

5D term origin of the excited triplet in LaCoO₃

Z. Ropka

Center for Solid State Physics, S^{mt} Filip 5, 31-150 Krakow, Poland

R. J. Radwanski*

*Center for Solid State Physics, S^{mt} Filip 5, 31-150 Krakow, Poland
and Institute of Physics, Pedagogical University, 30-084 Krakow, Poland*

(Received 26 December 2002; published 5 May 2003)

We provide the proof for the 5D term origin of an excited triplet observed in the recent electron-spin-resonance (ESR) experiments by Noguchi *et al.* [Phys. Rev. B **66**, 094404 (2002)]. We have succeeded to fully describe experimental ESR results both for the zero-field g factor, of 3.35, and the splitting D of 4.90 cm^{-1} , as well as for the magnetic field applied along different crystallographic directions within the localized electron atomiclike approach as originating from excitations within the lowest triplet of the $^5T_{2g}$ octahedral subterm of the 5D term. In our atomiclike approach the d electrons of the Co^{3+} ion in LaCoO_3 form the highly correlated atomiclike system $3d^6$ with the singlet ground state 1A_1 (an octahedral subterm of the 1I term) and the excited octahedral subterm $^5T_{2g}$ of the 5D term. We take the ESR experiment as confirmation of the existence of the discrete electronic structure for $3d$ electron states in LaCoO_3 in the meV scale.

DOI: 10.1103/PhysRevB.67.172401

PACS number(s): 76.30.Fc; 75.10.Dg

I. INTRODUCTION

LaCoO_3 has attracted much attention in the past 50 years due to its nonmagnetic ground state and the significant violation of the Curie-Weiss law at low temperatures^{1,2} often discussed in terms of successive changes of spin states with the increasing temperature. A great number of band-structure calculations,³⁻¹⁰ yielding the continuous energy spectrum for $3d$ states spread over 6 eV, as well as crystal-field (CEF) considerations with discrete, in the meV energy scale, energy spectrum¹¹⁻¹³ did not yield a final convincing solution for the magnetism, the electronic structure, and thermodynamics for LaCoO_3 . One can find a short comparative discussion of different modern theoretical approaches to LaCoO_3 in Ref. 14.

Recently Noguchi *et al.*¹⁵ have succeeded in the electron spin resonance (ESR) measurements for an excited triplet, the behavior of which under external magnetic field applied along different crystallographic directions of single-crystalline LaCoO_3 is very well described by an effective spin-Hamiltonian, Eq. (3.1) of Ref. 15, with the effective spin $S=1$ and with fitted values $g_{\parallel}=3.35$, $g_{\perp}=3.55$, and $D=+4.90 \text{ cm}^{-1}$ ($=7.056 \text{ K}=0.6 \text{ meV}$). This excited triplet has been discussed in connection to the intermediate-spin state in the standard description of LaCoO_3 in terms of low-spin (LS), intermediate-spin (IS), and high-spin (HS) states.^{4,16}

The aim of this paper is to provide the proof that the triplet state revealed in the recent ESR experiment of Noguchi *et al.* is the state originating from the atomiclike term 5D of the $3d^6$ electron system existing in the Co^{3+} ion. This 25-fold degenerate 5D term (in the $|LSL_zS_z\rangle$ space) and its 15-fold degenerate $^5T_{2g}$ octahedral subterm, we have studied in great details as we have considered its singlet as the ground state in our up-to-now description of LaCoO_3 ; see Fig. 1(c) of Ref. 12 and Fig. 2(c) of Ref. 13.

