11th International Conference
on Advanced Materials

Rio de Janeiro Brazil
September 20 - 25

ICAM2009

Spin-state ordering phenomenon in *L*$BaCo_2O_{5.5}$ cobalt oxides

D. D. Khalyavin(1)*, D. N. Argyriou(1), U. Amann(1), A. A. Yaremchenko(3) and V. V. Kharton(3)

(1) ISIS, Rutherford Appleton Laboratory, Didcot, UK, e-mail: dmitry.khalyavin@stfc.ac.uk
(2) Hahn-Meitner-Institut, Berlin, Germany
(3) CICECO, University of Aveiro, Aveiro, Portugal
* Corresponding author.

Abstract – Magnetic phase transitions in *L*$BaCo_2O_{5.5}$ (*L*=Nd, Tb and Y) cobaltites have been studied by neutron powder diffraction in combination with group-theoretical analysis. As a result, the crystal and magnetic structures in different phases were determined and successfully refined. In all cases, the proposed models involve a spin-state ordering between diamagnetic ($t_{2g}^6e_g^0$, S=0) and paramagnetic ($t_{2g}^4e_g^2$, S=2) Co^{3+} ions with octahedral coordination. In the compositions with *L*=Tb and Y a coexistence of two spin-state ordered phases was revealed below the critical temperature T_L~200 K. The concept of the spin-state ordering and electronic phase separation is consistent with the anomalous electrical properties and gives a clear picture for the magnetic behavior of these compounds.

Temperature evolution of the magnetic ground state in *L*$BaCo_2O_{5+\delta}$ attracts a great attention in recent years, after discovering their complex behavior related to a succession of the magnetic phase transformations [1-3] These cobaltites possess also other important properties, particularly giant magnetoresistance and high ionic/electronic conductivity. Several models have been proposed based on macroscopic measurements and theoretical calculations to explain the complex magnetic states, but no consensus has been reached. The present work was focused on neutron diffraction studies of compositions with different *L* and oxygen content close to 5.5. On the basis of symmetry arguments in combination with Rietveld refinement, we argue that the *L*$BaCo_2O_{5.5}$ cobaltites demonstrate spin-state ordering phenomenon related to translationally symmetric distribution of six-fold coordinated Co^{3+} ions in low and high spin-states (Fig.1). The crystal structure, in the temperature range 200<T<295 K, has an orthorhombic *Pmma* symmetry with $2a_p \times 2a_p \times 2a_p$ unit cell. Two non-equivalent 2*e* octahedral positions are occupied by diamagnetic (low-spin) and paramagnetic (high-spin state) Co^{3+} ions, forming chess-board like spin-state ordered (*ac*) planes. The five-fold coordinated Co ions in two independent 2*f* positions adopt the fixed high-spin electronic configuration. A long-range magnetic ordering appears below T_C~290 K. The magnetic structure above T_i~260 K has the wave vector $\boldsymbol{k}$=0 (Fig.2) and involves isotropic negative exchange interactions between the paramagnetic Co ions in both octahedral and pyramidal coordination. The spontaneous magnetisation originates from the spin-state ordering in the octahedral sublattice. At T_i, a magnetic phase transition to antiferromagnetic structure with the wave vector $\boldsymbol{k}=\boldsymbol{c}^*/2$ occurs. In the lower temperature magnetic phase, the coupling between the (*ab*) planes divided by [BaO] and [$LO_{0.5}$] layers is negative and positive, respectively. The driving force for the magnetic phase transition is a thermal excitation of magnetic moment on the diamagnetic cobalt ions. In the lower-temperature spin configuration, these excitations result in inevitable magnetic frustrations which may be avoided by transition to the structure with $\boldsymbol{k}$=0. Below T_L~200 K, the *Pmma* phase coexists with another orthorhombic *Bmmm* ($2a_p \times 2a_p \times 4a_p$) phase, where the type of spin-state ordering between the diamagnetic and paramagnetic octahedrally-coordinated Co^{3+} ions is different (Fig.1). The phase ratio, close to 1:1 at T_L, was found essentially temperature-independent. The new type of electronic ordering leads to a change in the magnetic structure (Fig.2). The conjugated spin-ordered configuration has the wave vector $\boldsymbol{k}$=0 and is favorable with respect to the exchange energy.

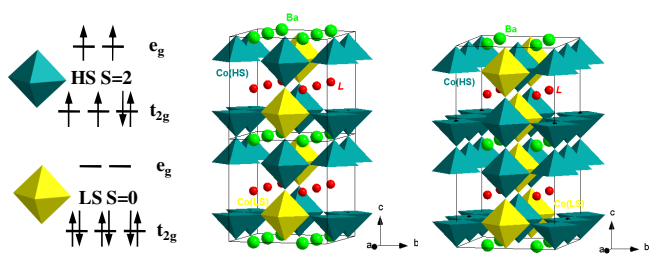

Figure 1: Electronic configuration of Co^{3+} ions in high and low spin-states (left), Crystal structures of *L*$BaCo_2O_{5.5}$ compositions with *Pmma* and *Bmmm* symmetries (middle and right, respectively).

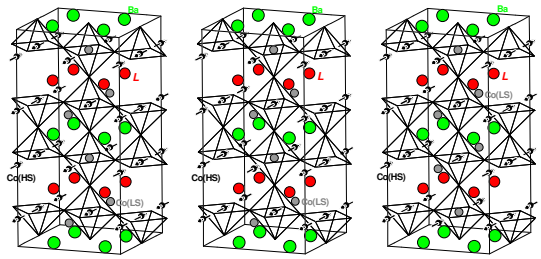

Figure 2: Magnetic structures of *L*$BaCo_2O_{5.5}$ compositions corresponding to different spin-state ordered phases: $\boldsymbol{k}$=0, phase with *Pmma* symmetry (left), $\boldsymbol{k}=\boldsymbol{c}^*/2$ phase with *Pmma* symmetry (middle) and $\boldsymbol{k}$=0, phase with *Bmmm* symmetry (right).

[1] A. A. Taskin, A.N. Lavrov, Y. Ando, Phys. Rev. Lett. 90 (2003) 2272011.
[2] D. D. Khalyavin, S. N. Barilo, S. V. Shiryaev, et al. Phys. Rev. B 67 (2003) 214421.
[3] A. Maignan, V. Caignaert, B. Raveau, D. Khomskii, G. Sawatzky, Phys. Rev. Lett. 93 (2004) 026401.