Spin-state transitions in Cobaltates

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Cobaltates containing Co^{3+} ions are of particular interest among transition-metal oxides, because the spin state of the Co^{3+} ions may comparatively easy be changed as a function of external parameters.

The perhaps prominent example in this context is the pseudo-cubic perowskite LaCoO₃, where the spin-state of Co^{3+} is known to change from nonmagnetic below about 50 K to paramagnetic above about 100 K. Although this spin-state transition is studied since decades, there is still some debate about the underlying microscopic mechanisms. Apart from temperature, the spin state can also be changed either by structural distortions when La is replaced by smaller rare-earth ions and/or by charge-carrier doping via the partial substitution of La by divalent alkaline-earth ions Ca, Sr, or Ba. In this talk, I will review the influence of the charge-carrier content and structural distortions on the thermodynamic and the transport properties.

Moreover, the closely related system $La_{2-x}Sr_xCoO_4$ is discussed. $La_{2-x}Sr_xCoO_4$ crystallizes in the single-layered perowskite structure of the K₂NiF₄ type. This layered system has been studied much less than the pseudo-cubic perowskites and rather contradictory suggestions for the spin states of the Co²⁺ and Co³⁺ ions can be found. Based on an analysis of the magnetic susceptibility and its anisotropy we can identify Co²⁺ to be in the high-spin state and Co³⁺ to be in the nonmagnetic low-spin state below about 400 K. For higher temperature our data yield clear evidence for a temperature-induced spin-state transition of Co³⁺ to the paramagnetic high- or intermediate-spin state.