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Experimental report (experiment number 01-02-737 in SNBL at ESRF)

Crystal structure study of $TbBaCo_2O_{5.5}$ across the metal insulator transition

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*We have successfully performed synchrotron diffraction study of a single crystal of $TbBaCo_2O_{5.5}$ across the metal insulator transition at **MAR 345** diffractometer in SNBL at ESRF. It was found, that below the metal-insulator transition there are weak superstructure reflections corresponcerning to a possible long-range ordering along a-direction in the crystal structure of $TbBaCo_2O_{5.5}$.*

A key aspect of cobalt oxides, which comes on top of the conventional charge, spin and orbital degrees of freedom, is the possible variety of the spin-states of the Co ions. Therefore cobalt layered perovskites represent a unique system that allows study the major open problems in this field, i.e. whether and to what extend the spin state degree of freedom affects the metal-insulator, charge- and spin-state transitions. In spite of enormous efforts invested by many groups, not only the magnetic and electronic states, but even details of the crystal structure of layered cobaltites are still controversial.

In the $R BaCo_2O_{5.5}$ structure cobalt cations exist in two coordination environments – pyramidal CoO_5 and octahedral CoO_6 in both having oxidation state 3+. Cobalt electron configuration $3d^6$ leads to a Jahn-Teller distortion of the oxygen octahedra and an orthorhombic distortion of the structure (*Pmmm* space group, cell a_c x $2a_c$ x $2a_c$, a_c being cell dimension of corresponding cubic prototype). These compounds display a metal-insulator transition (MIT) accompanied by structural changes. The driving force of this transition is closely related to the Co spin state and the corresponding electronic structure. Recently we have preformed high resolution neutron powder diffraction study of $HoBaCo_2O_{5.5}$ (both ^{16}O and ^{18}O substituted powder samples) [1] in the temperature range 250-390K. We found, that the metal-insulator transition occurs concomitantly with the melting of the orbital order in pyramids and increase of Co-O-Co bond angles together with a unit cell volume collapse. The positive isotope exponent on T_{MI} supported the idea that observed structure changes are caused by electron delocalisation above the transition. The transition does not affect the symmetry of the crystal structure and in the whole investigated temperature range crystal symmetry is described by *Pmmm* space group from neutron powder diffraction data.

Recently we have succeeded to grow high quality single crystals of layered cobaltite $TbBaCo_2O_{5.5}$. This achievement opens new possibilities to study a rich variety of cooperative phenomena including the MIT and the orbital-spin ordering anticipated in the layered cobalt perovskites. In this report we present the preliminary results of synchrotron diffraction study performed of single crystal of $TbBaCo_2O_{5.5}$ across the MIT in the temperature range 300 – 350 K. Below the MI transition we have observed a formation of superstructure reflections that correspond to $2a_c$ x $2a_c$ x $2a_c$ translations. Analysis of systematic absences for twinned crystal brings out another space group of this compound at room temperature (*Pmma* instead of generally accepted *Pmmm*) (Fig. 1). The superstructure reflections vanish after MI-transition implying that MI transition is accompanied by a structural transition (Fig. 2). Rare earth sub-lattices can differently influence to the whole crystal lattice and can change the balance between Hund's intra-atomic exchange and the energy splitting of the cobalt *3d* terms caused by crystal fields. The further single crystal studies with other layered cobaltites with Nd and mixed Tb,Dy are therefore very desirable.

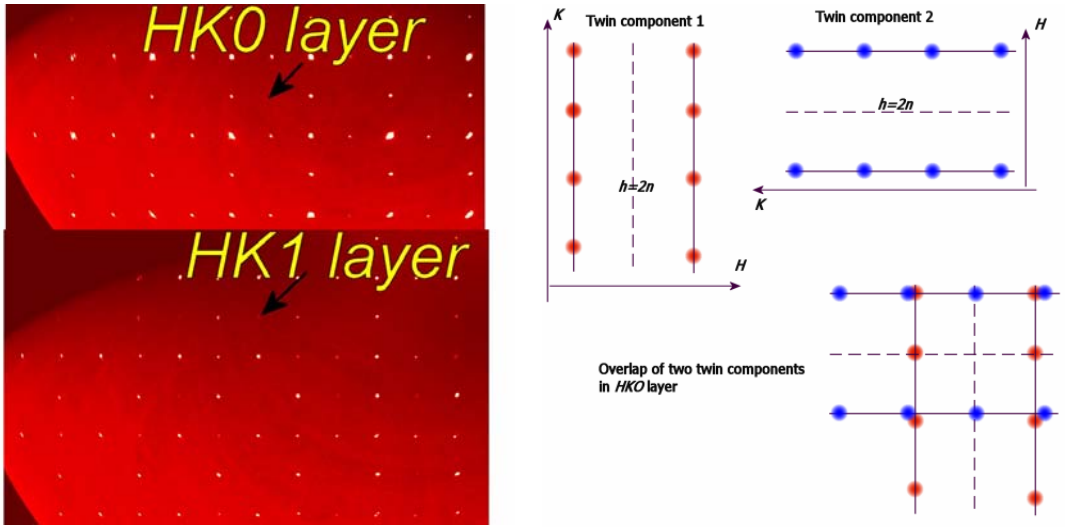
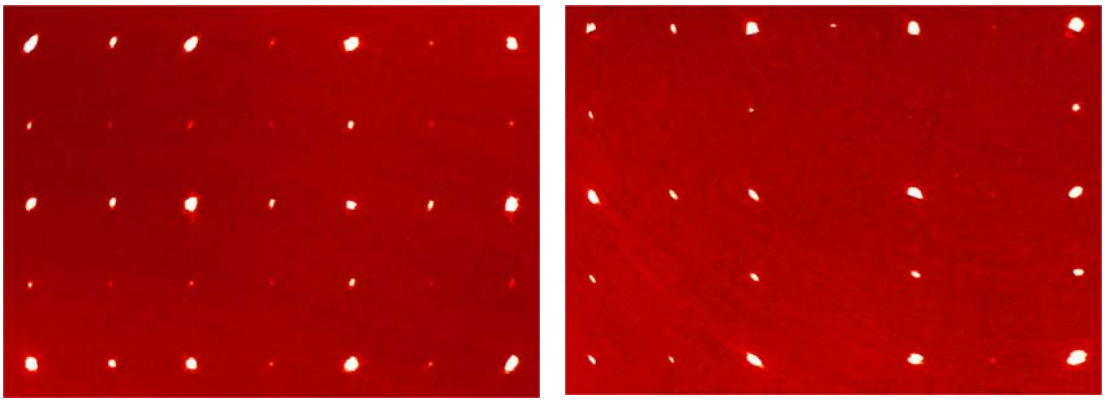


Fig.1 Left: superstructure reflections in the HK0 and HK1 reciprocal layers. Arrow in the HK0 layer indicates non-crystallographic systematic absences. Right: The overlap of two *Pmma* twin domains leading to similar diffraction pattern.



a) b)

Figure 2. Slices of reciprocal space in (hk2)-layer at 300K (a) and at 330K (b).

[1]. E. Pomjakushina, K. Conder, V. Pomjakushin, Prys. Rev. B **73**, 113105 (2006)