The existence of the fine electronic structure in LaCoO$_3$

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We argue that in LaCoO$_3$ exists the fine electronic structure associated with the atomic-like states of the Co^{3+} ions and caused by the crystal-field, the orbital magnetism and intra-atomic spin-orbit interactions. This low-energy fine electronic structure has to be taken into account for any meaningful analysis of electronic and magnetic properties of LaCoO$_3$. In our atomic-like approach the d electrons form the strongly-correlated system $3d^n$, $3d^6$ in case of the Co^{3+} ion in LaCoO$_3$, and have the discrete energy spectrum in contrary to the band picture that yields the continuous energy spectrum. Our studies indicate that the orbital moment has to be unquenched in the description of all $3d$-ion compounds.

Properties of LaCoO$_3$, a non-magnetic ground state and an anomalous temperature dependence of the magnetic susceptibility (χ), are still intriguing despite of more than 30 years of intensive theoretical and experimental studies. See, Refs [1–8] and the current literature in Phys. Rev. B and Phys. Rev. Lett.. LaCoO$_3$ belong to the class of compounds

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as $LaMnO_3$ which are known as Mott insulators. $LaMnO_3$-based compounds exhibit the giant magnetoresistance [9, 10]. The uniqueness of $LaCoO_3$ is mostly related with its non-magnetic ground state at low temperatures and the violation of the Curie-Weiss law [3]. Despite of enormous long lasting theoretical efforts the description of such compounds is still under very strong debate. The fundamental controversy "how to treat the d electrons" starts already at the beginning - should they be treated as localized or itinerant. Directly related with this problem is the structure of the states: do they form the continuous energy spectrum like it is in the band picture [3, 4], schematically shown in Fig. 1, or the discrete energy spectrum typical for the localized states.

The aim of this short paper is to put attention that in $LaCoO_3$ the fine electronic structure exists. This fine electronic structure is caused by the action of the crystal-field (CEF) and spin-orbit (s-o) interactions on the Co^{3+} ions. We make use of our general theoretical approach to a solid, from atomic physics to solid-state physics [11], considering the atomic-like states of the Co^{3+} ions. The direct motivation for this paper was a recent publication in Phys. Rev. Lett., Ref. [4], discussing the electronic structure in the energy scale of, say 15 eV, see Fig. 1, whereas we are convinced that the electronic structure should be discussed in the meV scale, i.e four orders of magnitude more accurate.

In the insulating $LaCoO_3$ compound the $3d$ cation (M) is in the trivalent state as is anticipated from the compensated valences $La^{3+}Co^{3+}O_3^{2-}$. In the perovskite structure the $3d$ cation is situated in the octahedral surrounding of the oxygen ions - thus it is reasonable to consider the cluster MO_6. The Co^{3+} ion has 6 d-electrons in the incomplete outer shell. These electrons we treat as forming the highly-correlated electron system $3d^n$, i.e like in the atom [12]. In a zero-order approximation these electron correlations within the incomplete $3d$ shell are accounted for by the phenomenological two Hund's rules. They yield for the $3d^6$ electron configuration the ground term ^5D with S=2 and L=2 [13]. Under the action of the dominant cubic crystal field, the ^5D term splits into the orbital triplet $^5T_{2g}$ and the orbital doublet ^5E_g spread over 2-3 eV. In the octahedral oxygen surrounding the orbital triplet $^5T_{2g}$ is lower, Fig. 2.

