The 3d-electron states in LaCoO$_3$

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Three fundamentally different electronic structures for 3d electron states in LaCoO$_3$, discussed in the current literature, have been presented. We are in favour of the localized electron atomic-like approach that yields the discrete energy spectrum associated with the atomic-like states of the Co$^{3+}$ ions in contrary to the continuous energy spectrum yielded by band theories. In our atomic-like approach the d electrons form the highly-correlated system 3d$^n$ described by S=2 and L=2.

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LaCoO$_3$ belong to the class of compounds known as Mott insulators. It appeals the scientific interest by more than 50 years. The uniqueness of LaCoO$_3$ is mostly related with its non-magnetic ground state at low temperatures and with the significant violation of the Curie-Weiss law at low temperatures [1,2]. Most of Co compounds are magnetic, even strongly. Despite of enormous long lasting theoretical efforts the description of LaCoO$_3$ 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 localised or itinerant. Directly related with this problem is the structure of the available states: do they form the continuous energy spectrum like it is in the band picture, schematically shown in Fig. 1, or the discrete energy spectrum typical for the localised states.

The aim of this paper is to show up the fundamentally different descriptions of LaCoO$_3$ appearing in the current literature by presenting 3 different electronic structures for the 3d
electrons. One is related with the band description and two with the localised description. There is a number of band-structure calculations [3-9] and the results are schematically shown in Fig. 1. The bands are not polarised with respect to the spin direction as LaCoO$_3$ does not order magnetically down to lowest temperatures. The same occupancy of the spin up and down states reproduces the experimentally-observed non-magnetic (diamagnetic) state at 0 K and is the realisation of the so-called low-spin (LS) state.

In the current literature, apart of the band picture, often appears a localized electronic structure like presented in Fig. 2 [10, 4]. At low temperatures the low-spin state (LS) is realized for 6 d electrons (spins) that is characterized by S=0. The electrons (spins) are put subsequently one by one on the single-electron states formed for 1 d electron in the octahedral crystal field: lower triplet $t_{2g}$ and higher doublet $e_g$. With increasing temperatures the LS state transforms to the high-spin (HS) state with S=2. Korotin et al. [4] pointed out the existence of the intermediate spin (IS) state with S=1 at the middle temperature region. The temperature-induced transformation of the LS state to the HS state has been originally inferred in Refs 1 and 2 from the temperature dependence of the paramagnetic susceptibility that exhibits an intriguing maximum at about 90 K.

The general shape of the bands presented in Fig. 1 can be understood knowing the localised states of Fig. 2. The continuous energy spectrum looks like the smooth convolution on the available localised single 3d electron orbitals $t_{2g}$ (occupied) and higher $e_g$ orbitals (empty). The similarity of the band density of states and the energy level scheme of Fig. 2 is related with the single-electron treatment of 3d electrons in both approaches.

Recently more complex electronic structure has been derived within the localized picture [11,12] that is presented in Fig. 3. The authors of Refs 11-12 have pointed out that the 6 d electrons form the highly-correlated atomic-like 3d$^6$ system. Two Hund’s rules yield the ground term $^5D$ with S=2 and L=2. This term is 25-fold degenerated. Its degeneracy is removed by the crystal field and spin-orbit interactions. Under the action of the dominant cubic crystal field, the $^5D$ term splits into the orbital triplet $^5T_{2g}$ and the orbital doublet $^5E_g$ with the energy separation about 2-3 eV. In the octahedral oxygen surrounding, realized in
the perovskite structure of LaCoO$_3$, the orbital triplet $^5T_{2g}$ is lower. The low-energy electronic structure has been calculated from the single-ion-like Hamiltonian considered within the 25-fold LS space containing simultaneously the crystal-field and spin-orbit coupling. The trigonal off-cubic distortion of the octahedral site, relevant to the situation realized in LaCoO$_3$, produces the non-magnetic singlet (in the $|LSL_zS_z\rangle$ space) ground state and two excited doublets that turn out to be highly magnetic, see Fig. 3. These excited states become thermally populated with the increasing temperature - as these states are strongly magnetic their thermal population manifests in the susceptibility experiment as a maximum that can be misleadingly interpreted as a temperature induced low-high spin transition.

It is worth noting that in our calculations we get the low- and high-spin state within the one term $^5D$ (for it, the intra-atomic spin-orbit coupling is essentially important [13]) in contrary to the two terms (LS, HS) or three terms (LS, HS, IS) considered within the single-electron approach of Fig. 2. Moreover, in the energy level scheme shown in Fig. 3 one can find the origin for the intermediate-spin state - the first and the second excited states of Fig. 3 one can try to describe by the effective spin of 1.16 and 1.83, respectively - these values are accidentally close to the ad hoc assumed values of $S=1$ and $S=2$. These states are in the discussed energy interval, up to 80 meV. The possibility of getting the non-magnetic ground state, discussed in the literature as the low-spin state, as well as the intermediate and highly-magnetic states within the same term we take as the great plus for our atomic-like approach. Surely the explanation involving one term only is physically simpler to be realized - according to the well-known Occam’s razor principle the simpler explanation is the better one.

