ELSEVIER

Physica B 312–313 (2002) 777–779

PHYSICA B

www.elsevier.com/locate/physb

The Jahn–Teller-effect formation of the non-magnetic state of the Co^{3+} ion in $LaCoO_3$

Z. Ropka[a,*], R.J. Radwanski[a,b]

[a] *Center for Solid State Physics, s^nt Filip 5, 31-150 Krakow, Poland*
[b] *Institute of Physics, Pedagogical University, 30-084 Krakow, Poland*

Dedicated to the 65th anniversary of the Jahn–Teller theorem

Abstract

It is shown that the Co^{3+} ion can have a non-magnetic ground state as the realization of the Jahn–Teller effect. This non-magnetic localized singlet ground state with a highly magnetic excited doublet is formed by the trigonal distortion of the local octahedral surrounding. Such structure is exactly accounted for by crystal-field interactions if the intra-atomic spin–orbit coupling is correctly taken into account. The presented crystal-field-based approach can be applied to other Co^{3+} and Fe^{2+} ion compounds.

PACS: 75.20.H; 71.70.E; 75.10.D

Keywords: Crystal-field interactions; Spin–orbit coupling; Jahn–Teller effect

$LaCoO_3$ has attracted scientific attention for almost 50 years due to its non-magnetic ground state [1] that gradually transforms with temperature showing a quite standard Curie–Weiss behavior with an effective moment exceeding $5\mu_B$. This phenomenon is attributed in the current literature to the temperature-induced transformation [1–4] from the 1ow-spin ($S=0$) to the intermediate ($S=1$) or/and high-spin ($S=2$) state of the trivalent cobalt ion. In current approaches the orbital moment is neglected [3–5].

The aim of this paper is to present a single-ion-like mechanism for the formation of the non-magnetic state of $LaCoO_3$. In our approach we take into account the spin and orbital momenta.

In the perovskite-like structure of $LaCoO_3$ the Co^{3+} ions are situated in an octahedral environment. The Co^{3+} ion has 6 d-electrons in the incomplete outer shell and here they will be treated as forming a highly-correlated electron system $3d^6$. In a zero-order approximation the electron correlations within the incomplete 3d shell we account for by the phenomenological Hund's rules that yield for the $3d^6$ electron configuration the term ^5D with $S=2$ and $L=2$ as the ground term. Under the action of the octahedral crystal field, the ^5D term splits [6] into the orbital triplet $^5T_{2g}$ and the orbital doublet ^5E_g. The ^5D term is 25-fold degenerate in the spin–orbit $|LSL_zS_z\rangle$ space. The removal of this degeneracy can be investigated by considering the single-ion-like Hamiltonian for the $3d^6$ system of the 3d ion [7].

The calculated low-energy electronic structure is shown in Fig. 1. From the figure it is clear that the trigonal lattice distortion causes the splitting of the lowest state that is triply degenerate in the $|LSL_zS_z\rangle$ space. The size of the splitting depends on the value of the trigonal-distortion parameter B_2^0, Fig. 1c. The singlet–doublet sequence depends on the kind of trigonal distortion, i.e the shrinkage or the elongation of the oxygen octahedron along the [1 1 1] axis seen as $\alpha > 60^\circ$ or $\alpha < 60^\circ$, respectively. The formation of the singlet–doublet sequence with the singlet lower is preferred by

*Corresponding author. Tel.: +48-12-6336146; fax: +48-12-6324012 .

E-mail address: sfradwan@cyf-kr.edu.pl (Z. Ropka).
URL: http://www.css-physics.edu.pl.