II. THEORETICAL OUTLINE

For the description of the excited triplet we apply exactly the same Hamiltonian as have been used by us in Refs. 11-13, namely Eq. (1) of Ref. 12 and of Ref. 13 for the term 5D with $S=2$ and $L=2$:

$$H_d = H_{cub}(L, L_z) + \lambda LS + B_2^0 O_2^0(L, L_z) + \mu_B(L + g_s S)B, \quad (1)$$

where $H_{cub} = B_4 \cdot (O_4^0 + 5O_4^4)$ for the z axis along the cube edge and O_m^n are the Stevens operators collected in, e.g., Ref. 17; Table 16, p. 863. The cubic CEF Hamiltonian takes, for the z axis along the cube diagonal, the form $H_{cub} = -\frac{2}{3}B_4 \cdot (O_4^0 - 20\sqrt{2}O_4^3)$. This latter form is useful for LaCoO_3 due to the experimentally observed rhombohedral (trigonal) distortion that can then be described by the parameter B_2^0 . For the $3d^6$ system in the oxygen octahedron $B_4 > 0$,¹¹⁻¹³ Ref. 17, p. 374. The last term in Eq. (1) allows studies of the influence of the magnetic field B , in the present case used for computer ESR experiments. The energy states, calculated for the dominant octahedral crystal field, weaker intra-atomic spin-orbit interactions, and the weakest trigonal distortion, are shown in Figs. 1(d) and Fig. 2(c) of Ref. 11 and in Fig. 1(d) of Ref. 18. According to us the observed triplet is the one shown as the lowest triplet in these figures.

III. RESULTS AND DISCUSSION

The splitting of the triplet, into the singlet and doublet, results from the trigonal distortion. This splitting, denoted as D in Ref. 15, is roughly proportional to the trigonal distortion B_2^0 parameter, Fig. 1. The magnetic moment, equal to the g factor in case of the triplet, of the doublet decreases with the increasing distortion from a value of $3.53\mu_B$ found for the purely octahedral crystal field in the presence of the spin-orbit coupling, Fig. 1(c) of Ref. 12. Figure 2 shows variation of the magnetic moment vs the splitting D for different val-

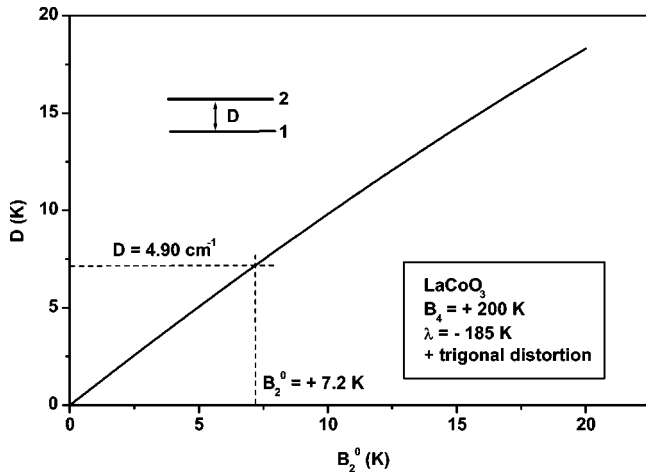


FIG. 1. Calculated dependence of the splitting of the excited triplet D on the distortion trigonal parameter B_2^0 in the presence of the octahedral crystal field $B_4 = +200$ K and the spin-orbit coupling $\lambda = -185$ K.

ues of the spin-orbit coupling in the presence of the octahedral crystal field described by the octahedral parameter $B_4 = +200$ K. The experimentally observed values $D = 4.90 \text{ cm}^{-1}$ and $g = 3.35$ are obtained for $\lambda = -185$ K and $B_2^0 = +7.2$ K. Practically the same curves are obtained for larger values of B_4 —it is related to the fact that B_4 determines the splitting of the 5D term and the 2–3-eV energy scale.

