Reprinted from Acta Physica 2 (2007) 24-26

# 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 $LaCoO_3$ (LQK1020)

*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 the author's right protection of the American Physical Society
from March 28, 2006 LQK1020 - rejected, see following article, pp 14-32;
cond-mat/0603812 30 March 2006;
published 29 January 2007 in Acta Physica **2** (2007) 24-26;
online: www.actaphysica.eu)

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.

PACS: 75.10.Dg; 71.70.Ch;
Keywords: $3d$ compounds, electronic structure, crystal field, spin-orbit coupling, $LaCoO_3$

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 $t_{2g}^5 e_g^1$ 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

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

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 $t_{2g}^4 e_g^2$ ($S$=2) state, by the trigonal distortion in the presence of the spin-orbit coupling.

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 $\sim$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.

[1] 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); cond-mat/0512030 (2005).
[2] Z. Ropka and R. J. Radwanski, Phys. Rev. B **67**, 172401 (2003).
[3] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B **66**, 094404 (2002).
[4] 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).
[5] A. Ishikawa, J. Nohara, and S. Sugai, Phys. Rev. Lett. **93**, 136401 (2004).
[6] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Gruninger, T. Lorenz, P. Reutler, and A. Revcolevschi, Phys. Rev. B **66**, 020402(R) (2002); **71**, 019902(E) (2005).
[7] R. J. Radwanski, R. Michalski, and Z. Ropka, Acta Phys. Pol. B **31**, 3079 (2000).
[8] Z. Ropka R. Michalski, and R. J. Radwanski, Phys. Rev. B **63**, 172404 (2001).

# Submission of Comment to PRL LQ1020: origin of the excited state in LaCoO3

after rejection 23.03.2006 of
"LaCoO3 - from first principles" LQ10665

–=====—-=====—-=====—-=====—-=====—-=====—-=====

Od: esub-adm@aps.org ⟨esub-adm@aps.org⟩
Do: prltex@ridge.aps.org ⟨prltex@ridge.aps.org⟩
Copy to: zofiaropka@fizyk.instytut.serwery.pl
Data: 28 marca 2006, 12:24:22; Pliki: ⟨none⟩
Temat: Manuscript es2006mar28_052 has been submitted to Phys. Rev. Lett.
JNL: prl TEMPID: es2006mar28_052
RECVD: Tue Mar 28 06:24:22 2006
TITLE: Comment on a Phys. Rev. Lett. paper: the origin of the excited state in LaCoO3

AUTHORS: Radwanski, R. J./Ropka, Z./
EMAIL: zofiaropka@fizyk.instytut.serwery.pl
ADDRESS: Center of Solid State Physics
Snt Filip 5, 31-150 Krakow, Poland

ART_TYPE:Comment/Reply; OBJECT: SECTION:L7-? TYPE:TH
PACS1: 75.10.Dg; PACS2: 71.70.-d;
NFIGS: 0 COLORFIGS: no, EFIG: No figures
NTABLES: 0 COPY: STANDARD
LENGTHCHECK: 115 lines (1.0 pages)
REFCHECK: No errors detected

NOTES: Dear Editor,
We submit Comment on recently published paper in Phys. Rev. Lett. Our paper on this subject
LQ10665 "$LaCoO_3$ - from first principles"
has been quickly, 24 March 2006, rejected.

Thus we submit Comment in order to correct the origin of the excited state in $LaCoO_3$. The publication of Comment is obligation of each scientific journal. We would appreciate publication of our Comment that enables open and normal scientific discussion.
Sincerely Yours,
R. J. Radwanski and Z. Ropka
Krakow, 28.03-2006

# Rejection of LQK1020 with the response of the commented authors Dr D. Louca

–=====—=====—=====—=====—=====—=====—=====

From: Physical Review Letters ⟨prl@ridge.aps.org⟩
To: zofiaropka@fizyk.instytut.serwery.pl
Data: 18 kwietnia 2006, 18:56:31
Temat: Your_manuscript LQK1020 Radwanski
Pliki: ⟨none⟩

–=====—=====—=====—=====—=====—=====—=====

Re: LQK1020
Comment on "Nanomagnetic droplets and implications to orbital ordering in $La_{1-x}Sr_xCoO_3$": the origin of the excited state in $LaCoO_3$ by R. J. Radwanski and Z. Ropka

Dr. Z Ropka
Center of Solid State Physics
Snt Filip 5, 31-150 Krakow, POLAND

Dear Dr. Ropka,

In accordance with our usual policy for Comments, the above manuscript was sent to the author(s) of the work being commented on. Their reaction is enclosed. If the criticism is valid, publication is not indicated.

