

LaCoO₃ - from first principles

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LaCoO₃ from first principles, assuming the atomistic construction of matter and the electrostatic origin of the crystal-field splitting. In our atomic-like approach QUASST the d electrons of the Co³⁺ ion in LaCoO₃ form the highly-correlated atomic-like system $3d^6$ with the singlet ground state 1A_1 (an octahedral subterm from the 1I term) and the excited octahedral subterm $^5T_{2g}$ of the 5D term. In the spin-orbital space, being physically adequate, this high-spin state is Jahn-Teller active. We take the ESR experiment of Noguchi *et al.*, Phys. Rev. B **66**, 094404 (2002), as confirmation of the existence of the discrete electronic structure for $3d$ electron states in LaCoO₃ in the meV scale postulated in QUASST.

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LaCoO₃ exhibiting non-magnetic ground state and the significant violation of the Curie-Weiss law at low temperatures [1] often discussed in terms of successive changes of spin states (low- (LS), intermediate- (IS) and high-spin (HS) states) with the increasing temperature attracts much attention in recent 50 years. Despite of large activity, both theoretical and experimental, there is still enormous chaos in theoretical understanding of its properties. We would expect that the problem of LaCoO₃, of the origin of the excited

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state in particular, has been clarified in 2003 in our paper [2], making use of experimental results of Noguchi *et al.* [3], but recently has appeared a paper in Phys. Rev. Lett. of Phelan *et al.* [4] with a claim that i) the excited state in LaCoO₃ is the intermediate-spin S=1 state of a $t_{2g}^5 e_g^1$ configuration. Moreover, they have claim that ii) the HS state $t_{2g}^4 e_g^2$ (S=2), in contrary to the IS state, is not Jahn-Teller active and that iii) the t_{2g} - e_g splitting in LaCoO₃ is small. The appearance of the paper of Phelan *et al.* in Phys. Rev. Lett. is a direct motivation for this paper. The aim of this paper is to clarify above mentioned erroneous claims and to present a consistent understanding of LaCoO₃ within the localized atomistic paradigm. We understand atomistic ionic paradigm as the most natural and physically adequate approach to transition-atom compounds.

The IS state as the first excited state has been introduced to the LaCoO₃ problem in year of 1996 by band calculations of Korotin *et al.* [5] as an **opposite** view to the ionic view being a base for the Tanabe-Sugano diagrams known from years of 1954 and 1970 [6]. The Tanabe-Sugano diagram for the $3d^6$ configuration, Fig. 1, has yielded, accepting the relatively strong crystal field $Dq/B > 2$, the excited state to be the HS $t_{2g}^4 e_g^2$ state and this view was the base for a model of Goodenough [1]. The IS-state concept of Korotin *et al.* became highly popular with hundreds of citations [7–12]. In the band calculations of Korotin *et al.* the IS state becomes the first excited state as an effect of the especially strong $d-p$ hybridization. However, we claim that if at present, in year of 2006, one wants to still claim that the IS state is an excited state has to present a quantitative band-based or hybridization-based interpretation of the Noguchi *et al.* experiment.

In a situation of the dominant band view in LaCoO₃ problem, in general in 3d oxides [5, 7–12], and of continuous claiming of the IS state as the first excited state we feel necessary to present our understanding of properties of the magnetism and electronic structure of LaCoO₃ in the localized atomistic paradigm. This our understanding is based on well-known physical concepts like the crystal-field (CEF), spin-orbit (s-o) coupling, local distortions and other terms known from the ionic language. We present this view being aware that the ionic picture and crystal-field considerations are at present treated as the "old-fashioned" and contemptuous physics in times of wide spreading omnipotent band theories of different versions LDA, LSDA, LDA+U, LDA+GGA, DMFT and many, many others. We gave a name of QUASST for our approach to a solid containing transition-metal atoms from Quantum Atomistic Solid State Theory pointing out that the physically adequate description of properties of a 3d/4f/5f solid the best is to start from analysis of the electronic structure of constituting atoms.

Schematic steps of the QUASST approach to LaCoO₃ can be written as:

1. we accept the atomistic structure of matter, i.e. atoms preserve much of their atomic properties becoming the full part of a solid like, for instance, in NiO or LaCoO₃. In LaCoO₃ during the formation of compound there occurs an electron transfer of three electrons from La and Co to O with the simultaneous formation of the perovskite lattice with the ionic charge