The calculated dependence of the triplet states under the action of the external magnetic field applied along different crystallographic directions, denoted in Fig. 1 of Ref. 15, is shown on Figs. 3–5 together with the ESR transitions f_o , f_1 , and f_2 for selected frequencies. For clarity, we have performed calculations of all 25 states in the $|LSL_2S_z\rangle$ space,¹⁹

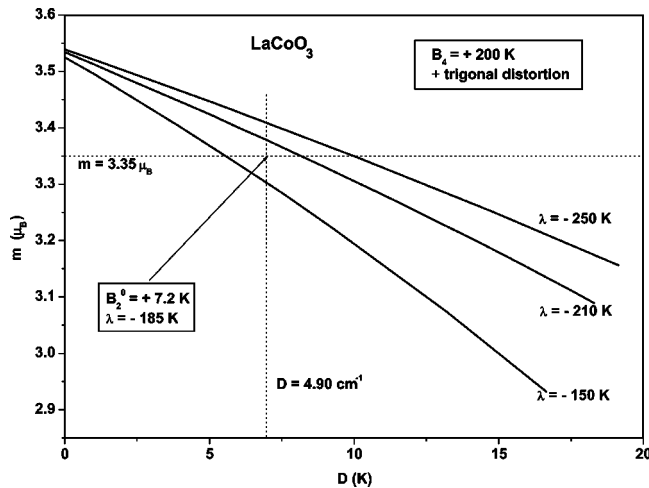


FIG. 2. Calculated dependence of the magnetic moment of the excited doublet on the splitting D for different values of the spin-orbit coupling λ in the presence of the octahedral crystal field $B_4 = +200$ K. Values of $g_{\parallel} = 3.35$ and $D = +4.90 \text{ cm}^{-1}$ ($= 7.056 \text{ K} = 0.6 \text{ meV}$) are reproduced by $\lambda = -185$ K and the trigonal distortion parameter $B_2^0 = +7.2$ K. Curves for a larger value of $B_4 = +260$ K are only slightly above (less than 1%).

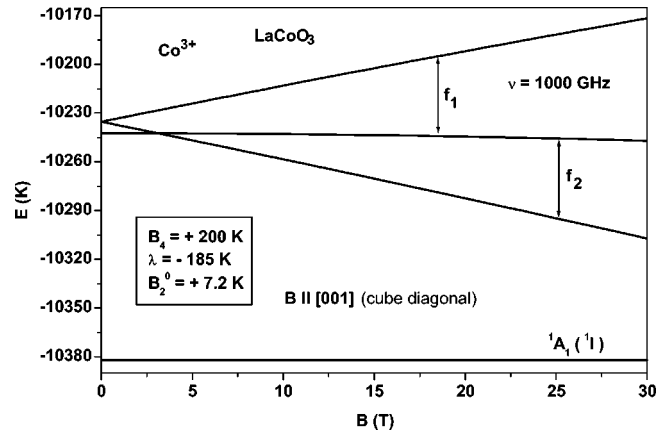


FIG. 3. Calculated field dependence of the three lowest states, the quasitriplet, of the 25-fold degenerate 5D term for the octahedral crystal field $B_4 = +200$ K and the spin-orbit coupling $\lambda = -185$ K and the distortion trigonal parameter $B_2^0 = +7.2$ K for external magnetic fields applied along the diagonal of the cube of the perovskite structure of LaCoO_3 . The ESR transitions f_1 and f_2 for the frequency of 1000 GHz ($= 48$ K) are shown. The zero energy is at the level of the unsplit 5D term.

but only the three lowest states are shown in Figs. 3–5. The energy structure of the 15 lowest states, originating from the ${}^5T_{2g}$ subterm, is shown in Fig. 6. It is predominantly determined by the spin-orbit interactions that define the 0.1-eV energy scale. The comparison of our Fig. 3 with Fig. 4 of Ref. 15, Fig. 4 with Fig. 5(a) of Ref. 15, and Fig. 5 with Fig. 5(b) of Ref. 15 illustrates a perfect reproduction of the experimental ESR results. In particular, we would like to bring attention to the reproduction of the behavior for the cubic-edge direction (Fig. 4) and for the direction perpendicular to the cube diagonal (Fig. 5). For the cubic direction the reso-

