

**Comment****Comment on Phys. Rev. B paper:**

*" $t_{2g}$  versus all 3d localization in LaMO<sub>3</sub> perovskites  
(M=Ti-Cu): First-principles study"*

*R. J. Radwanski\**

*Center of Solid State Physics; S<sup>nt</sup> Filip 5, 31-150 Krakow, Poland  
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland*

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Solovyev *et al.* [1] have presented results of band-structure calculations for LaMO<sub>3</sub> perovskites (M=Ti-Cu) within the local-density approximation. I point out that these calculations have little correspondence to the reality as they do not take into account i) the spin-orbit (s-o) coupling and ii) the Zeeman effect. It is claimed that the spin-orbit coupling has to be taken into account for any meaningful discussion of 3d paramagnetic ions because it substantially modifies the electronic structure, its low-energy part in particular, the local ground state and its magnetic moment.

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Solovyev *et al.* [1] have presented results of band-structure calculations for LaMO<sub>3</sub> perovskites (M=Ti-Cu) within the LDA+U method, where LDA means the local-density approximation. Solovyev *et al.* have developed an own version, called LDA+U<sub>2</sub>, with the treatment of d- $t_{2g}$  electrons as localized. These calculations have, however, little correspondence to the reality as they do not take into account i) the spin-orbit (s-o) coupling and ii) the Zeeman effect. The neglect of the spin-orbit coupling is clearly admitted on p. 7164, left column, 16 lines bottom, "We leave the effects of the spin-orbit coupling for future investigations". One of the consequence of leaving off the s-o coupling is that the authors can calculate the spin moment only (Table III). The calculated spin-only moment has been found to overestimate very much the experimentally observed values for LaTiO<sub>3</sub> and LaVO<sub>3</sub> compounds, in particular.

\* <http://www.e-physica.pl>; Email: [sfradwan@cyf-kr.edu.pl](mailto:sfradwan@cyf-kr.edu.pl)

I claim that the spin-orbit coupling has to be taken into account for any meaningful discussion of 3d paramagnetic ions. In particular, by theoretical models those want to describe their magnetism. **It is the spin-orbit coupling that makes a d electron different from the free-like electron.** It is of particular importance, if d electrons are treated as localized, as is the way in LDA+U approaches. To make clear my standpoint - I am in favour for the picture for Mott insulators with **all** d electrons localized. According to me, the s-o coupling has very large influence on the electronic structure, its low-energy part in particular, the local ground state and its magnetic moment. Thus, the s-o coupling has to be taking into account from the beginning.

The inability to calculate properly the local ground state unables the reproduction the magnetic moment clearly seen for LaTiO<sub>3</sub> and LaVO<sub>3</sub> compounds. The effect of the spin-orbit coupling for these early 3d transition-metal ions can be quite easily explained using an argument of the 3<sup>rd</sup> Hund's rule, that becomes fully valid in case of extremely strong s-o coupling as happens for 4f ions. According to the 3<sup>rd</sup> Hund's rule the orbital and spin contributions to the magnetic moment of the ground state are opposite for these less half-filled d ions.

This qualitative explanation can be exactly calculated if one accepts the two first Hund's rules and considers a single-ion-like Hamiltonian of the form [2, 3]:

$$H_d = H_{CF} + H_{s-o} = B_4^0(O_4^0 + 5O_4^4) + \lambda L \cdot S + \mu_B(L + g_s S)B_{ext}$$