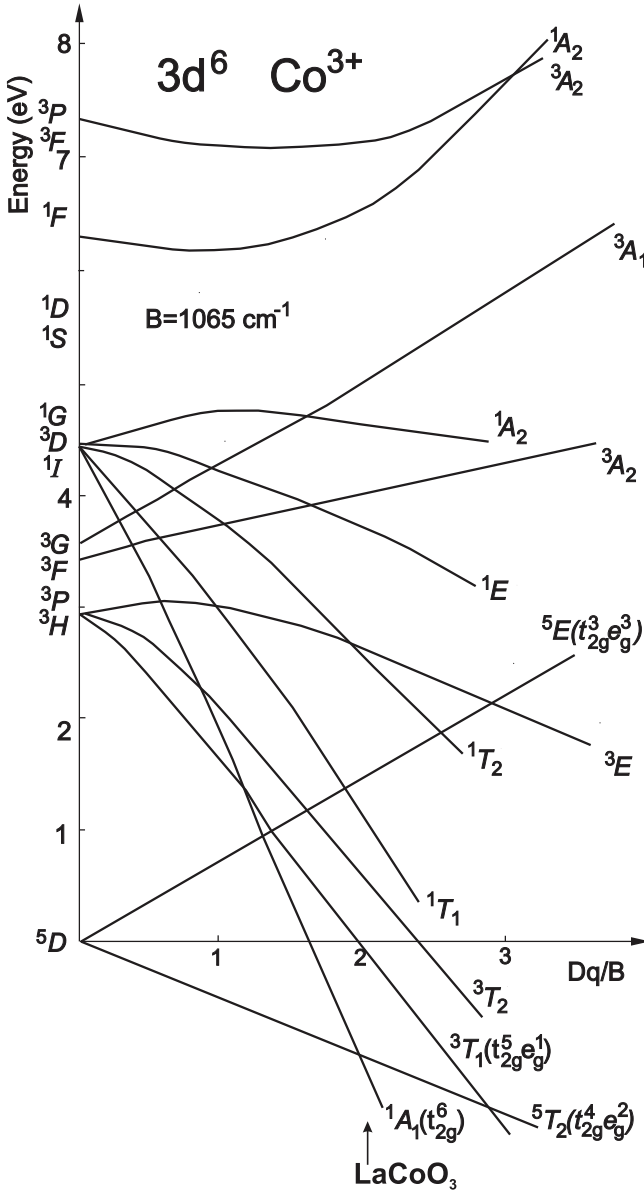


FIG. 1: A modified Tanabe-Sugano diagram for the Co^{3+} ion ($3d^6$ configuration) showing the effect of the octahedral crystal field on the electronic terms of the free Co^{3+} -ion. The electronic structure of cubic subterms, corresponding to $Dq/B = 2.025$, relevant to LaCoO_3 is marked by an arrow. 3

distribution $\text{La}^{3+}\text{Co}^{3+}\text{O}_3^{2-}$,

2. all magnetism of LaCoO_3 is related to the Co^{3+} ion with six electrons outside close configuration ^{18}Ar because both O^{2-} and La^{3+} ions have closed shells,

3. six electrons of the Co^{3+} ion form strongly-correlated atomic-like system, $3d^6$; its electronic structure is known from the atomic physics,

4. from the perovskite structure of LaCoO_3 we learn that:

a) all Co sites are equivalent,

b) the local symmetry of the Co ion is octahedral,

c) the Co ion is surrounded by six nearest neighbours oxygens forming almost perfect octahedron,

d) there appears small off-octahedral distortion with a lowering temperature.

5. influence of the octahedral crystal field on the free-ion electronic terms,

6. influence of the intra-atomic spin-orbit coupling on the local electronic structure,

7. influence of the rhombohedral distortion, octahedral crystal field on the local electronic structure,

8. magnetic interactions are not considered in LaCoO_3 because LaCoO_3 up to lowest temperatures does not form magnetically-ordered state,

9. having determined the local electronic structure with the eigenfunctions we have the zero-temperature properties as well as the free energy $F(T)$,

10. the zero-temperature properties are related to the properties of the local ground state; the free energy $F(T)$ enables calculations of the whole thermodynamics. See, for instance, our description of FeBr_2 , an exemplary of $3d$ compounds.

Ad. 1. An assumption about the atomistic construction of matter seems to be obvious but we would like to point out that band-structure calculations (LDA, LSDA, ..) disintegrate $3d$ atoms completely starting from consideration of $3d$ electrons as independent electrons in the octahedral crystal field. According to us these one-electron calculations has to reproduce, before calculations of properties of a solid, the electronic structure of the given ion. In our approach we simply accept the term electronic structure known from the atomic physics as is clearly written in p. 3 pointing out the importance of strong electron correlations among d electrons for the formation of the intraatomic term structure.