The existence of this fine electronic structure is generally neglected, see e.g. Refs [4–6] despite that the above-mentioned knowledge about the formation of the ^5D term can be found in text books [13]. This neglect of the fine electronic structure is in fact related with the neglection in the literature of the s-o coupling and the orbital magnetism. We argue that the s-o coupling and the orbital magnetism have to be taken into account for any meaningful analysis of electronic and magnetic (e-
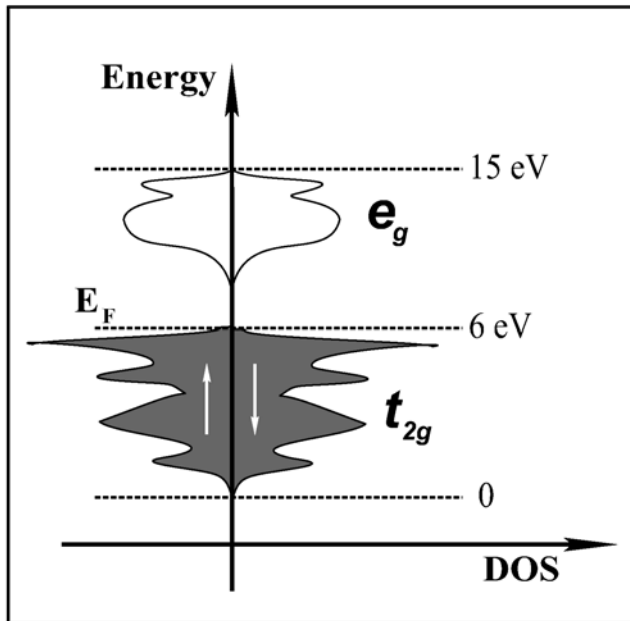
FIG. 1: Description of the d states in $LaCoO_3$ within the band approach - there is the continuum energy spectrum spread over 15 eV. After Ref. 4.

m) properties of compounds containing $3d$ ions like it is for rare-earth compounds [14–18]. This can be easily understood. The overall splitting of the $^5T_{2g}$ ground subterm by the s-o coupling amounts approximately to 5λ. With λ of 20 meV it means that there exists 15 discrete levels within the 100 meV range. It yields an average energy separation of 7 meV. The calculated by us the fine electronic structure of the Co^{3+} ion in the slightly distorted octahedral site, relevant to the situation realized in $LaCoO_3$, is shown in Fig. 2 taken after our Ref. [19]. There is the non-magnetic singlet (in the $|LSL_zS_z\rangle$ space) and two excited doublets that turn out to be highly magnetic. These excited states become thermally populated with the increasing temperature.

The existence of such discrete levels affects electronic and magnetic properties, as we know well from rare-earth compounds [14–18]. In particular, some anomalies of the heat capacity (c) and of the magnetic susceptibility occur at temperatures comparable with the first energy separations. In the present case it is below 120 K ($\approx$ 11 meV). The experimentally observed anomalies in $\chi(T)$[8] and $c(T)$[1] we are taking
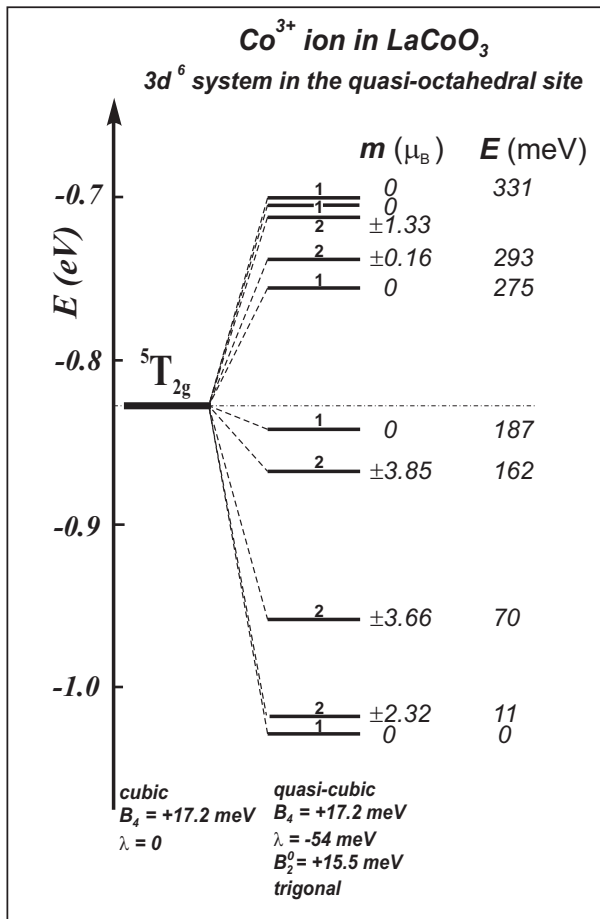
FIG. 2: The lowest part of the fine electronic structure of the Co^{3+} ion in $LaCoO_3$ originating from the cubic subterm $^5T_{2g}$. Other 10 states of the ^5D term originating from the ^5E_g cubic subterm are 2.0-3.0 eV above - they practically do not influence the magnetic and electronic properties of $LaCoO_3$. In such an electronic structure one can find the non-magnetic ground state as well as the intermediate and high-magnetic states. After Ref. [19]. [According to our recent paper, Phys. Rev. B 67 (2003) 172401, this structure lies 12 meV above the $^1A_1$ cubic subterm].