If you feel that you can overcome or refute the criticism, you may resubmit to Physical Review Letters. With any resubmittal, please include a summary of changes made and a brief response to all recommendations and criticisms. An independent referee will be consulted if needed.

Yours sincerely,

Yonko Millev
Assistant Editor
Physical Review Letters

Attached: Response of Dr D. Louca to the Comment

# Response of Dr Louca to the Comment – LQK1020/Radwanski

Dear Dr. Millev

Thank you for your correspondence on April 3, 2006 regarding a comment written on our manuscript that was recently published in Physical Review Letters (Phelan *et al.*, PRL 96, 027201 (2006)). At this stage, we would like to simply respond to the comment and if the comment gets accepted after the refereeing process, we would then proceed with a formal reply.

In our recent publication, we presented high resolution, elastic and inelastic neutron scattering results that provided evidence for a distinct low-energy excitation coincident with the thermally induced magnetic transition as well as coexisting strong ferromagnetic and weaker antiferromagnetic dynamic, short-ranged correlations in pure LaCoO3. The excitation was assigned to a transition within the temperature induced magnetic state, split in zero-field because of the trigonal distortion. The observation of both FM and AFM correlations was interpreted as evidence for dynamic orbital correlations between intermediate spin (IS) S=1 states, as well as evidence that the first excited thermal induced state is the IS. To this date, we are not aware of any other mechanism that could explain our observations. We further reported on the evolution of the magnetic correlations upon hole doping, and found that while the AFM correlations rapidly disappear, the FM correlations become static and form nanosized isotropic droplets.

In their comment, Radwanski and Ropka claimed, based on a simple crystal field calculation, that the first excited state is a high-spin state while the purpose of the comment is to "correct our claim [that of an IS state as the first excited state]". The view presented in the comment has been published by the same authors in the past, and the comment does not present any new insight. Moreover, the comment does not invalidate any of our experimental observations, and actually cannot explain any major point of our Letter such as the observation of simultaneous FM and AFM correlations, which are incompatible with the high-spin (HS) state, the disappearance of the local excitation and AFM correlations upon doping, and the formation of nanosize FM droplets upon doping. We therefore do not see any merit in publishing this comment.

Furthermore, the claims presented in the comment are based on the flawed assumption that covalency and hybridization are irrelevant even for an atomistic discussion of the energy levels of the Co-ions. The authors use a plain vanilla crystal field calculation for the trivalent Co

ions, and by giving it a fancy new name they would like us to believe it explains all the unusual phenomena that have excited condensed matter physicists for many decades. While the crystal field in its plain form as used by the authors is known to often work for 4f electrons (because they are well shielded by the closed 5s and 5p shells), and much less so for 5f systems, it has long been known that covalency strongly influences the crystal field and magnetic properties of transition metal ions. Reviews on this matter date as far back as 1966 (e.g. Owen and Thornley, Rep. Prog. Phys. 29, 675). The effects of covalency can completely change the energy levels and have to be taken into account for meaningful atomistic calculations. Accordingly, atomic multiplet calculations that take hybridization with the ligand oxygen into account as in Potze *et al.*, Phys. Rev. B 51, 11501 (1995) were the first to point out the possibility of even an intermediate-spin 3T1 ground state for the d6 configuration, and formed the basis for later assignments of the IS state as the first excited state in LaCoO3. Therefore, in contrast to the comment's claim, the atomistic view is not opposing the IS state as the first excited state, but the authors' oversimplification and inability to recognize the shortcomings of their model in reproducing ours and others experimental facts are.

D. Louca
12 April 2006