Research Article

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Comment on a Phys. Rev. Lett. paper: "Orbital Excitations in $LaMnO_3$: $3d$ levels of a free transition-metal atom"♠

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(under the authors rights and law protection of the Phys. Rev. Lett. and of the American Phys. Society from 14.02.2002 (LNK810);
the direct motivation for this Comment was continuous rejection of our papers written within the standard ionic paradigm;
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In a recent Letter [1] Van den Brink has studied theoretically orbital excitations in $LaMnO_3$. By this Comment [2] we point out that the already introductory statement "In a free transition metal atom the $3d$ energy levels are fivefold orbitally degenerate" is incorrect. If it could be true for an atom with one d electron it surely is not true for an atom with a larger number of d electrons, in particular not for the Mn^{3+} ion considered in the commented Letter dealing with $LaMnO_3$.

In the Mn^{3+} ion, having four d electrons, there is, as is well-known from the atomic physics, 210 states. The NIST Atomic Spectra Database [3] provides for the free Mn^{3+} ion (Mn IV in the atomic-physics notation) experimental evidence for the 7 terms with the ground term ^5D. These 7 terms contain already 161 states. States of the ^5D ground term are grouped into 4 multiplets with energies at 0, 12.3, 35.6, 68.5 and 109.8 meV. The ground term ^5D is in agreement with two Hund's rules yielding for the $3d^4$ electron system S=2 and L=2. The

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total number of states in the 4 multiplets is 25. The multiplet structure, as is well-known in the atomic physics, results from the spin-orbit coupling. The experimentally derived energies, shown above, if described by the Hamiltonian $H_{s-o}=\lambda_{s-o}L\cdot S$ in the LS coupling scheme yield with S=2 and L=2 the spin-orbit coupling λ_{s-o} of (average) 11.6 meV (=135 K = 94 cm^{-1}).

In a solid the Mn^{3+} ion experiences the crystal field, that splits further these 25 states. In $LaMnO_3$ the crystal field has predominantly the octahedral symmetry due to the local MnO_6 octahedron. The effect of the crystal field on the atomic Mn^{3+} states, with taking into account the intra-atomic spin-orbit coupling, has been already studied in great details [4–6]. The effect of an off-cubic distortion on the fine atomic-like electronic structure and the formation of the magnetic ordering is also very important, but it goes beyond the present Comment.

In a conclusion, the commented Letter contains fundamental errors about 3d levels in the free transition-metal atom. As a consequence, considerations of 3d levels for the Mn^{3+} ion with the incorrect nature puts fundamental doubts, saying it gently, on the proposal of Ref. 1 about the (orbiton) nature of peaks observed in the Raman scattering for $LaMnO_3$. According to us before inventing a new phenomenon it is necessary to check phenomena known in the atomic physics and check, whether peaks observed in Raman scattering experiments are not related to the atomic-like states. The discussion of the Raman spectra goes, however, beyond the present Comment that criticizes the understanding of Ref. 1 about the 3d free-atom levels being in the sharp conflict with the atomic physics.

[1] J. van den Brink, Phys. Rev. Lett. **87**, 217202 (2001).

[2] We do not like to write a Comment, in which as the editorial obligation one has to criticize or correct somebody's paper - thus please treat the Comment as a part of the normal scientific discussion. We are forced to write the Comment due to a hardly understandable and inacceptable politics of the Editors of Phys. Rev. Lett., that find some papers, on the electronic structure and the magnetism of 3d-ion compounds, pointing out the importance of the spin-orbit coupling and the orbital moment, as inappropriate and unsuitable for the publication in Phys. Rev. Lett.. The relevant correspondence of PRL-LNK810 is attached here - the long discussion has led to a scientific bet for 1 million US dollars as is written in arXiv:cond-mat/0211153v1. It is coming time when we will approach this amount of money for support of the Polish physics.

[3] NIST Atomic Spectra Database, in http://physics.nist.gov.

[4] R. J. Radwanski and Z. Ropka, arXiv:cond-mat/9907140; this paper was originally submitted 30.05.1997 to Phys. Rev. Lett. getting the code number LE6925 *Relativistic effects in the electronic structure for the 3d paramagnetic ions.*
[5] R. J. Radwanski and Z. Ropka, Physica B **281&282**, 507 (2000).
[6] R. J. Radwanski and Z. Ropka, arXiv:cond-mat/0201153; this paper was originally submitted 27.01.1997 to Phys. Rev. Lett. getting the code number LA6567 *Influence of spin-orbit interactions on the cubic crystal-field states of the d^4 system.*

♠ This Comment has been submitted to Phys. Rev. Lett. on 14.01.2002, getting a code LNK810, but it has been rejected by the Editor as "not suitable" despite of our extensive arguments that the open scientific discussion of the electronic structure and magnetism of $LaMnO_3$ is very important, in particular in the situation when the electronic structure and properties of $LaMnO_3$ are widely discussed in many prestigious physical journals and we came out with the novel electronic structure. We have argued that such arbitrary decisions of the Editor of Phys. Rev. Lett. violate fundamental scientific rules and the publication of Comment is simply the scientific obligation of each journal, regarding itself to be scientific. Otherwise, it is a manipulation of Science by Editors of Phys. Rev. Lett. as we have pointed out in "Open letter to the Editor: The manipulation of Physics by the Editor of Phys. Rev. Lett. - the role of the spin-orbit coupling in 3*d*-atom containing compounds", submitted to Phys. Rev. Lett. 30.12.2000 getting a code number LA8178, also put 7.01.2001 as arXiv:cond-mat/0101027. Here is the full text of the rejection email of 30.01.2002 for the present Comment.

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RE:from Editor of Phys.Rev.Lett. 30.01.2002:

LNK810; Comment on "Orbital excitations in $LaMnO_3$: 3*d* levels of a free transition-metal atom"

Dear Dr Ropka,

Your manuscript has been considered. We regret to inform you that we have concluded that it is not suitable for publication in Physical Review Letters. I see no possible benefit from futher correspondence regarding this paper, and will not engage in any.

Yours sincerely,

Reinhardt B. Schuhmann,

Editor of Physical Review Letters

NY, 30 January 2002.

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Our resubmission on 10 June 2002 stays up to 7.04.2003 without any reaction of the Editor. Here is our accompanied letter:

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On line