0921-4526/02/$ - see front matter
PII: S0921-4526(01)01207-8

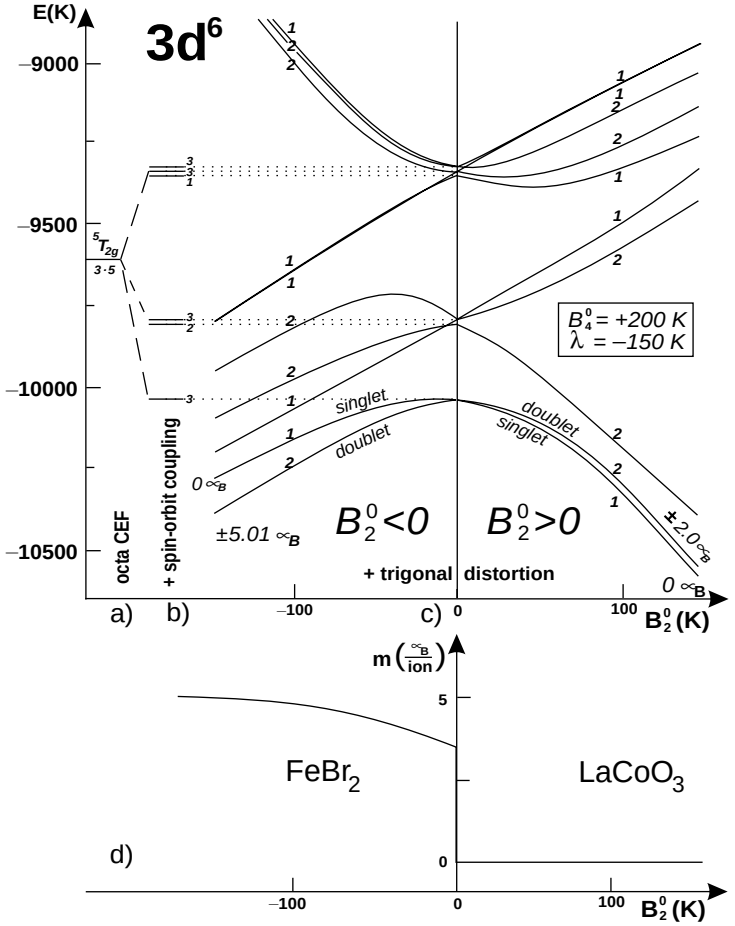

Fig. 1. The influence of the strength and of the type of the trigonal distortion on the electronic structure and the ground state magnetic moment of the $3d^6$ system. (a) the 15-fold degenerated $^5T_{2g}$ sub-term formed by the octahedral crystal field, (b) effect of the spin–orbit coupling, (c) the influence of the trigonal distortion on the electronic structure and (d) the ground state magnetic moment.

Nature. It is the realization of the Jahn–Teller theorem. Such a sequence fulfills the 3rd thermodynamic law and gains the extra energy.

The computations have been performed for the parameters $B_4 = +17.2$ meV, $\lambda = -54$ meV and $B_2^0 = +15.5$ meV. The result concerning the nonmagnetic atomic state of the Co^{3+} ion does not depend on the parameters chosen provided the sign of the parameters is kept. The derived electronic structure, Fig. 2, is quite peculiar. It has (i) a non-magnetic singlet ground state and (ii) highly magnetic excited doublet states. The magnetic moment of the first and the second doublets amounts to $\pm 2.32\mu_B$ and $\pm 3.66\mu_B$. In the electronic structure presented in Fig. 2c one can find the single-ion microscopic base for the low-, intermediate- and high-spin states postulated in theoretical discussions [1–5]. At zero temperature only the lowest state is occupied causing the diamagnetism of $LaCoO_3$. With increasing temperature, the higher states become thermally populated with the population given by Boltzmann statistics. This peculiar atomic structure with a spin-like energy gap results in the anomalous temperature dependence of the magnetic susceptibility with a very pronounced maximum resembling experimental data.

In conclusion, a novel single-ion view on the origin of the non-magnetic state of $LaCoO_3$ has been proposed. It is associated with the non-magnetic singlet ground state of the Co^{3+} ion being situated in the slightly trigonally-distorted octahedral crystal field in $LaCoO_3$. This non-magnetic state can be theoretically revealed provided the spin–orbit coupling is correctly taking into account. The non-magnetic singlet state results from the off-cubic trigonal distortion and is the physical realization of the Jahn–Teller theorem. In the anti-Jahn–Teller effect the doublet state would be pushed lower. But such the doublet ground state is good for the realization of the