The first term is the cubic CEF Hamiltonian with the Stevens operators  $O_n^m$  that depend on the orbital quantum numbers  $L, L_z$ . The second term accounts for the spin-orbit interactions with  $\lambda$  as the s-o coupling constant. The last term accounts for the influence of the magnetic field, external or internal in case of the magnetically-ordered state. The Ti<sup>3+</sup> ion is the 1 d-electron system with  $S = 1/2$  and  $L = 2$  whereas the V<sup>3+</sup> ion is the 2 d-electron system with  $S = 1$  and  $L = 3$ . By direct diagonalization of the 10×10 matrix (Ti<sup>3+</sup> ion) associated with the Hamiltonian (1) considered in the  $|LSL_z S_z\rangle$  base [4] I have obtained that in case of the octahedral cubic CEF surroundings the 6-fold degenerated  $t_{2g}$  state splits into a lower quartet and a higher doublet, [2, 3] separated by about 330 K ( $\approx \frac{3}{2}\lambda$ ). The magnetic moment of the lower quartet is quite small. In fact, it is close to zero. This result is already known in an approximate form by more than 25 years, Ref. [2], p. 422, but ignored by nowadays band-structure theories. An orthorhombic distortion and the Zeeman- effect in the magnetically-ordered state increase this moment. A very important consequence of the approach of Hamiltonian (1) is that there appears the fine electronic structure with a number of

closely-lying localized levels. For the  $Ti^{3+}$  ion there is 6 localized levels within 30 meV.

The Hamiltonian (1) is written for the lowest term LS given by two Hund's rules. It yields the many-electron states of the whole  $d^n$  system [3] in contrary to one-electron states discussed in band-theories, including the LDA+ $U_2$  theory. I claim that not one-electron states but many electron states are of fundamental importance for description of magnetic and electronic properties of  $3d$  ions at low and room temperatures. In fact, I follow here Sir N. F. Mott, who already almost 50 years ago has realized inadequacies of one-electron approaches to  $3d$ -ion compounds that stay insulators (Mott insulators) despite of the unfilled  $d$  band.

At the end I would like to express my acknowledgements to the authors for the scientific honesty - most of authors do not write openly about used approximations. It allows, however, for the scientific discussion.

Concluding, I claim that the spin-orbit coupling has to be taken into account for any meaningful discussion of  $3d$ -ion compounds as it produces the fine electronic structure within 30 meV and has enormous influence on the ground-state magnetic moment. I claim that one-electron calculations as performed in the commented paper have little correspondence to the reality unless they are not providing indications for temperature dependence of the specific heat and magnetic susceptibility as well as the magnetic-ordering temperature.

Note added after reading the Solovyev *et al.*'s answer:

I fully maintain all my objections to [1]. I am fully aware of all problems arisen by them. I can also add that I do not have difficulties with the understanding of their work.

This discussion clearly shows that i) the understanding of  $3d$ -ion compounds is far from being consistently understood and that ii) there exists, apart of LSDA approaches completely another approach (with localized discrete states). These facts were the main goals of my Comment. Editors of *Phys. Rev. B* and *Phys. Rev. Lett.*, making use of the band-structure people referee reports, prohibit this localized point of view to be propagated. The name of Solovyev appears as I have been informed in May 1997 by the Editor of *Phys. Rev. Lett.* that "The author (i.e. me) should learn about the spin-orbit coupling from the papers of Solovyev." In such the circumstances I have found that Solovyev, despite of the applied complex theory, does not take into account the spin-orbit coupling [1]. Some arisen points touch fundamental problems of the modern solid-state physics (e.g. consistent description of Mott insulators) - they cannot be answered in a short letter. Thus,

please leave these problems open for the future, but with keeping our scientific views. I am ready for further scientific confrontation and/or open discussion. Here I only can say that just due to the s-o coupling the one-electron states for the  $Ti^{3+}$  ion within the LDA approaches substantially differs from my states for this ion. A value of 30 meV has been chosen as it refers to the room-temperature energy, that arbitrarily ends the low-temperature region and low-energy excitations. The cubic crystal-field Hamiltonian can be easily extended to lower symmetries. The effect of 30 meV for  $LaTiO_3$  is really important despite of its very small value compared to the LSDA band-width  $W$  of 2 eV.

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- [1] I. Solovyev, N. Hamada, and K. Terakura, *Phys. Rev. B* **53**, 7158 (1996).
  - [2] A. Abragam and B. Bleaney, in: *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford) (1970).
  - [3] R. J. Radwanski, *Molecular Physics Reports* **15/16**, 113 (1996).
  - [4] the computer program is available on the written request to the author.