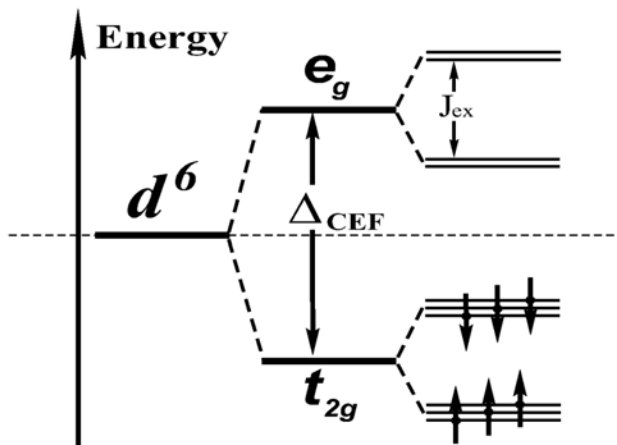as the confirmation of the presence of the fine-electronic structure in

FIG. 3: Energy spectrum of the Co^{3+} ion in $LaCoO_3$ in the low-spin state, after ref. 2, which we claim to be very oversimplified.

$LaCoO_3$. The calculations [20], resembling those presented in Refs [14–18], reveal the Schottky-type maximum in the c(T) curve at about 60 K and the rounded maximum in the $\chi(T)$ curve at 90 K.

In conclusion, we argue that in $LaCoO_3$ exists the fine electronic structure associated with the atomic-like states of the Co^{3+} ions and caused by the crystal-field (CEF) and intra-atomic spin-orbit (s-o) interactions. This fine electronic structure has to be taken into account for any meaningful analysis of electronic and magnetic properties of $LaCoO_3$. Our atomistic approach provides in the very natural way the non-magnetic low-temperature state (the $3d^6$ highly-correlated system is a non-Kramers system) and the insulating state in $LaCoO_3$. The present calculations correct the electronic-structure considerations presented in Refs [1–8]. In particular, it turns out that the low-energy electronic structure is much more complex than that the one recalled in Fig. 3 from Ref. [2] and points out the existence of the discrete states in contrary to the continuum energy-band structure derived in Ref. [6] (Figs 1 and 2), in Ref. [3] (Figs 1-3, 7) and in Ref. [5].

We would like to point out that our approach should not be considered as the treatment of an isolated ion - we consider the cation in the oxygen octahedron MO_6. The perovskite structure is built up from the corner sharing octahedra MO_6 - thus such the atomic structure occurs at each cation. There is growing number of experiments which confirm that

even in the macroscopic crystalline system such the atomic structure is largely preserved. These observations give the base for the developed by us the quantum atomic solid-state theory (QUASST). The present calculations prove the importance of the intra-atomic s-o coupling, the local scale off-cubic lattice distortions and the orbital magnetism for the description of low-temperature properties of compounds containing $3d$ ions. Our approach allows the calculations of the eigenfunctions and spin and orbital moments.

The note added during the referee process of BBR734 (15.05.2000).

1. The present approach, pointing out the existence of the discrete energy spectrum, fundamentally differs from the continuum energy-band structure considerations discussed recently in Refs [3, 4].

2. We would like to point out that our approach should not be considered as the treatment of an isolated ion only - we consider the Co^{3+} ion in the oxygen octahedron. The physical relevance of our treatment to $LaCoO_3$ is obvious - the perovskite structure is built up from the corner sharing Co^{3+} octahedra.

3. We do not agree with the referee that the splitting of only 11 meV can be easily exceeded by the exchange interaction between Co ions leading to the magnetically-ordered ground state of $LaCoO_3$.

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[20] the computer program can be obtained on the written request to the authors