

Ground state of the Mn^{3+} ion in $LaMnO_3$ [♠] - 5E_g or $t_{2g}^3e_g^1$?

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ABSTRACT, 31.07.2006 (Acta Physica 3, 35 (2007)), also here, preceding page;
see also arXiv:cond-mat/0403714, March 29, 2004;
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We have shown that the ground state of the Mn^{3+} ion in $LaMnO_3$ is the 5E_g cubic subterm. It is a 10-fold degenerated state belonging to the $t_{2g}^3e_g^1$ configuration. The description by the 5E_g ground state is more specific information than by the $t_{2g}^3e_g^1$ configuration. An optical transition at 2 eV is the 5E_g - ${}^5T_{2g}$ transition. Its energy is determined by the strength of the crystal-field interactions of the Mn^{3+} ion and it is the energy needed for the on-site t_{2g} - e_g promotion from the $t_{2g}^3e_g^1$ configuration to the $t_{2g}^2e_g^2$ one.

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Keywords: 3d oxides, crystal field, spin-orbit coupling, Mn^{3+} ion, $LaMnO_3$

$LaMnO_3$ is a solid with a high application potential in spintronics after a partial substitution of La atoms by Ca or Sr ones [1–6]. These substitutions lead to the ferromagnetic state and, what is more important, to increase of temperature of the magnetic ordering close to room temperature what enables its practical application. The ground state of $LaMnO_3$, in particular of the Mn^{3+} ion in $LaMnO_3$, is/was a subject

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of a long lasting controversy. Results of our calculations, confirming earlier crystal-field theory calculations, yielding the 5E_g state as the ground state of the Mn^{3+} ion in LaMnO_3 did not get appreciation in year of 2002, at the SCES-02 Conference. Opponents have raised an argument that other researchers gave a picture with the ground state as $t_{2g}^3 e_g^1$, with the t_{2g} states as the lowest and the e_g state lying higher, Fig. 1. Despite of our long explanation our paper has been rejected from the publication by the SCES-02 Committee with clear message that according to them the 5E_g ground state was erroneous in physics of manganites. The present paper is devoted only to solve this scientific problem because when too many problems are addressed in one paper the reader (and the referee) can be lost with an understanding of the subject of the paper. We mention only that our approach provides a physical explanation for the 2 eV peak observed in optical absorption spectra and discussed recently within the orbitally degenerate Hubbard model [7] as well as in the spin-orbital model [6]. In the present contribution we explain that the 5E_g state is one of 80 states of the $t_{2g}^3 e_g^1$ configuration of the Mn^{3+} . A misunderstanding is likely related to the fact that the notation $t_{2g}^3 e_g^1$ uses the one-electron picture in contrary to the many-electron crystal-field notation used by us. In one-electron picture subsequent electrons are put on the octahedral crystal-field states derived for one d electron. For the one $3d$ electron ($3d^1$) octahedral crystal field split its 10-fold degenerated states into t_{2g} states, lying lower, and excited e_g states. The 5E_g notation underlines the symmetry of the state [8, 9] and for the four d electrons relevant to the Mn^{3+} ion it refers to the many-electron states of the whole $3d^4$ system. We point out that this **many – electron** crystal-field approach is more physically adequate and that the formation of the 5E_g state is a sign of strong electron correlations.

There is in total 210 possibilities to put four electrons on the 10 spin-orbital states. It is the physical situation realized in the Mn^{3+} ion. These states can be schematically written as $t_{2g}^3 e_g^1$, t_{2g}^4 , $t_{2g}^2 e_g^2$, $t_{2g}^1 e_g^3$ and e_g^4 configurations with 80, 15, 90, 24 and 1 states, respectively. These states can be also divided as high-spin, intermediate spin and low-spin states taking into account a quantum number S . These states are further modified in the crystal field, predominantly of the octahedral symmetry in LaMnO_3 . Among 80 states belonging to the configuration $t_{2g}^3 e_g^1$ there are 10 states of the 5E_g symmetry. Thus, the description by the 5E_g ground state gives more specific information than the $t_{2g}^3 e_g^1$ configuration. The four d electrons of the Mn^{3+} ion in the incomplete $3d$ shell in LaMnO_3 form the strongly correlated intra-atomic $3d^4$ electron