Ad. 3. From the atomic physics we know that for the $3d^6$ configuration of the Co^{3+} ion 210 states are grouped in 16 terms: 5D (25 states), 3H (33), 3G (27), 3F (21), 3F (21), 3D (15), 3P (9), 3P (9), 1I (13), 1G (9), 1G (9), 1F (7), 1D (5), 1D (5), 1S (1) and 1S (1). These terms are shown in Fig. 1 in the energy scale. The two Hund rules ground term of the free Fe^{2+} and Co^{3+} ions is 5D , a number of excited terms are at least 3 eV above. Experimental energies of the free-ion terms have been tabulated in NIST [14]. To these $L-S$ coupling terms an effect of the $j-j$ coupling can be added, if necessary.

Ad. 4. For more complex structures there will be a few $3d$ sites, each of them having own electronic structure.

Ad. 5. Influence of the octahedral crystal field on the free-ion electronic terms has been calculated by Tanabe and Sugano in a year of 1954 already [6]. The splitting of electronic terms to octahedral subterms in a function of the strength of the octahedral CEF parameter Dq/B (B - intra-ionic Racah parameter introduced for in order to account theoretically the arrangement of the free-ion terms determines the energy scale) is known as Tanabe-Sugano diagrams. A modified Tanabe-Sugano diagram for $3d^6$ is presented in Fig. 1. A problem was and still is with the evaluation of the value of Dq/B on this diagram for a given compound. Numerous qualitative indications, starting already at fifties of the XX century, have not been conclusive. In the crystal-field theory parameter $10Dq$ ($\cong 120 \cdot B_4$) in the simplest form is the multiplication of the octupolar charge moment of the lattice A_4 and of the involved cation caused by anisotropic charge distribution of the own incomplete shell. Thus Dq (B_4) can be calculated from first principles provided the octupolar charge moment, $\beta \langle r^4 \rangle$ of the involved ion is known. β is the fourth-order Stevens coefficient.

The octahedral crystal field coefficient A_4 that is the octupolar charge moment of all surrounding charges at the Co site can be calculated from the point-charge model which is first-principles elementary calculations. Taking the charge of oxygen as $-2e$ and the cation-oxygen distance of 192.5 pm [12, 13] in LaCoO_3 we obtain a value of A_4 of $+432 \text{ Ka}_B^{-4}$, a_B is the Bohr radius. Taking for the Co^{3+} ion $\beta = +2/63$ and $\langle r_d^4 \rangle = 2.342 \text{ a}_B^4$ [15] we get $B_4 = +32 \text{ K}$. This value is eight times smaller than the recent evaluation of B_4 of $+260 \text{ K}$ [2]. In Ref. 2 we pointed out that despite this difference the most important is that 1) these *ab initio* calculations give the proper sign of the B_4 parameter because it determines the ground state in the oxygen octahedron and 2) the experimentally derived strength of crystal-field interactions turns out to be much weaker than it was thought so far in literature for justification of the strong crystal-field approach in which one-electron approach becomes more physically adequate. Here we would like to explain this 8-times difference by attributing it to a large underestimation of $\langle r_d^4 \rangle = 2.342 \text{ a}_B^4$ in Hartree-Fock calculations from a year of 1965 [15]. Good agreement is obtained if $\langle r_d^4 \rangle$ would be about 18 a_B^4 . This later larger value is in agreement with recent calculations. Korotin *et al.* [5] have used a value for r_d of 1.26 \AA yielding approximately $\langle r_d^4 \rangle = 32.2 \text{ a}_B^4$. Recently Solov'yev [16], p. 5, has calculated for the Ti^{3+} ion $\langle r_d^2 \rangle$ of 2.27 \AA^2 ($= 8.11 \text{ a}_B^2$), which approximately yields $\langle r_d^4 \rangle$ even of 65 a_B^4 . Thus we think that a value of 18 a_B^4 needed for the ionic electrostatic-origin of the crystal-field splitting in LaCoO_3 is fully reasonable. Concluding, we think that too small values obtained so far for the CEF parameters were largely due to too small values taken for the octupolar moment of the transition-metal atom, in particular for $\langle r_d^4 \rangle$.

Ad. 6. In the simplest form the spin-orbit Hamiltonian takes the form $H_{s-o} = \lambda_{s-o} L \cdot S$ for the given term or with a parameter ξ for the whole configuration. Values for λ_{s-o} for different configurations of free $3d$ ions have been collected in text-books [17]. Of course, the s-o coupling in a compound can be different from the free-ion value.

Ad. 7. LaCoO_3 develops below 1610 K a slight rhombohedral (trigonal) distortion reaching an angle 60.79 degrees at 4 K [1, 5]. It means that the local oxygen octahedron is compressed along the diagonal. We have calculated that for such distortion the parameter B_2^0 is positive like it was found in Ref. [2]. The distortion is small and causes a slight splitting of the lowest quasi-triplet with $D = 4.9 \text{ cm}^{-1}$ as has been revealed experimentally by Noguchi *et al.* and described by us in Ref. [2] by a trigonal parameter B_2^0 of +7.2 K.

