

Reprinted from *Acta Physica* 5 (2007) 35-36

**Comment on a Phys. Rev. Lett. paper
"Spin State Transition in LaCoO₃ studied
using Soft X-ray absorption spectroscopy
and Magnetic Circular Dichroism":
physics of LS, IS and HS spin states (LAK1030)**

*R. J. Radwanski**

*Center of Solid State Physics; S^{nt} Filip 5, 31-150 Krakow, Poland
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland*

Z. Ropka

Center of Solid State Physics; S^{nt} Filip 5, 31-150 Krakow, Poland

(under protection of the American Physical Society from January 3, 2007
(Phys. Rev. Lett. LAK1030 - rejected, see following article pp 35-41)
published 30 April 2007 in *Acta Physica* 5 (2007) 35-36)

We argue that the energy level diagram of a CoO₆ cluster presented in Fig. 2 in the recent Phys. Rev. Lett. **97** (2006) 176405 paper is physically inadequate to LaCoO₃ and that the description of the HS, IS and LS spin states in LaCoO₃ is oversimplified.

PACS: 75.10.Dg : 71.70.

Keywords: spin states, crystal field, LaCoO₃, 3d compounds

In a recent paper Haverkort *et al.* [1] have come to a conclusion that the first excited state in LaCoO₃ is the high-spin (HS) state in contrary to overwhelmed by last 10 years flurry of studies claiming the intermediate-spin (IS) state. At beginning we congratulate authors of Ref. [1] that they have managed to publish in Phys. Rev. Lett. a Letter with the excited HS state, instead of the IS state. There was quite recently a paper [2] claiming the IS state as the first excited state but our Comment did not get appreciation of the Phys. Rev. Lett.'s Editor and its referees (we cannot write more on our 10-years discussion on magnetism, electronic structure and orbital magnetism of 3d oxides). After congratulations, because it is necessary for a Comment to make critics or corrections, we express our view that the energy-level diagram of a CoO₆ cluster shown in the commented letter in Fig. 2 is physically inadequate to LaCoO₃ and that the description of the HS, IS and LS states in LaCoO₃ is oversimplified. The splitting of the HS state, which is 15-fold degenerated state, has been exactly calculated in

* <http://www.e-physica.pl>; Email: sfradwan@cyf-kr.edu.pl

our paper [3] taking into account strong intra-atomic correlations, the spin-orbit coupling and off-octahedral distortions. In the ionic many-electron crystal-field description the HS state is ${}^5T_{2g}$ cubic subterm [4] of the $t_{2g}^4 e_g^2$ configuration. In the cluster description of [1] the HS state has the same degeneracy as in the ionic description ${}^5T_{2g}$ cubic subterm. A physical inadequacy of Fig. 2 is related to many things. Here we mention only the atomic limit of the cluster calculations with results presented in Fig. 2. When one extrapolates the LS, IS, HS dependence, they seem to be straight lines, to $Dq \rightarrow 0$ the energy of HS, IS₁, LS and IS₂ states can be found as 0.30, 0.69, 0.70 and 0.88 eV (meaning of the zero energy in Fig. 2 is unclear). These energies yield the relative energies with respect to the free atomic HS ground state of the Co³⁺ ion as 0.39, 0.40 and 0.58 eV, respectively. In the reality in the Co³⁺ ion, however, the 1I term, the source of the LS, 1A_1 subterm, lies 4.45 eV above the HS (5D) term [5], i.e. more than 10 times higher in energy. Similarly, the 3H term being the source of the IS states in the ionic picture, lies 3.1 eV above the HS ground state. Here we follow a Tanabe-Sugano thinking from a year of 1954 [4] and we consider the many-electron crystal-field approach as generally physically adequate also for 3d compounds. Please note that the concept of the IS excited state, resulting from band calculations of Korotin *et al.* [6], was formulated in year of 1996 in contrary to the well-known Tanabe-Sugano ionic picture. We would like to mention a paper by Kyomen *et al.* [7] who have succeeded to describe both the magnetic susceptibility and heat capacity of LaCoO₃ taking into account the energy-level diagram of our paper [3].

In conclusion, we question the physical adequacy of the energy level diagram of a CoO₆ cluster to LaCoO₃ as well as to other Co³⁺ oxides.

-
- [1] M. W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N. B. Brookes, H. H. Hsieh, H. -J. Lin, C. T. Chen, and L. H. Tjeng, *Phys. Rev. Lett.* **97**, 176405 (2006); cond-mat/0606285 (2006).
 - [2] D. Phelan, D. Louca, S. Rosenkranz, S. -H. Lee, Y. Qiu, P. J. Chupas, R. Osborn, H. Zheng, J. F. Mitchell, J. R. D. Copley, J. L. Sarrao, and Y. Moritomo, *Phys. Rev. Lett.* **96**, 027201 (2006).
 - [3] Z. Ropka and R. J. Radwanski, *Phys. Rev. B* **67**, 172401 (2003).
 - [4] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **9**, 753 (1954).
 - [5] R. J. Radwanski and Z. Ropka, *Physica B* **359**, 1354 (2005); R. J. Radwanski and Z. Ropka, *Physica B* **345**, 107 (2004).
 - [6] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, *Phys. Rev. B* **54**, 5309 (1996).
 - [7] T. Kyomen, Y. Asaka, and M. Itoh, *Phys. Rev. B* **71**, 024418 (2005).