Research Article

Comment on a Phys. Rev. Lett. paper: "Nanomagnetic droplets and implications to orbital ordering in $La_{1-x}Sr_xCoO_3$": the origin of the excited state in $LaCoO_3$

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In contrary to a claim of the recent Phys. Rev. Lett. **96** (2006) 027201 paper we maintain that the first excited state in $LaCoO_3$ is the high-spin (HS) state (a lowest quasi-triplet from the octahedral subterm $^5T_{2g}$ of the ^5D term, Phys. Rev. B **67** (2003) 172401) in agreement with the Tanabe-Sugano diagram.

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In a recent paper Phelan *et al.* [1] claim that the excited state in $LaCoO_3$ is the intermediate-spin (IS) S=1 state of a $t_{2g}^5e_g^1$ configuration.

By this Comment we would like to correct this claim. We would expect that the problem of the excited state in $LaCoO_3$ has been clarified in a year of 2003 in our paper [2], making use of experimental results of Noguchi *et al.* [3], but authors of the commented paper likely did not notice this paper. They have cited our first paper about $LaCoO_3$ from a year of 1999 in Ref. 22 - in fact this paper dealt with the splitting of of the ^5D term, belonging to the high-spin $t_{2g}^4e_g^2$ (S=2) state, by the trigonal distortion in the presence of the spin-orbit coupling.

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In Ref. [2] we have proved that the excited state (quasi-triplet) originates from the $^5T_{2g}$ subterm of the ^5D term belonging to the HS $t_{2g}^4 e_g^2$ (S=2) configuration. We have perfectly reproduced the magnetic-field behaviour of the quasi-triplet and the anisotropic g factor experimentally revealed by Noguchi *et al.* [3]. The ground state is a many-electron subterm $^1A_1$ originating from the ^1I term, which in the free Co^{3+} ion lies 4.45 eV above the ground term ^5D. The 13-fold degenerated ^1I term is split by the octahedral crystal field and the subterm $^1A_1$ is strongly pushed down, by relatively strong crystal field, due to its very large orbital quantum number L=6, as occurs on the Tanabe-Sugano diagram for Dq/B=2.025.

The IS state as the first excited state has been introduced to the $LaCoO_3$ problem in year of 1996 by band calculations of Korotin *et al.* [4] as an **opposite** view to the atomistic view being a base for the Tanabe-Sugano diagrams known from years of 1954. The Tanabe-Sugano diagram for the $3d^6$ configuration has yielded the excited state to be the HS state and this view was the base for a model of Goodenough. The IS-state concept has become highly popular [5, 6]. In the band calculations of Korotin *et al.* the IS state becomes the first excited state as an effect of the especially strong $d-p$ hybridization. However, we claim that if at present, in a year of 2006, one wants to still claim that the IS state is an excited state he/she has to present a quantitative band-based or hybridization-based interpretation of the Noguchi *et al.* experiment. In the atomic physics $t_{2g}^5 e_g^1$ (S=1) state is 24-fold degenerated - thus there is a question about a degeneracy left in $LaCoO_3$ and its characteristics.

In the ionic atomistic picture the discrete atomiclike electronic structure is preserved also in transition-metal solid (QUASST) [7]. For instance, the meV-scale splitting of the 15-fold degenerated $^5T_{2g}$ (HS) subterm by the trigonal distortion in the presence of the spin-orbit coupling has been presented in Ref. [2] for $LaCoO_3$ and for the Fe^{2+} ion in $FeBr_2$ [8].Thus the HS state is Jahn-Teller active equally as the IS state is. In means that the basis for the final conclusion of Phelan *et al.* [1], the need of the J-T active excited state, is incorrect. We note that the meaning and the degeneracy of the LS, IS and HS states in the band picture is understood differently than in the ionic (QUASST) picture. Thus, we think that the basic problem of $LaCoO_3$ is associated with a consideration of d states as localized (ionic, QUASST) or as delocalized forming a wide energy ∼10 eV band like in Ref. [4] and to settle down the d occupation/valency of 6/+3 or 7.3/+1.7. Within the localized picture the estimation of the strength of the octahedral crystal-field interactions is decisive.

In conclusion, we claim that the origin of the excited state in $LaCoO_3$ has been already established to be the high-spin state, namely levels originating from the $^5T_{2g}$ (^5D)subterm.

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