Ad. 8. The formation of the magnetic state we have described in numerous compounds - let mention exemplary 4f/3d/5f compounds ErNi_5 , FeBr_2 , NiO , CoO , UPd_2Al_3 and UGa_2 , results of which have been published starting from 1992. In all these cases the magnetic energy is much smaller than the overall CEF splitting. They are both ionic (FeBr_2 , NiO , CoO) and intermetallic (ErNi_5 , UPd_2Al_3 , UGa_2) compounds [18].

We appreciate very much Refs [4, 5] but in contrary to a claim of Ref. 4 that ii) the high-spin HS state $t_{2g}^4 e_g^2$ ($S=2$) is not Jahn-Teller active in contrary to the IS state we argue that the HS state ($S=2$) is Jahn-Teller active, see Fig. 2 of Ref. [19], Fig. 1 of Ref. [20] and Fig. 6 of Ref. [2]. We have claimed that the Jahn-Teller effect has to be considered in the spin-orbital space, but not in the orbital space only [21]. In contrary to a claim of Ref. 4 that iii) the $t_{2g}-e_g$ splitting in LaCoO_3 is small we argue that the crystal-field is relatively strong, the best described as intermediate. In contrary to a result of Ref. 5 revealing the spin polarization in the IS and HS state in the paramagnetic state we argue that in the reality there is no spin polarization. We do not agree with a claim that "the crystal-field energy is determined by the $3d - 2p$ hopping parameters, ..." - in our understanding the crystal-field splitting results from conventional electrostatic interactions of the multipolar character, it means it has the same origin as Stark effect known in the atomic physics. Finally we note substantial difference of our approach with that of Ref. [5] with respect to the actual d -shell occupation. Instead of the six-electron configuration in the ionic model considered by us Ref. [5] yields 7.3 d electrons in average. It means that Korotin *et al.* calculations provide much smaller electron transfer and realization of the smaller valency.

We would like to note that all of the used by us parameters (dominant octahedral CEF parameter B_4 , the spin-orbit coupling λ_{s-o} , lattice distortions) have clear physical meaning and can be calculated from first-principles. The most important assumption is the existence of very strong correlations among $3d$ electrons preserving the atomistic ionic integrity of the Co^{3+} ion also in the solid when this cation becomes the full part of a solid in LaCoO_3 . The electronic structure of the transition-metal atom predominantly determines the macroscopic properties of the whole compound containing transition-metal $3d/4f/5f$ atoms. With pleasure we notice the good reproduction of experimental magnetic susceptibility and heat capacity with our energy level structure [2] by recent paper of Kyomen *et al.* [22].

In **conclusions**, we have calculated from first-principles the low-energy electronic structure of LaCoO_3 which determines its macroscopic properties. The electronic structure originates from the Co^{3+} ions taking into account the

calculated octahedral CEF interactions, the intra-atomic spin-orbit coupling and a relatively weak trigonal distortion and assuming the atomistic integrity in LaCoO_3 of the Co^{3+} ion with the $3d^6$ configuration.

Our calculations explain the non-magnetic ground state as related to the ionic 1A_1 (1I) subterm, the first-excited state as related to the HS $^5T_{2g}$ (5D) and insulating ground state. Our calculations confirm the physical adequacy of the Tanabe-Sugano diagrams and we quantify the strength of the octahedral CEF parameter of the Co^{3+} ion in LaCoO_3 as $B_4 = +260$ K ($Dq/B=2.025$ on the Tanabe-Sugano diagram).

The crystal-field interactions are relatively strong in LaCoO_3 but not so strong to destroy the ionic integrity of the $3d$ -electrons as is postulated in QUASST. Our model can be classified as an ionic model but we have got a number of nontrivial results not obtained so far in the ionic model like the excited HS state magnetic moment of 0 and $\pm 3.35 \mu_B$ instead of $4 \mu_B$ expected for $S=2$ state. We are fully aware of many oversimplifications of our approach but we strongly believe that it is a physically adequate model to be further developed. 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.

Dedicated to all researchers of LaCoO_3 - in our understandings we have benefited from all conducting integral research, both theoretical and experimental.

This paper has been rejected by Editor of Phys. Rev. Lett. LQ10665, who claims that this paper is not suitable and not of wide interest to people (see following rejection letter). Both of these reasons are obviously nonsense. There are hundreds of papers devoted to LaCoO_3 every year what proves that people are working on LaCoO_3 and are interested in this subject. The rejection is a further evidence for the scientific discrimination in Phys. Rev. Lett.

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