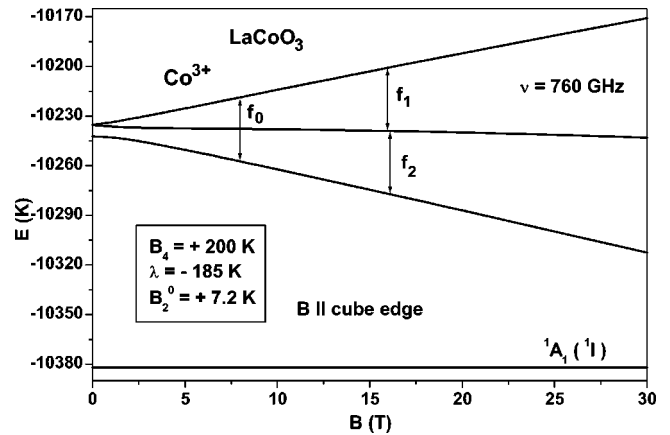


FIG. 4. Calculated field dependence of the three lowest states of the 5D term for the octahedral crystal field $B_4 = +200$ K and the spin-orbit coupling $\lambda = -185$ K and the distortion trigonal parameter $B_2^0 = +7.2$ K for external magnetic fields applied along the edge of the cube of the perovskite structure of LaCoO_3 . The ESR transitions f_o , f_1 , and f_2 for the frequency of 760 GHz ($= 36.5$ K) are shown. The ESR transitions f_1 and f_2 occur practically at the same magnetic field, what is a characteristic feature for the cubic direction.

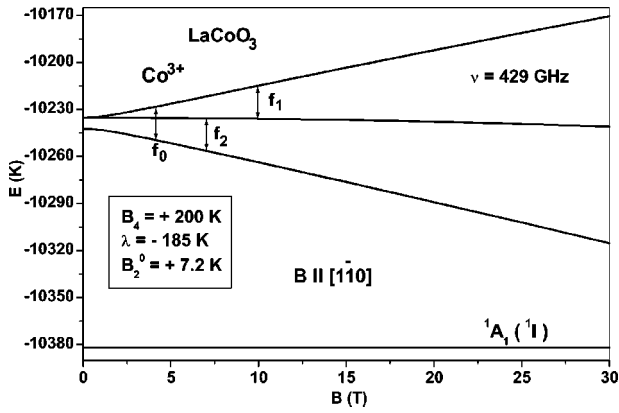


FIG. 5. Calculated field dependence of the three lowest states of the 5D term for the octahedral crystal field $B_4 = +200$ K and the spin-orbit coupling $\lambda = -185$ K and the distortion trigonal parameter $B_2^0 = +7.2$ K for external magnetic fields applied along the $[110]$ direction, i.e., perpendicular to the diagonal of the cube of the perovskite structure of LaCoO_3 . The ESR transitions f_0 , f_1 , and f_2 for the frequency of 429 GHz ($=20.6$ K) are shown.

nance fields f_1 and f_2 are the same which is not the case for the perpendicular direction. For the $[001]$ direction, the cube diagonal, the resonance fields are shifted by 6 T, Fig. 3, in agreement with the experimental observation.

