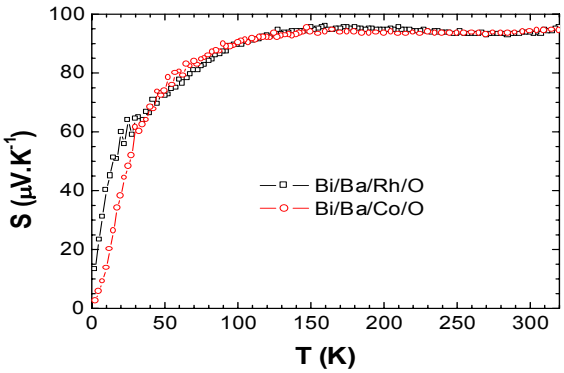
Misfit and perovskite cobaltites: crucial role of cobalt cation spin-states upon transport and magnetic properties

A. Maignan, S. Hébert, D. Pelloquin, V. Pralong, V. Caignaert, S. Malo, M. Hervieu and B. Raveau*
Laboratoire CRISMAT, UMR 6508 CNRS/ENSICAEN,
6 bd du Maréchal Juin, 14050 CAEN Cedex 4 - France.

The different spin-states of the cobalt cations provide an additional degree of freedom compared to the degrees of freedom in CMR manganites. The control of the Co crystal field allows to induce various physical properties. To illustrate that point, the recent achievements obtained for the misfit cobaltites used as p-type thermoelectric materials will be reviewed. Their CoO_2 layers isostructural to those of Na_xCoO_2 favors the Co^{3+}/Co^{4+} low-spin (LS) states which are essential to obtain large Seebeck (S) coefficient. The discovery of misfit rhodates with similar S values [1], containing Rh^{3+}/Rh^{4+} LS cations confirm that point (Figure).



T dependence of the Seebeck coefficient for two isostructural misfit oxides containing either Rh (squares) or Co (circles) in the CdI_2-type layer.

The oxygen deficient perovskite cobaltites deriving from $SrCoO_3$ will also be described. By substituting ions at either strontium ($Sr_{1-x}L_xCoO_{3-\delta}$) or cobalt ($SrCo_{1-y}M_yO_{3-\delta}$) sites, it is possible to make insulating antiferromagnets (AF) ($Sr_{2/3}Y_{1/3}CoO_{2.66}$, T_N = 320K [2]) or ferromagnets (F) ($Sr_{2/3}Y_{1/3}CoO_{2.70}$, T_C = 170K [2]; $Sr_{0.9}Th_{0.1}CoO_{2.79}$ T_C = 200K [3]). The F samples exhibit negative magnetoresistance (MR) near T_C. Furthermore, the presence of M = Sc^{3+} [4], Ti^{4+} [5], Mn^{3+4+} [6] at the cobalt site, creates a disordered (DIS) magnetic state. Upon external magnetic field application, the induced DIS to F transition creates a second type of MR. All these oxygen-deficient crystallize in complex structures related to the oxygen ordering phenomena [3]. The coexistence of alternating layers of CoO_4 tetrahedra (and/or CoO_5

tetragonal pyramids) with CoO_6 octahedra, is thought to stabilize an e_g orbital ordering responsible for the AF insulating state found for $\delta \approx 1/3$ [2, 7].

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* Corresponding author : Antoine Maignan, Laboratoire CRISMAT/ENSICAEN, 6 bd Maréchal Juin, 14050 CAEN Cedex 4 - France, E-mail : antoine.maignan@ensicaen.fr , Tel.: +33-231-45-2634, fax : +33-231-95-1600