Experimental Report

20/11/2013

Proposal: **5-24-534** **Council:** 10/2012

Title: Neutron diffraction study of the pressure effect on crystal structurein La0.5Ba0.5CoO2.8

This proposal is a new proposal

Researh Area: Physics

Main proposer: **SIKOLENKO Vadim V.**

Experimental Team: SIKOLENKO Vadim V.
EFIMOV Vadim

Local Contact: RITTER Clemens
HANSEN Thomas

Samples: La0.5Ba0.5CoO2.8

Instrument	Req. Days	All. Days	From	To
D20	3	3	21/02/2013	25/02/2013

Abstract:

The main goal of this proposal is a detailed neutron powder diffraction study on La0.5Ba0.5CoO2.8 to refine relaible the crystal and magnetic structure at 100 K under the action of pressure up to 50 kbar. The obtaned result could provide key insights into most probable model explaining the nature of the anti- and ferromagnetic phase separation observed at the border of the spin state and concomitant ferro-antiferromagnetic transition.

The combination of this NPD study with XAFS/XMCD-spectroscopy results at the Co K-edge (ESRF,ID24 beamline) will give us an opportunity to analyze the crystal and magnetic structure changes of lattice parameters as well as local atomic and electronic(spin-state change & magnetic moment of cobalt ions) structure distortions near Co ions in order to establish the correlation between local and long-range order of crystal and magnetic structure changes as well as magnetic and transport properties in a wide temperature range.

These NPD experiments plan to perform on the high-intensity(!) two-axis D20 diffractometer with reasonably good resolution at the 1.54 Å using the Paris-Edinburg cell at P = 0, 20, 50 kbar upon increasing and decreasing pressure.

Experimental report
5-24-534

Neutron diffraction study of the pressure effects on crystal and magnetic structure of the $La_{0.5}Ba_{0.5}CoO_{2.8}$

The Co ions in octahedral symmetry may have either high (HS), intermediate (IS) or low spin state (LS) as the energies of the crystal-field splitting of both the Co 3*d* states (E_{cf}) and the Hund's rule exchange energy (E_{ex}) are comparable. Cobaltites are very sensitive to external pressure as the crystal-field splitting energy E_{cf} strongly depends on variations in the Co-O bond length and Co-O-Co angle. Applied pressure should lead to stabilization of the insulating nonmagnetic LS state because the gap between t_{2g} and e_g levels increases with decreasing Co-O bond length, causing depopulation of the magnetic e_g state. Pressure effect on ferromagnetic transition temperature T_C was found to be very different for various compositions. However, there is no data to pressure effects on antiferromagnetic state of cobaltites with simple perovskite structure. We have performed an experiment on anion-deficient $La_{0.5}Ba_{0.5}CoO_{2.8}$ using D20 diffractometer (λ = 1.3 Å) equipped with Paris Edinburg cell in the pressure region till 6.5 GPa and temperature from 50 to 300 K.

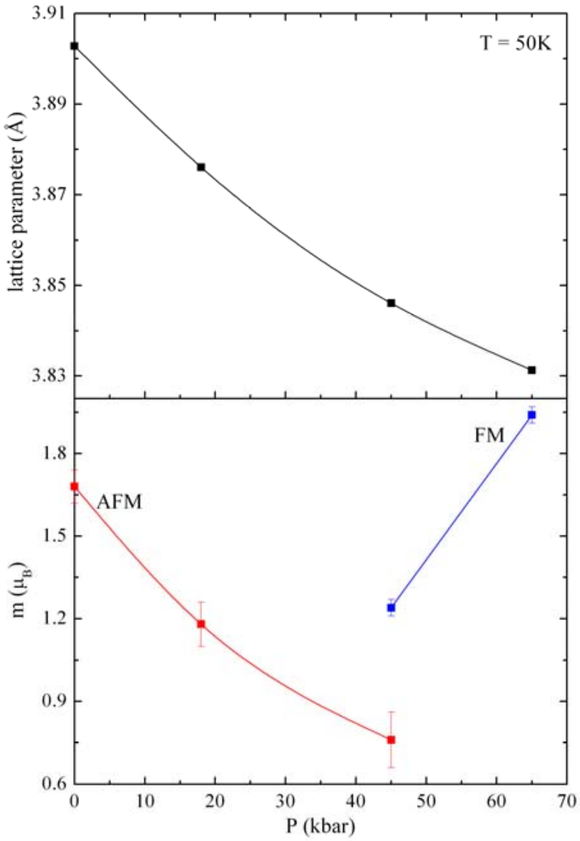

Fig.1 Lattice parameter vs. pressure (upper panel) and antiferromagnetic/ferromagnetic moment vs. pressure (lower panel) for the $La_{0.5}Ba_{0.5}CoO_{2.8}$ at T = 50 K

