

Electronic structure and spin transitions in cobalt oxides

Karel Knížek

Laboratoř oxidových materiálů, Fyzikální ústav AVČR, v.v.i., Cukrovarnická 10, 162 00 Praha 6

knizek@fzu.cz, [lom.fzu.cz](mailto:knizek@fzu.cz), www.fzu.cz/oddeleni/24

Electronic structure of cobalt oxides, in particular with Co ion in valence states 3+ or 4+, is strongly influenced by the subtle balance between crystal field energy (Δ_{CF}), on-site Coulomb repulsion (expressed by Hubbard parameter U) and the energy of charge transfer between Co and oxygen (Δ_{Co-O}). Therefore Co^{3+} ion in oxides can exist in 3 spin states: low (LS, $S=0$, $t_{2g}^6 e_g^0$), intermediate (IS, $S=1$, $t_{2g}^5 e_g^1$) and high (HS, $S=2$, $t_{2g}^4 e_g^2$). The materials, studied in our laboratory, can be divided into two groups. 1) Perovskites with mixed valency of cobalt 3+/4+, which undergoes spin transitions depending on temperature, external pressure or doping. Based on our calculations and experiments on $La_{1-x}Sr_xCoO_3$ we have developed a two step LS-LS/HS-IS scenario consisting of a local excitation of HS in LS matrix, which is followed by reversal of the thermally populated HS/LS pairs into the IS states. A special case is a system derived from $Pr_{0.5}Ca_{0.5}CoO_3$, where the spin transition and simultaneous metal-insulator transition is conditioned by the charge transfer between Pr^{3+} and Co^{4+} . 2) Layered cobaltates with a promising thermoelectric properties. Electronic structures of Na_xCoO_2 and $CuCoO_2$ and their implications for thermoelectric properties will be presented. The calculations were made with the WIEN2k program. This program is based on the density-functional theory (DFT) and uses the full-potential linearized augmented plane-wave (FP LAPW) method with the dual basis set – atomic-like function in the atom spheres and the plane wave in the interstitial region between spheres. For the exchange correlation potential, the GGA (Generalized Gradient Approximation) form was adopted.