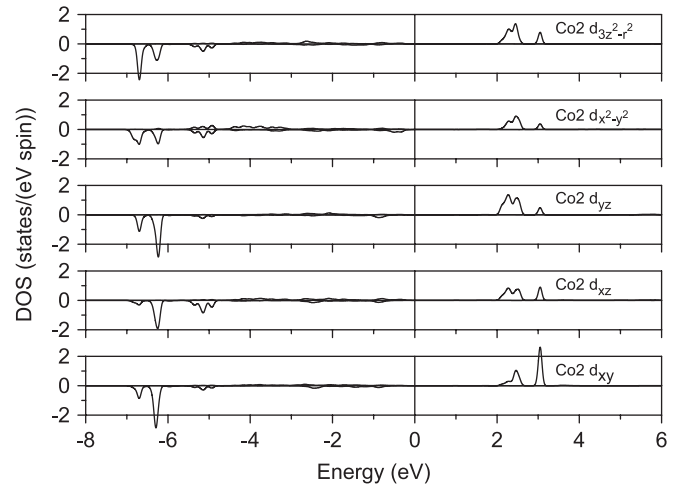


Fig. 4. Partial d DOS plots for Co2, in a distorted tetrahedral symmetry. A HS state can be observed. Upper (lower) panels correspond to spin-up (down) levels.

We have studied different magnetic arrangements for the Co atoms, always considering a HS state for the magnetic ions in the material. The AF G-type solution (each Co atom is AF coupled to all its neighbors) is more stable than a ferromagnetic (FM) solution by about 130 meV/Co. We also tried an A-type (FM planes coupled AF) and C-type (FM chains coupled AF) solution. These are 80 and 90 meV/Co less stable, respectively. These results are for GGA + U with $U = 4$ eV, with the non-orbitally dependent part of the exchange-correlation potential modeled utilizing the Perdew–Burke–Ernzerhof scheme [8]. These results, the big stabilization energy of the G-type AF phase, are consistent with the very high Néel temperature observed (537 K).

The magnetic moments calculated inside the muffin-tin spheres are $3.0\mu_B$ for both Co atoms. Considering the values of the OAM calculated, the effective magnetic

moment would be $3.5\mu_{\text{B}}/\text{Co}$, consistent with the experimental measurements reported [7].

This work was supported by the Ministry of Science and Education of Spain (MEC) through the project MAT2006-10027. We are thankful to the CESGA (Centro de Supercomputación de Galicia) for the computing facilities. P.M.B. thanks the financial support from the MEC under the program Juan de la Cierva.

References

- [1] K. Schwarz, P. Blaha, *Comp. Mat. Sci.* 28 (2003) 259.
- [2] K. Takada, et al., *Nature (London)* 422 (2003) 53.
- [3] K. Schwarz, P. Blaha, *Comp. Mat. Sci.* 28 (2003) 259.
- [4] V. Anisimov, et al., *J. Phys.: Condens. Matter* 9 (1997) 767.
- [5] P.M. Botta, et al., *Phys. Rev. B* 74 (2006) 214415.
- [6] Y. Ito, et al., *J. Am. Ceram. Soc.* 85 (2002) 969.
- [7] T. Takeda, H. Watanabe, *J. Phys. Soc. Japan* 33 (1972) 973.
- [8] J.P. Perdew, et al., *J. Phys. Rev. Lett.* 77 (1996) 3865.