

# Doping induced spin state transition in $\text{Li}_x\text{CoO}_2$ as studied by the GGA + DMFT calculations

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Lithium cobalt oxide  $\text{LiCoO}_2$  is a famous material in batteries production [1].  $\text{LiCoO}_2$  exhibits no long range magnetic order down to 5 K and Curie–Weiss behavior in high temperature region [2]. The local magnetic moments emerging in  $\text{Li}_x\text{CoO}_2$  with decrease of lithium concentration  $x$  (hole doping) reduces Li mobility. This can be related to the coupling between Li and magnetic Co, which leads to lowering of battery efficiency. Therefore the study of the origin of magnetism in hole doped  $\text{Li}_x\text{CoO}_2$  is quite important and can help in improvement of existing batteries characteristics and may suggest new ideas in searching of novel battery materials.

The parent compound,  $\text{LiCoO}_2$ , is a quasi-two-dimensional system with the Co ions forming a triangular lattice (in  $ab$ -plane). The Co–Co in-plane distance is two times smaller than the interplane one. The Co ions are in the  $\text{CoO}_6$  octahedra, which share their edges. The Li ions are in between of the  $\text{CoO}_2$  planes and donate additional  $x$  electrons to these  $\text{CoO}_2$  layers in  $\text{Li}_x\text{CoO}_2$  with  $x < 1$ . As a result in doped material Co valence reduces from  $4+$  ( $d^5$  configuration) to  $3+$  ( $d^6$  configuration) upon changing  $x$  from 0 in hypothetical  $\text{CoO}_2$  to 1 in stoichiometric  $\text{LiCoO}_2$ . Both configurations may exist in different spin states. High spin (HS,  $S = 2$  for  $d^6$  and  $S = 5/2$  for  $d^5$ ), intermediate spin (IS,  $S = 1$  for  $d^6$  and  $S = 3/2$  for  $d^5$ ) and low spin (LS,  $S = 0$  for  $d^6$  and  $S = 1/2$  for  $d^5$ ) states.

Due to octahedral surrounding Co  $3d$  band splits on  $t_{2g}$  and  $e_g$  sub-bands, while the trigonal distortions (due to layered structure) lead to further splitting of the  $t_{2g}$  band on the higher lying  $a_{1g}$  singlet and two  $e_g^\pi$  states having lower energy. In the ionic model competition between  $t_{2g} - e_g$  crystal-field splitting,  $\Delta_{CFS}$ , and intra-atomic Hund's rule exchange,  $J_H$ , defines, which spin state is stabilized in a system under consideration at given conditions [3]. The transitions between differ-

ent spin states (spin state transition) typically occur due to variation of temperature (as in  $\text{LaCoO}_3$  [4]) or pressure (external, like in  $\text{FeO}$  [5], or internal, like in  $\text{RCoO}_3$  [6]), while more exotic mechanisms such as isotope effect is possible [7]. Moreover, doping may also trigger the spin state transition. Indeed, in  $\text{Li}_x\text{CoO}_2$  the Co–O distance [2] shrinks with decrease of the Li content, i.e., with decrease of  $x$ : Co–O bond length is 1.922 Å for  $x = 1$ , 1.921 Å for  $x = 0.94$ , and 1.906 Å for  $x = 0.75$ , which leads to increase of the  $t_{2g} - e_g$  crystal field splitting and may result in the spin state transition.

Indeed, Hertz et al. analyzing experimental magnetic data of  $\text{Li}_x\text{CoO}_2$  proposed a spin state transition for  $\text{Co}^{4+}$  ions, while  $\text{Co}^{3+}$  was assumed to retain nonmagnetic LS state at any  $x$  [2]. The magnetic susceptibility shows Curie–Weiss behavior for any doping level, which is in accord with this scenario, but effective magnetic moment,  $p_{\text{eff}}$ , was found to be strongly nonlinear with  $x$ . Hertz et al. suggested change of the spin localization and onset of the two-phase region for  $0.8 \lesssim x \lesssim 0.95$  to explain this feature. In addition to this scenario there are other models based of analysis of different experimental data supposing that all Co ions are in the LS state across all doping values [8] or involving IS state [9]. Therefore, a thorough theoretical study is needed to describe evolution of  $\text{Li}_x\text{CoO}_2$  magnetic properties with doping.

Our calculations carried out within the DFT + DMFT method with using of AMULET code package [10] show that there is the high spin to low spin transition  $\text{Li}_x\text{CoO}_2$  with decrease of lithium concentration (see Fig. 1). One may see that with decrease of the doping level,  $x$ , and modification of the crystal structure the essential changes in contribution of different electronic configurations (see Fig. 1) occurs. The contribution of configurations, which have the largest possible magnetic moment becomes smaller. At the same time the contribution of the IS and LS states increase. This is in strong contrast to the case of  $\text{Co}^{3+}$

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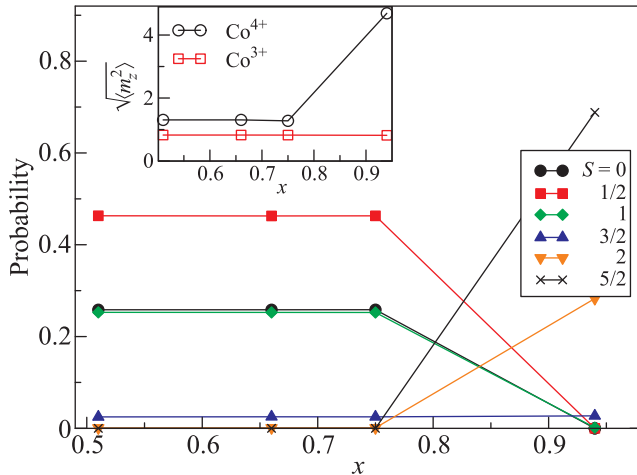


Fig. 1. (Color online) Probabilities of electronic configurations with different spins in the case, when all Co were supposed to have 4+ charge state (corresponding number of electrons is  $N_d + 2N_p = 5 + 12 = 17$  per unit cell), as calculated in GGA + DMFT for  $x = 0.94, 0.75, 0.66,$  and  $0.51$ . Inset shows local magnetic moments  $\sqrt{\langle m_z^2 \rangle}$ , if all Co ions are in 4+ or 3+ charge states

( $d^6$ ), where the LS state was found to be dominating for all Li concentrations (see inset in Fig. 1).

The nature of this transition is a delicate balance between crystal splitting and Hund's rule interaction, which is tilted with decrease of the doping level due to change of the crystal structure. The decrease of the Co–O distance results in increase of crystal field splitting that makes the LS configuration of both  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  more preferable. Thus, reduction of the Co–O bond length can stabilize the LS state in  $\text{Li}_x\text{CoO}_2$  and hence can help to avoid appearance of magnetic traps, which improves ionic conductivity. This idea can be used

in fabrication of  $\text{Li}_x\text{CoO}_2$  thin films batteries by appropriate choice of a substrate.

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