We are in favour of the atomic-like approach. It enables the calculations of whole thermodynamics in remarkably good agreement with experimental results [11,12]. The diamagnetic state of LaCoO$_3$ is associated with the non-magnetic singlet ground state of the Co$^{3+}$ ion realized in the high-spin state ($S=2$) in the presence of the orbital magnetism and the intra-atomic spin-orbit coupling. This non-magnetic Co$^{3+}$ state differs significantly from the low-spin nonmagnetic state with the term $^1A_1$, the LS configuration in Fig. 2. Such low-spin
state is thought in the current literature to be realized by the strong crystal field (strong CEF approach). Our nonmagnetic state is found within the weak crystal-field regime, i.e. when the crystal field does not break the intra-atomic arrangement about the total S and L, thus preserving the atomic structure. This weak crystal-field approach, known within the rare-earth CEF community as the CEF approach, has been successfully applied to 3d-ion doped systems, when 3d ions are introduced as impurities [14-17]. Such systems have been successfully studied in electron paramagnetic resonance (EPR) experiments [14-17]. In Refs. 11 and 12 we have applied this approach to a 3d-ion system where Co ions are the part of the solid, LaCoO$_3$ in this case.

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 octahedral crystal field. This octahedral crystal field is predominantly associated with the oxygen octahedron CoO$_6$. The perovskite structure is built up from the corner sharing octahedra CoO$_6$ - thus such the atomic structure occurs at each cation due to the translational symmetry. The strength of the crystal field interactions is determined by the whole charge surroundings, not only by the nearest oxygen octahedron. It makes that the CEF approach looks like a single-ion approach but in fact describes coherent states of the whole crystal.

Within the single-electron approaches, both the band theory and the strong CEF approach, the realization of the LS and HS state results from an interplay of the CEF and exchange interactions ($\Delta_{CEF}$ and $J_{ex}$ in Fig. 2). The different strength of CEF and exchange interactions in different compounds is reasonable but the postulated their significant change with temperature in LaCoO$_3$ is, according to us, hardly scientifically acceptable.

In conclusion, we have presented 3 fundamentally different electronic structures for 3d electron states in LaCoO$_3$ discussed in the current literature. We are in favour of the localized electron atomic-like approach that yields the discrete energy spectrum associated with the atomic-like states of the Co$^{3+}$ ions. This approach bridges the atomic physics and the solid-state physics. It reveals very strong correlations of the local magnetic moment and the local symmetry (of the crystal field). Our 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$_3$. Good description of many electronic and magnetic properties indicates that the band-structure calculations have to be oriented into the very strong intra-atomic d-d correlation limit in order to get the ground state in agreement with two Hund’s rules and take into account the orbital magnetism.

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**Figure caption:**

Fig. 1. Schematic description of the d states in LaCoO$_3$ within the band approach - there is the continuous energy spectrum.

Fig. 2. Single-electron discrete energy spectrum of the Co$^{3+}$ ion in LaCoO$_3$ for the low-spin (LS, S=0), intermediate-spin (IS, S=1) and high-spin state (HS, S=2). According to the current literature these spin states are subsequently realized with the increasing temperature.

Fig. 3. a) The fine electronic structure of the Co$^{3+}$ ion in LaCoO$_3$ produced by the octahedral crystal field and the intra-atomic spin-orbit coupling. b) The lowest part of the fine electronic structure of the Co$^{3+}$ ion in LaCoO$_3$ originating from the cubic subterm $^5T_{2g}$ with further splittings by the trigonal distortion. The non-magnetic ground state as well as the intermediate and high-magnetic states should be noticed. According to the CEF approach these spin states are increasingly populated with the increasing temperature.
LaCoO$_3$

$\text{Co}^{3+}$

$cubic - octa$

$B_4 = +200 \text{ K}$

$\lambda_\text{o} = -210 \text{ K}$

$E_g$

$120 B_4$

$2 \text{ eV}$

$L = 2$

$S = 2$

$T_{2g}$

$1052 \text{ K}$

$120 B$

$4$

$2$
LaCoO$_3$

$^{5}T_{2g}$

\[ m (\mu_B) \quad E (K) \]

- $1$  \quad $0$  \quad $3836$
- $2$  \quad $\pm 1.33$  \quad $3401$
- $3$  \quad $\pm 0.16$  \quad $3186$

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$cubic$

$B_4 = +200 \, K$

$\lambda_0 = 0$

$\gamma = 3$

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$cubic$

$B_4 = +200 \, K$

$\lambda_0 = -210 \, K$

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$cubic$

$B_4 = +200 \, K$

$\lambda_0 = -210 \, K$

$\gamma = 3$

$B_2^0 = +180 \, K$

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$trigonal$

$a)$

$b)$

$c)$