ActAPhysica/0709.06 30 Sep 2007

Od Prof. Spaltek
23-12-02 13:15 RJR

OO 15 PO Praca odrzucona ze wzgledu
na brak dyskusji uwag recenzentki
w recenzji, niejasnym jest dlaczego
struktura poziomow $t_{2g}-e_g$ jest odwrócona
Wzpladem tego, co otrzymate wielu autorow

Jozef Spaltek
31/X/02

OO 15

SCES-02 Krakow
July 10-14, 2002

Electronic structure and magnetism of LaMnO_3 *

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system
Final: Rejected
J. Spaltek
20/12/02

We claim that in LaMnO_3 exists low-energy electronic structure originating
from ~~the atomic-like states~~ ^{the} highly-correlated $3d^4$ electronic system occur-
ring in the Mn^{3+} ion. Our studies indicate that the intra-atomic spin-orbit cou-
pling and the orbital magnetism are indispensable for the physically adequate de-
scription of electronic and magnetic properties of LaMnO_3 .

PACS numbers: 71.70E, 75.10D

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configuration of

1. Introduction

The present study is a continuation of our systematic investigations on the elec-
tronic structure and magnetic properties of compounds containing ~~the~~ transition-
metal atoms. ~~Problem of the Mn^{3+} ion containing compounds is of particular~~
interest.

LaMnO_3 is an insulating antiferromagnet with the Neel temperature of 140
K [1, 2, 3, 4]. The Mn ions in the perovskite structure sit in the almost perfect
oxygen octahedron with some small further distortions. The basis for all theories
is the description of the Mn^{3+} ion and its electronic structure.

The aim of this paper is to present a consistent description of the low-energy
electronic structure and magnetism of LaMnO_3 on the atomic scale. In our un-
derstanding, formulated as the Quantum Atomistic Solid State Theory (QUASST)
[5, 6], this low-energy electronic structure is related to the atomic-like electronic
structure of the highly-correlated $3d^4$ electronic system occurring in the Mn^{3+} ion.
In our description the orbital magnetism and the intra-atomic spin-orbit coupling
play the ~~the~~ ^{the} fundamentally important role.

* Presented at the Strongly Correlated Electron Systems Conference, Kraków 2002

FIG. 1: Controversy on the description of the electronic structure of the $3d$ states in the Mn^{3+} ion in LaMnO_3 . The calculated by us E_g ground state has been rejected on SCES-02, because it "is reversed with respect to the $t_{2g}-e_g$ structure obtained by many authors" as is written in Polish.

