ESRF	**Experiment title:** *Pressure-induced spin-state and phase transitions in the mono-$LaCoO_3$ and multi-valent metastable $La_{0.5}Ba_{0.5}CoO_{2.87}$ with one modified by pulsed huge-field*	**Experiment number:** **HC-5265**
Beamline: **ID-15B**	**Date of experiment:** from: **10.05.2023** to: **13.05.2023**	**Date of report:** 01.08.2023
Shifts: 9	**Local contact(s):** **Michael Hanfland**	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists)

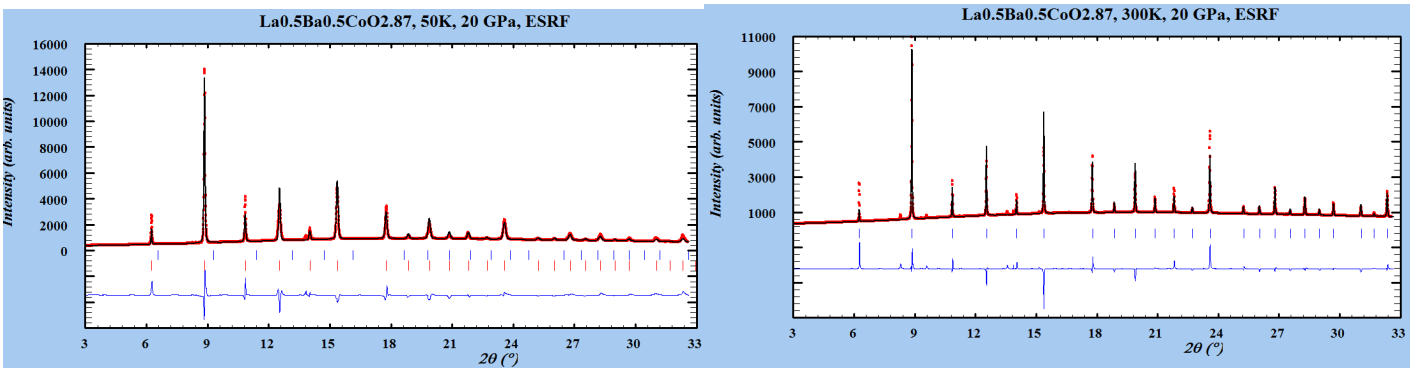
Dr. Stanislav Savvin* - ILL, Grenoble, France

Dr. Dmitry Khakyavin - Laboratory SFTC - Rutherford Appleton Laboratory ISIS Facili

Dr. Anrew Sazonov - Laboratory European Spallation Source (ESS)

Dr. Vadim Sikolenko - Karlsruhe Institute of Technology Institute for Applied Geoscience

The cobaltites with perovskite structure are systems with fascinating transport and magnetic properties [1-11]. The parent compound $LaCoO_3$ (LCO) is a paramagnetic (PM) insulator at low temperature (LT). As temperature increases a gradual spin transition (ST) from a low-spin (LS, $t_{2g}^6e_g^0$) to intermediate (IS, $t_{2g}^5e_g^1$) or high (HS, $t_{2g}^4e_g^2$) spin-state occurs, accompanied with insulator to metal transition at ~550 K [1-5]. Previous studies showed that chemical substitutions in LCO can induce a long-range antiferromagnetic (AFM) or ferromagnetic (FM) order [2-11]. For example, low doped $La_{1-x}Ba_xCoO_{3-d}$ ($LBCO_{3-d}$) becomes an AFM insulator [4,7,8,10,11]. One possible explanation for these phenomena is stabilization of the HS state [6, 11]. Surprisingly, the T_c of these compositions increases under applied pressure [7,8,10,11] while the origin of the magnetostructural phase transition is still unclear. In a medium doped oxygen deficit compound $La_{0.5}Ba_{0.5}CoO_{\mathbf{2.75}}$ all cobalt atoms are in AFM state whereas $La_{0.5}Ba_{0.5}CoO_{\mathbf{2.87}}$ has a mixture FM+AFM phases at low temperatures. It leads to a large magnetic anisotropy inducing a giant magnetoresistance as well as transformation of crystal structure including the separation into two different pseudocubic phases with sp.gr. *Pm-3m* at 50 K and one cubic phase at 300 K (**Fig.1b, c**).



a) **b)**

Fig. 1. The Rietveld refinement of the synchrotron X-ray diffraction data for $La_{0.5}Ba_{0.5}CoO_{2.87}$ measured at 20 GPa at 50 K (**a**) and 300 K (**b**), with experimental data in open circles, the calculated pattern in blue, and the difference curve in blue. The tick marks indicate Bragg peak positions for two *Pm*-3*m* (blue + red) phases at 50 K and one *Pm*-3*m* (blue) phase at 300 K.