It is worthwhile to point out that for the description shown

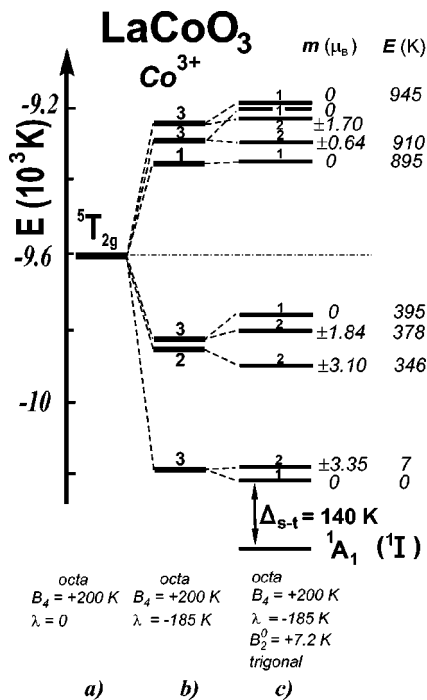


FIG. 6. Calculated low-energy electronic structure of the Co^{3+} ion in LaCoO_3 originating from the ${}^5T_{2g}$ cubic subterm with the 1A_1 singlet ground subterm put 140 K below the lowest ${}^5T_{2g}$ state. Such the structure is produced by the dominant octahedral crystal field and the intra-atomic spin-orbit coupling (b). (c) shows the splitting produced by the trigonal distortion. The states are labeled by the degeneracy, the magnetic moment, and the energy with respect to the lowest state of the 5D term.

we use only three parameters: B_4 (not so sensitive provided that it is positive and it is in the range 50–300 K), λ , and B_2^0 , that have been selected as shown in Figs. 1 and 2. All of them have clear physical meaning. In fact, the most important is the choice of the term, the term 5D with $S=2$ and $L=2$ in the present case. In this choice we have been oriented by our assumption of the fulfilling of two Hund's rules also in case of solids. The spin-orbit coupling parameter is by 12% smaller than the free-ion value, which is reasonable. But in fact, the most important “unwritten” assumption is an assumption about the significant surviving of the atomic states of the $3d^6$ system—it corresponds to the very strong correlations among $3d$ electrons. Thanks to these strong intra-atomic correlations the atomiclike terms of the Co^{3+} ion survive also in the solid when this cation becomes the full part of a solid.

IV. CONCLUSIONS AND REMARKS

We proved that the excited triplet, revealed in the ESR experiment by Noguchi *et al.*,¹⁵ originates from the 5D term, more exactly the lowest triplet of its ${}^5T_{2g}$ subterm. The zero-field g factor and the singlet-doublet splitting as well as the ESR excitations for different crystallographic directions have been very well described by taking into account the octahedral CEF interactions, the intra-atomic spin-orbit coupling and a relatively weak trigonal distortion. Such a good and very consistent description with a so limited number of parameters provides significantly large confidence to the found physical origin of the excited triplet. It is worthwhile to add that the same approach we have used for FeBr_2 and the term 5D has been found to be the ground term of the Fe^{2+} ion.¹⁸ The value of D was derived to be -33 K and also results from the trigonal distortion B_2^0 of -30 K. The splitting D in both compounds is of the same size in the

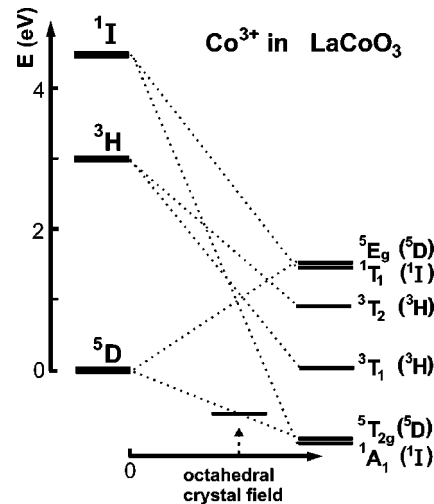


FIG. 7. Electronic structure of cubic subterms of the Co^{3+} ion in the octahedral crystal field inferred from Tanabe-Sugano diagrams for $Dq/B = 2.025$ relevant to LaCoO_3 . The arrow indicates the strength of the octahedral crystal field considered by us in the previous studies. The crystal field is stronger but not so strong as to destroy the atomic discrete structure of the d -electron states.

absolute value. However, in LaCoO_3 the 5D term is the excited term, as due to the activated character of the ESR spectra, we became sure that there is an extra singlet at $\Delta_{s-t} = 140$ K below—as is shown in Fig. 6. This singlet is a state 1A_1 . It originates from the 1I term, that in the free Co^{3+} (Co IV) ion lies 4.43 eV above the ground term.²⁰ The 13-fold degenerate term 1I splits under the action of the octahedral crystal field into six states and the singlet state 1A_1 is strongly pushed down due to its very large value of the orbital quantum number $L=6$. The situation with the 1A_1 subterm being slightly lower than ${}^5T_{2g}$ subterm occurs for $Dq/B=2.025$ on the Tanabe-Sugano diagrams presented on p. 388 of Ref. 17. Assuming the Racah parameter B of