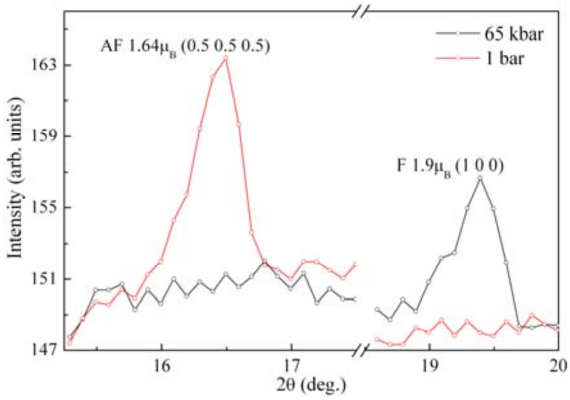

Fig.2. Intensity of antiferromagnetic and ferromagnetic peaks vs. pressure for the $La_{0.5}Ba_{0.5}CoO_{2.8}$ at 50 K

Rietveld refinement assumes cubic symmetry of the lattice (Pm-3m space group). We did not observe significiant changes of the nuclear structure upon cooling down to 2K. Magnetic ordering below 200K can be described as G-type AF. External pressure leads to a gradual drop in the intensity of the antiferromagnetic peaks which practically dissapear at 6.5 GPa and 50K. Starting from 4 GPa the intensities of the (100) and (110) peaks are strongly enhanced with the appearance a ferromagnetic component with a propagation vector k = 0. this indicates that the two magnetic components coexists at around 4GPa. However, we did not observed any microscopic structural separation as we have found in $La_{0.5}Ba_{0.5}CoO_{2.87}$ at ambient pressure.

The valence of the cobalt ions in $La_{0.5}Ba_{0.5}CoO_{2.8}$ is close to 3+, with formally small amount of Co^{4+} ions. By analogy with well good studied manganites one can expect a destruction of the magnetic ordering or a stabilization of the antiferromagnetic state at high pressure. However we have observed a clear transition from antiferromagnetic to ferromagnetic state at high pressure. We suggest that the pressure effect on the magnetic ground state in cobaltites can be considered in terms of cobalt spin state crossover. In the simplest scheme the magnetic ground state is determined by the spin state of cobalt ions which strongly depends on the unit cell volume, doping level and 3d(Co)-2p(O) hybridization. Pressure is expected to favor the populaion of the LS state since the ionic redius of LS-Co^{3+} is smaller than that of IS-Co^{3+}. Similarly the ionic radius of HS-Co^{3+} is larger than that of IS-Co^{3+}. The IS state in cobaltites is realized via large 3d(Co)-2p(O) hybridization which should be increase under pressure. This means that the high pressure should induce also a transition from HS to IS. The superexchange interaction between cobalt ions in the HS state is strong and negative according to the Goodenough-Kanamory rules. The observed magnetic moment value in ferromagnetic phase (1.9 μ_B/Co) is very close to the ferromagnetic moment for the nearly stoichiometric $La_{0.5}Ba_{0.5}CoO_3$, which indicates that cobalt ions are in the IS state. Finally, we can conclude that our results are in agreement with a model according to which the origin of the transition is associated with the cobalt ions spin state crossover from a mixed HS/IS into IS/LS state. Magnetic interaction between cobalt ions in HS are antiferromagnetic whereas they are ferromagnetic if the ions are in the IS state

Results oft he 5-24-534 experiment has been published in:

I.O.Troyanchuk, M.V.Bushinsky, V.Sikolenko, V.Efimov, C.Ritter, T.Hansen, D.M.Többens, *Pressure induced antiferromagnet-ferromagnet transition in $La_{0.5}Ba_{0.5}CoO_{2.8}$ cobaltite* Eur.Phys.J. B86 (2013), 435