ESRF	**Experiment title:** **Nature of metal-insulator transition in $TbBaCo_2O_{5.5}$ cobaltite**	**Experiment number:** **HE-1288**
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Shifts: 18	**Local contact(s):** Dr. A. Bombardi	*Received at ESRF:*

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Report:

$TbBaCo_2O_{5.5}$ belongs to the family of oxygen-deficient Ba – doped cobaltites with perovskite structure $RBaCo_2O_{6-\delta}$ (R= rare earth ions, δ~0.5). Their crystal symmetry belongs to the orthorhombic ***Pmmm*** space group [1,2]. In these perovskites R and Ba cations build alternate planes perpendicular to the ***c*** – direction, and oxygen vacancies are located in R – planes and ordered, forming channels in ***a*** – direction [1,2]. One half of the Co are located in oxygen octahedra, the other one – in square pyramids. Bulk samples of $TbBaCo_2O_{5.5}$ show on heating at T_{MI}=350 K metal-insulator (M-I) first order phase transition [1-3]. Orbital ordering (OO) was proposed as one of the possible mechanisms for this transition. The d_{x^2}/d_{y^2} type of OO was suggested on the basis of the analysis of the Co-O interacomic distances in ***a***, ***b***, and ***c*** – directions below T_{MI} [2]. On the other hand, band structure calculations predict d_{xy}/d_{xz} type orbital order [4].

We have studied OO in $TbBaCo_2O_{5.5}$ using resonant X-ray scattering measurements at the Co K-edge (7.709 keV for pure CO). This method has recently been successfully applied to study charge and orbital order in different compounds (See [5, 6] and references therein). The experiment was carried out at the ID20 beam line. Polarization analysis was made using a graphite (006) analyzer crystal. Since single crystal samples are very difficult to grow, with only one report in literature [7], we have used for our experiment epitaxial ***c*** - axis oriented films with a thickness of ~ 750 Å, grown by a pulsed laser ablation method [8].

The ***Pmmm*** space group does not have any forbidden peaks, which could be allowed due to alternative ordering of the 3d orbitals in the same crystallographic site. However, the intensities of superstructure Bragg peaks (***h k l***), where ***k*** and/or ***l*** are odd, are weak and it is reasonable to expect a high ratio between resonant and non-resonant intensity. Using computer simulations we found, that the strongest azimuthal dependences are expected for peaks (***h k l***) with ***k*** – odd, ***l*** – even.

Energy scans of scattered intensity of the superstructural peaks show a sharp resonance at E=7.722 keV in the $\sigma\rightarrow\pi$' channel independent on azimuth. Both, resonant scattering and strong absorption have been seen in the $\sigma\rightarrow\sigma$'channel. [9]. Several examples of these scans for the (016) and (116) peaks for different

azimuthal angles and polarizations are presented in Fig. 1 a, b. The energy E=7.722 keV corresponds to the maximum of fluorescence (Fig. 1 c).

Azimuthal dependences of the integrated intensity of the (016) and (116) peaks, both in σ→σ' and σ→π' channels are presented in Fig. 2 a, b. Correction of the experimental data by absorption and Lorentz factors are included. As one can see, the measured signal shows strong azimuthal oscillations.

Temperature dependences of the integrated intensity for the peak (016) in σ→π' channel as well as the fundamental reflection (004) have been measured on warming up to M-I phase transition temperature. It has been found, that with increasing temperature (i) the (016) peak decreases more strongly than the (004) reflection; (ii) azimuthal oscillations of the (016) peak decrease appreciably (Fig.3). This indicates that the anisotropy of the average form factor of Co is strongly affected by this transition.

The components of the tensors of anomalous form factor for the Co – ions in both sublattices have been obtained from the fit of the azimuthal dependences of the integrated intensity, using the formalism described in the *Ref. 5*. On basis of the obtained results it was argued, that only the theoretically predicted d_{xy}/d_{xz} model of OO [4] can describe the experimental results under certain limitations for the anomalous scattering tensor components [9].

The weakening of the azimuthal oscillations of scattered intensity with increasing temperature (Fig. 3) indicates a decrease of the orbital order parameter [10]. Therefore we suggest an orbital order-disorder or order-order transition as a possible mechanism of the M-I phase transformation.

Unfortunately, due to some technical problems we were not able to measure in detail the azimuthal dependence of the scattered intensity above T_{MI} and therefore the asymmetry of the anomalous scattering factor of Co in the metallic state.

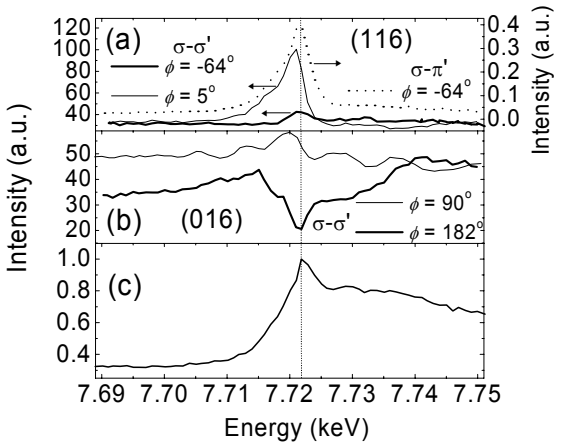

Fig1. (a), (b) – typical energy scans of the (016) and (116) Bragg peaks for different azimuthal angles and polarizations; (c) – X-ray fluorescence close to the Co K-edge. Dotted line indicates the position of the maximum of the fluorescence.

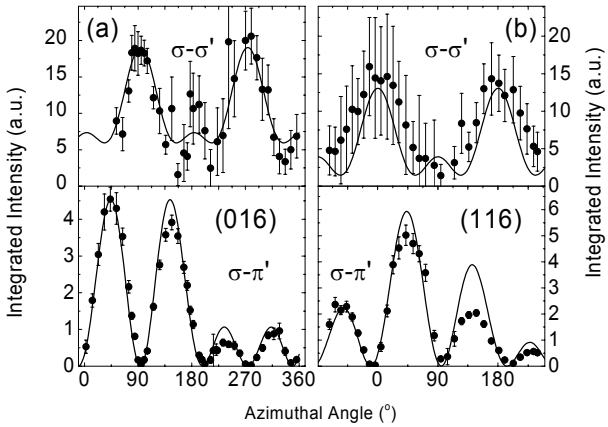

Fig2. Azimuthal oscillations of scattered intensity for (016) and (116) peaks. Solid lines present the fit results using the d_{xy}/d_{zx} model of the orbital ordering.

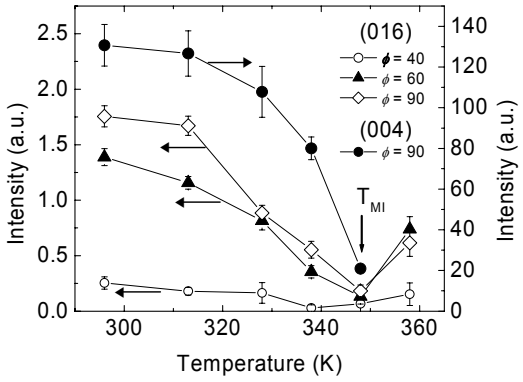

Fig.3. Temperature dependence of the intensity of (004) fundamental Bragg peak and (016) reflection in σ→π' channel at different azimuthal angles. The units for the left and right axes are different.

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