1065 cm^{-1} one gets $Dq=2156 \text{ cm}^{-1}$ and consequently $B_4 = +260$ K. This value is only slightly larger, by 30%, than we used previously^{11–13} and in the calculations of ESR dependencies on Figs. 3–5. Thus the crystal-field interactions are strong in LaCoO_3 but not so strong to destroy the atomic discrete electronic structure of the $3d$ -electron states. The inferred electronic structure, in the 4-eV scale, of cubic subterms of the Co^{3+} ion in the octahedral crystal field, relevant to LaCoO_3 , is shown in Fig. 7. Surely, our long-lasting studies as well as growing number of more and more sophisticated experiments indicate that it is the highest time to “unquench” the orbital moment in the solid-state physics for description of the magnetism and the electronic structure of $3d$ -atom containing compounds.²¹

*Electronic address: sfradwan@cyf-kr.edu.pl, <http://www.css-physics.edu.pl>

¹P.M. Raccach and J.B. Goodenough, *Phys. Rev.* **155**, 932 (1967).

²V.G. Bhide, D.S. Rajoria, G. Rama Rao, and C.N.R. Rao, *Phys. Rev. B* **6**, 1021 (1972).

³S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, *Phys. Rev. B* **53**, R2926 (1996).

⁴M.A. Korotin, S.Yu. Ezhov, I.V. Solovyev, V.I. Anisimov, D.I. Khomskii, and G.A. Sawatzky, *Phys. Rev. B* **54**, 5309 (1996).

⁵I. Solovyev, N. Hamada, and K. Terakura, *Phys. Rev. B* **53**, 7158 (1996).

⁶M. Zhuang, W. Zhang, C. Hu, and N. Ming, *Phys. Rev. B* **57**, 10 705 (1998); **57**, 10 710 (1998).

⁷P. Ravindran, P.A. Korzhavyi, H. Fjellvag, and A. Kjekshus, *Phys. Rev. B* **60**, 16 423 (1999).

⁸D.D. Sarma, N. Shanti, and P. Mahadevan, *Phys. Rev. B* **54**, 1622 (1996); T. Saitoh, T. Mizokawa, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, *ibid.* **55**, 4257 (1997).

⁹H. Takahashi, F. Munakata, and M. Yamanaka, *Phys. Rev. B* **57**, 15 211 (1998).

¹⁰M.R. Ibarra, R. Mahendiran, C. Marquina, B. García-Landa, and J. Blasco, *Phys. Rev. B* **57**, R3217 (1998).

¹¹R.J. Radwanski and Z. Ropka, *Solid State Commun.* **112**, 621 (1999); cond-mat/9906437 (unpublished).

¹²R.J. Radwanski and Z. Ropka, *Physica B* **281&282**, 507 (2000).

¹³Z. Ropka and R.J. Radwanski, *Physica B* **312 & 313**, 777 (2002).

¹⁴Z. Ropka and R.J. Radwanski, cond-mat/0012228 (unpublished).

¹⁵S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, *Phys. Rev. B* **66**, 094404 (2002).

¹⁶P.G. Radaelli and S.-W. Cheong, *Phys. Rev. B* **66**, 094408 (2002).

¹⁷A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

¹⁸Z. Ropka, R. Michalski, and R.J. Radwanski, *Phys. Rev. B* **63**, 172404 (2001).

¹⁹The used home-made computer program BIREC for $3d$ is available on our web-site: <http://www.css-physics.edu.pl>

²⁰NIST Atomic Spectra Database, in <http://physics.nist.gov>.

²¹R.J. Radwanski, R. Michalski, and Z. Ropka, *Acta Phys. Pol. B* **31**, 3079 (2000).