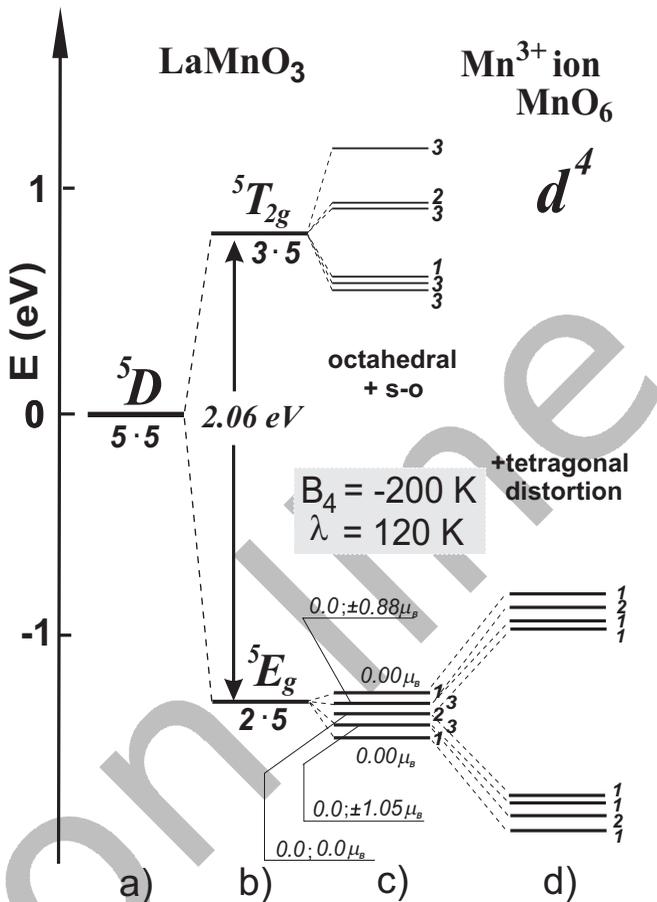


FIG. 2: Calculated electronic structure of the lowest 5D term (a) of the $3d^4$ electronic system occurring in the Mn^{3+} ion realized in LaMnO_3 , produced by the octahedral crystal field (b), the intra-atomic spin-orbit coupling (c) and the tetragonal distortion (d). The degeneracy and the magnetic moment of the states are shown. The fine splitting is not to the left-hand scale. This figure is the same as submitted to the SCES-02.

system. These strong correlations among the $3d$ electrons we account for by two Hund's rules, that yield the 5D ground term, Fig. 2a. In the oxygen octahedron surroundings, realized in the perovskite structure of LaMnO_3 , the 5D term splits into the orbital doublet 5E_g as the ground

subterm, Fig. 2b, and the excited orbital triplet ${}^5T_{2g}$. For physically adequate description of states we have to take into account the intra-atomic spin-orbit coupling, Fig. 2c (because it is always present in the ion) and off-octahedral distortions, Fig. 2d.

The E_g ground subterm comes out from *ab initio* calculations for the octupolar potential, the A_4 coefficient and the B_4 parameter in the crystal-field theory, acting on the Mn^{3+} ion from the oxygen negative charges. In a solid such the atomic-like $3d^4$ system interacts with the charge and spin surroundings. The interaction with the charge surroundings are described by means of the crystal-field interactions. Fig. 2c shows the energy level scheme of the $3d^4$ system in the octahedral crystal field and in the presence of the spin-orbit, in the spin-orbital space, originating from 25-fold degenerated 5D term. The dominating octahedral crystal field leaves 10 lowest states well separated from others. These 10 states are split into two quintets by the tetragonal distortion, see Fig. 2d. The splitting of two quintets is of order of 100 meV. This fine electronic structure predominantly governs the electronic and magnetic properties of real $3d$ -ion systems. To such electronic structure the Nature superimposes the spin-dependent interactions in order to lower energy of a lattice of Mn^{3+} ions by producing a magnetic state. The appearance of the magnetic state is associated with the spin polarization and the temperature dependence of the energy of the levels. The self-consistent calculations have been performed similarly to those presented in Ref. [10] for $FeBr_2$.

The relevant parameters for $LaMnO_3$ are: the octahedral CEF parameter $B_4 = -200$ K, tetragonal distortion $B_2^0 = +100$ K, the spin-orbit coupling parameter $\lambda_{s-o} = +120$ K and the molecular-field coefficient $n = 26.3$ T/ μ_B . This molecular field coefficient yields T_N of 140 K in agreement with experiment. The octahedral CEF parameter $B_4 = -200$ K yields the CEF splitting of 2.06 eV between 5E_g and ${}^5T_{2g}$ states. It corresponds to a $t_{2g}-e_g$ promotion from the $t_{2g}^3e_g^1$ configuration to the $t_{2g}^2e_g^2$ one. This excitation is a physical reason for the 2-eV optical absorption discussed in Ref. [7]. The above-mentioned value of B_4 places $LaMnO_3$ on the Tanabe-Sugano diagram [11] at $Dq = 0.2$ eV, i.e. at the intermediate crystal-field regime. The octahedral crystal-field interactions are slightly smaller in $LaMnO_3$ compared to $LaCoO_3$ due to a larger mean Mn-O distance of 201 pm (190 and 218 pm in the a-b plane and 196 pm along c axis) compared to the Co-O distance of 192.5 pm in $LaCoO_3$ (0.27 eV in Ref. [12]).