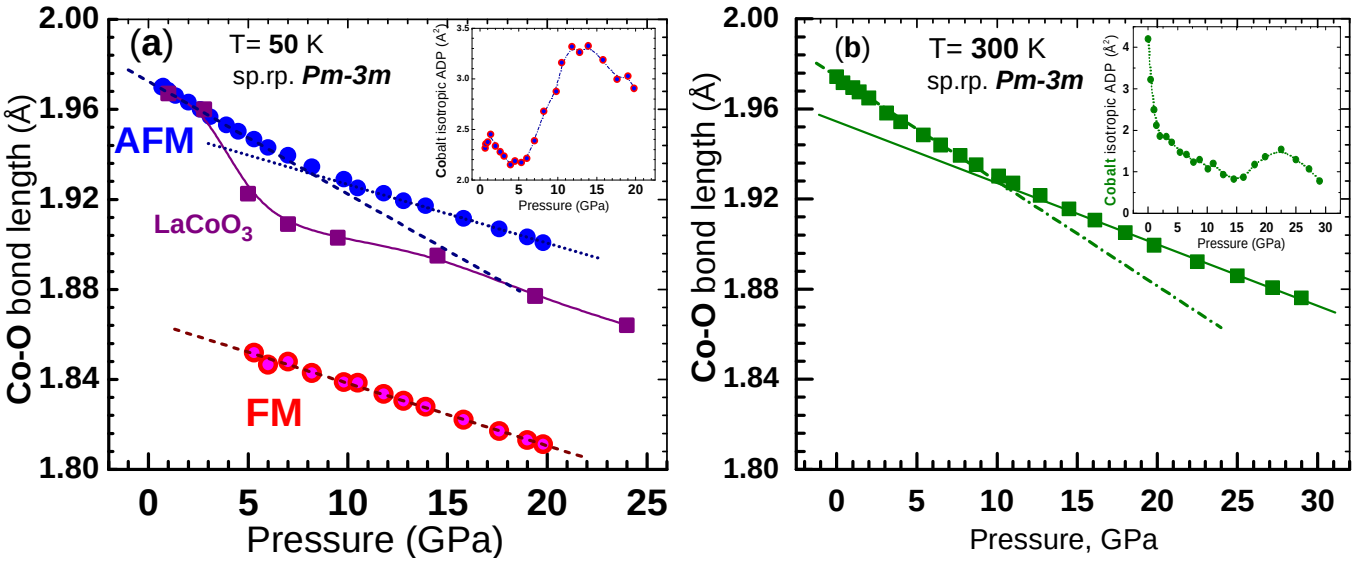


Fig. 2. The pressure dependence of the two (**a**) and one (**b**) Co-O bond length for $LaCoO_3$ with $La_{0.5}Ba_{0.5}CoO_{2.87}$ at 50 K and 300 K, respectively; both insets show an cobalt isotropic ADP.

When pressure is applied, the Co-O bond length of the $LaCoO_3$ & $La_{0.5}Ba_{0.5}CoO_{2.87}$ is gradually decreasing at 50 K and 300 K (**Fig.**2a,b). However, above pressure 5 GPa at 50 K for $LaCoO_3$ & $La_{0.5}Ba_{0.5}CoO_{2.87}$ the Rietveld refinement confirmed a sharply falling of the Co-O bond length and the transformation of one cubic phase into the two ones, respectively (**Fig.**2a). Moreover, the isotropic ADP of Co for $La_{0.5}Ba_{0.5}CoO_{2.87}$ shows a sharply and weakly growth above 7 GPa at 50 K and above 15 GPa at 300 K, respectively (**Fig.2**a,b, insets). It interesting to note that these pressure points in both cases corresponds to the bending between higher and lower slopes of Co-O bond length. Similar bending behavior is possibly an indication of the HS→IS spin-state transition of Co^{3+} ions with IS→LS one of Co^{4+} at 50 K and IS→LS one of both Co^{3+} and Co^{4+} ions at room temperature. The drop of the cobalt isotropic ADP at lower pressures is associated to the lattice compression with further beginning of the HS→IS spin-state transition of Co^{3+} ions and IS→LS one of Co^{4+}. We suppose that such spin-sate transitions are best described by a mixture of HS, LS and IS multivalent cobalt ions. It is well documented by R.D.Shanon that the Co^{3+} ionic radius of the HS state (0.61 Å) is significantly larger than that of the LS (0.54 Å) and IS (0.56 Å) states and especially with Co^{4+} ones of the IS (0.54 Å) and LS (0.53 Å).

References

1. J.B. Goodenough and J.S. Zhou, Structure and Bonding (Springer, New York, 2001), pp. 17–113.
2. J. Wu and C. Leighton, *Phys. Rev. B* **67**, 174408 (2003).
3. I.O. Troyanchuk, I. Fita, R. Szymczak, R. Puzniak,et.al, Phys. Rev. B **71**, 214404 (2005).
4. D. Novoselov, V. Křápek, P. Novák,, Dm. M. Korotin, and V. I. Anisimov, **Phys. Rev. B 86, 195104 (2012)**.
5. M. Karolak, M. Izquierdo, S. Molodtsov and A. Lichtenstein, Phys. Rev. Lett. 115, 046401 (2015).
6. M. Feygenson, V. Sikolenko, A. Sazonov, D. Novoselov, et al., **Phys. Rev. B 100**, **054306 (2019)**.
7. V. Sikolenko et.al *Pressure induced AF-FM transition on* $La_{0.5}Ba_{0.5}CoO_{2.8}$, Eur. Phys. J. B**86** 435 (2013).
8. V.Sikolenko,et.al *Pressure effects on oxygen-deficient Ba-substituted cobaltites*.Powder diffr.**28** S126 (2013).
9. V. Sikolenko, et.al *High pressure induced spin state crossover in* $Sr_2CaYCo_4O_{10.5}$, J.Phys.Cond.Mat.**27** 046005 (2015).
10. V. Sikolenko, et.al.,*High pressure effects on magnetic and crystal structure of* $La_{0.75}Ba_{0.25}CoO_3$ .Mat. Chem. Phys. **181** 78 (2016).
11. M. Feygenson, S. Savvin, M. Hanfland, F.Porcher, V. Sikolenko, et al, *Pressure-induced structural and magnetic phase transitions in* $La_{0.75}Ba_{0.25}CoO_{2.9}$ *studied with scattering methods and first-principle calculations* **Phys. Rev. B 104, 144107 (2021).**
12. Dong Li, Hongguang Wang, at.al., **Nature Communications** 14, 3638 (2023).