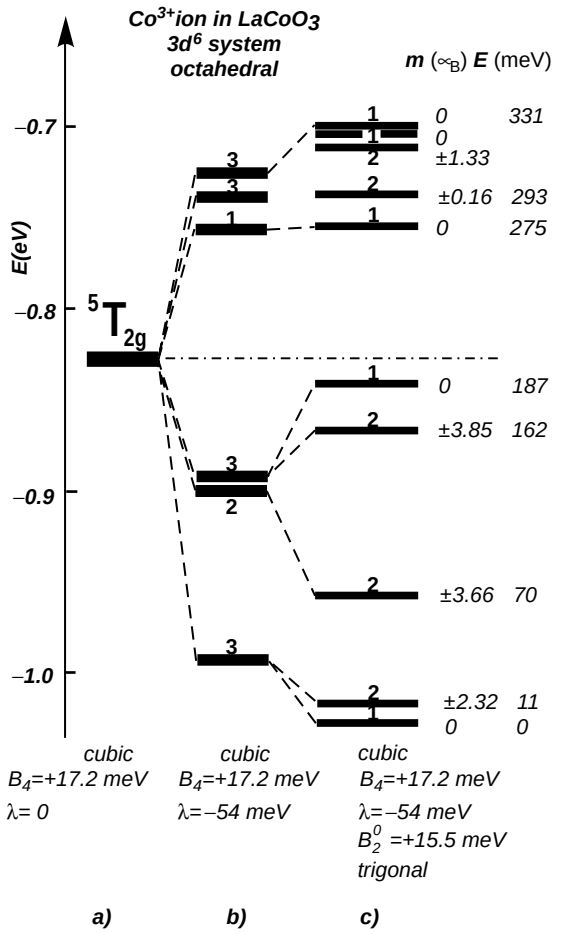

Fig. 2. The influence of the trigonal distortion (a) on the octahedral CEF states and (b) on the CEF + spin–orbit states ($\lambda = -54$ meV, $B_4 = +17.2$ meV) of the orbital-triplet $^5T_{2g}$ ground cubic sub-term. (c) The trigonal distortion, $B_2^0 = +15.5$ meV, produces the fine electronic structure with a nonmagnetic singlet ground state and a closely lying, at 11 meV, strongly magnetic excited state. The states are labelled with the degeneracy, the magnetic moment and the energy with respect to the ground state.

magnetic state — we expect this situation to be realized in magnetically ordered Co^{3+} and Fe^{2+}-ion compounds like $FeBr_2$ [8], for instance. Our atomic-like explanation for the nonmagnetic state of $LaCoO_3$ is based on the symmetry and well-known physical mechanisms. Our model provides a detailed low-energy electronic structure and allows for quantitative explanation of the temperature dependence of physical properties like the specific heat and the magnetic susceptibility. According to the quantum atomistic solid-state theory [9], the discrete atomic structure is preserved in solids — the obtained good reproduction of experimental results in numerous compounds confirms a posteriori this atomic assumption. The slight trigonal distortion with $\alpha = 60.8^\circ$ has actually been experimentally observed in $LaCoO_3$ [1,3]. This observation correlates well with the opposite distortion observed in CoF_3 ($\alpha = 57.9^\circ$) that is strongly magnetic ($T_N = 460$ K). The present model can be applied to other Co^{3+} and Fe^{2+} ion compounds and the analysis of other Co/Fe systems is underway.

References

[1] V.G. Bhide, et al., Phys. Rev. B 6 (1972) 1021.
[2] D.D. Sarma, et al., Phys. Rev. Lett. 75 (1995) 1126.
[3] M. Abbate, et al., Phys. Rev. B 49 (1994) 7210.
[4] M.A. Korotin, et al., Phys. Rev. B 54 (1996) 5309.
[5] Min Zhuang, et al., Phys. Rev. B 57 (1998) 10705.
[6] A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon, Oxford, 1970, pp. 365–471.
[7] R.J. Radwanski, Z. Ropka, Phys. B 281&282 (2000) 507.
[8] Z. Ropka, et al., Phys. Rev. B 63 (2001) 172404.
[9] R.J. Radwanski, et al., Acta Phys. Pol. B 31 (2000) 3079.