In conclusion, we have shown that the ground state of the Mn^{3+} ion in $LaMnO_3$ is the 5E_g cubic subterm. This 10-fold degenerated state belongs to the 80-fold degenerated $t_{2g}^3e_g^1$ configuration. The 5E_g cubic

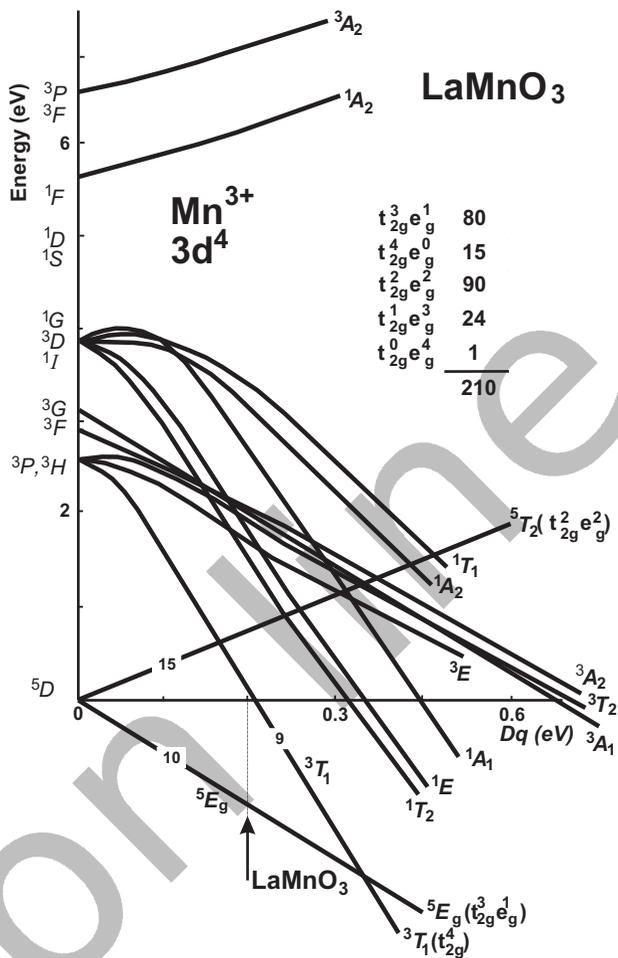


FIG. 3: Tanabe-Sugano diagram for the Mn³⁺ ion. It shows the influence of the strength of the octahedral crystal field on the ionic states of the Mn³⁺ ion. The value of $B_4 = -200$ K places LaMnO₃ on the Tanabe-Sugano diagram at $Dq = 0.2$ eV, i.e. at the intermediate crystal-field regime.

subterm is the high-spin state with $S=2$. An optical transition at 2 eV is the ${}^5E_g \rightarrow {}^5T_{2g}$ transition. Its energy is determined by the strength of the crystal-field interactions of the Mn³⁺ ion and it is the energy needed for the on-site $t_{2g} \rightarrow e_g$ promotion from the $t_{2g}^3 e_g^1$ configuration to the $t_{2g}^2 e_g^2$ one.

♠ - this paper did not get appreciation of Prof. J. Spalek to be published in the Proceedings of the XII Conf. KSN12 - *Acta Phys. Pol.* vol. 111, No 4 and 5 (October 2007). It is a continuation of the rejection unscientific politics about LaMnO_3 and the ionic description starting on SCES-02 by Prof. Prof. J. Spalek, A. M. Oles, H. Szymczak and J. Morkowski (the chairmen of SCES-02). About this unscientific decision at SCES-02 the whole International Committee was informed.

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