

Magnetic, magnetostructural and magnetoelectric properties of cobalt-based oxides

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Cobalt-based oxides are attracting the interest as strongly coupled spin-lattice-charge systems due to the relevance of the cobalt spin state for their functional properties. In addition, different inorganic structures containing cobalt are being investigated as multiferroic systems or responsive magnetoelectric compounds. The relationship between the crystallographic and functional properties of some cobalt-based oxides presenting simple and complex structures is discussed in the light of neutron and x-ray scattering studies, as a function of temperature and under application of external magnetic fields. Examples will be presented with cobalt cations having different coordination, oxidation and spin states.

The spin-state (SS) of trivalent cobalt is being examined in a variety of cobalt oxides due to its proven ability to condition their electric transport, magnetic and electronic properties. The properties of Pr_{0.50}Sr_{0.50}CoO₃ (PSCO) differ from those in Pr_{0.50}Ca_{0.50}CoO₃ (PCCO), where a spin-state change has been proved to induce a partial Pr³⁺ to Pr⁴⁺ valence shift and an exotic metal-insulator transition. We have investigated the evolution of the crystal and magnetic structures in PSCO across the unexpected magnetostructural transition at TS ~120 K. Coupled structural and magnetic symmetry changes (from Im'm'a to Fm'm'm) are reported.

The charge-ordered Co²⁺/Co³⁺ cobaltite Ba₂Co₉O₁₄ (BCO) presents a more complex structure with five independent Co sites. Three possible magnetic groups are compatible with the low temperature antiferromagnetic intensities. The magnetic symmetry, structural properties and spin-state transitions at certain cobalt sites in Ba₂Co₉O₁₄ were investigated by neutron diffraction and x-ray spectroscopies in relation to the abrupt conductivity changes around 567 K. Results provide a coherent description of all changes in the system that covers the range 5-800K.

Finally, the competition between magnetic anisotropies and frustrated magnetic orders is enhanced by the presence of Co²⁺ octahedra (with a strong magnetocrystalline anisotropy) in some magnetoelectric oxides (for example the Mn_{1-x}Co_xWO₄ multiferroics).

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