ESRF	**Experiment title:** Study of the $Bi_{0.5}Sr_{0.5}MnO_3$ and $Bi_{0.5}Ca_{0.5}MnO_3$ charge ordered phases by x-ray resonant scattering at the Mn K-edge?	**Experiment number**: HS 2555
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Report:

A resonant x-ray scattering study at the Mn K-edge of $Bi_{0.5}Sr_{0.5}MnO_3$ perovskite was performed to determine its charge-ordering (CO) pattern. Bismuth-based Bi-Sr-MnO_3 manganites show CO at room temperature, being the CO transition at abnormally high temperatures (T_{CO}~500 K for x=0.5). The ordered phase of $Bi_{0.5}Sr_{0.5}MnO_3$ has been proposed to consist of either double stripes of MnO_6 octahedra [1] or Zener pairs [2] in contrast to the conventional checkerboard model found in most of the half-doped lanthanide manganites.

(0 k 0) with k=3,5, denoted as charge-order reflections, and (0 k/2 0) with k=5,7, denoted as orbital-order reflections, in the *Ibmm* setting, were observed in a single-crystal cut with [001] surface normal at room temperature. Twin mosaic was inevitable in the crystal so both, (0 1 0) and (1 0 0) domains, were detected at the same scattering angle. The characteristic dependence of the intensity of these superlattice reflections on the azimuthal angle and on the polarization of the incident beam (by means of a Cu (220) analyzer) were investigated in detail.

Figure 1 shows the intensity of (030) charge-order and (0 5/2 0) orbital-order reflections as a function of the photon energy at different azimuthal angles for the σ-polarized and the π-polarized scattering beam, respectively. A strong resonance is observed at 6551.7 eV, within 1 eV respect to the Mn K-absorption edge, for the (0 5/2 0) reflection. No Thomson scattering intensity is detected at energies below the absorption edge for this reflection. Scattering intensity is only observed in the σ–π' polarization chanel and shows a strong azimuthal dependence disappering completely at ϕ=0. The energy dependence of the (030) reflection, instead show non-resonant Thomson scattering and a resonant contribution at the absoption edge. The resonant peaks are located at 6553 eV and 6554.3 eV for ϕ=90 and ϕ=0, respectively. The polarization analysis indicates that this reflection is mainly of σ–σ' character. A π periodicity of the resonant intensity on the azimuthal angle ϕ has been found for both types of reflections.

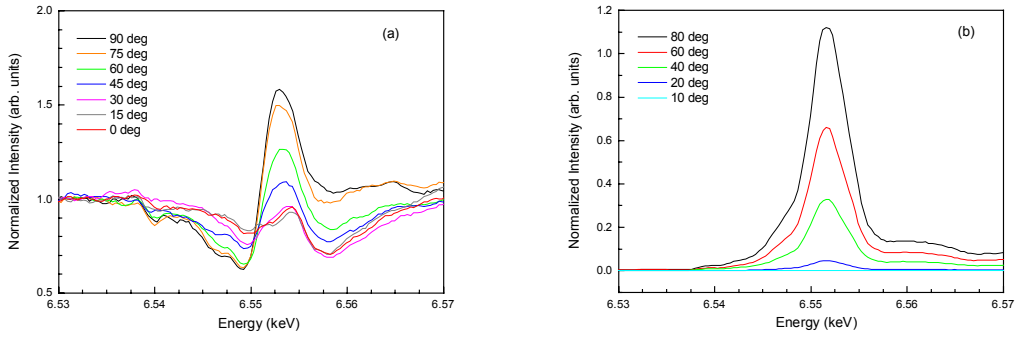

Figure 1. (a) Energy dependence of the polarization-resolved (σ→σ) intensity of the charge (030) reflection of $Bi_{0.5}Sr_{0.5}MnO_3$ sample at the Mn K absorption edge at different azimuthal angles. **(b)** Energy dependence of the polarization-resolved (σ→π) intensity of the orbital (05/20) reflection of $Bi_{0.5}Sr_{0.5}MnO_3$ sample at the Mn K absorption edge at different azimuthal angles.

We have also measured the temperature evolution of both superlattice reflections on heating above T_{CO}. Figure 2 reports the evolution of the integrated intensity of (030) and (05/20) reflections with temperature across the charge-ordering transition (T_{CO}~500 K). Its evolution confirms that the (010) and (01/20) structural modulations appear near 480 K, signaling the onset of the charge-orbital ordering transition.

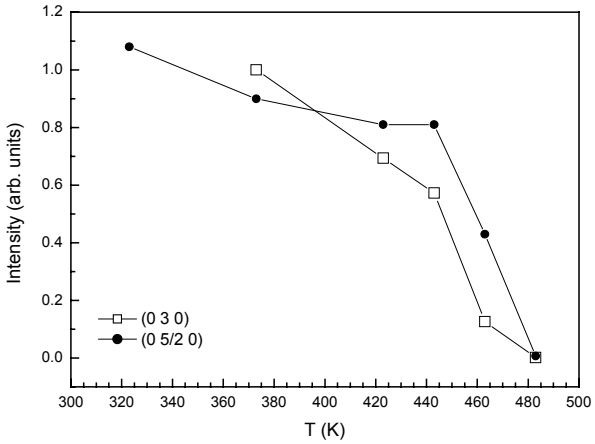

Figure 2. Integrated intensity of the (030) and (05/20) superlattice peaks as a function of temperature.

The main experimental results of this study are perfectly described within the framework of our structural model [3] based on a checkerboard pattern of two Mn atoms with different local geometrical structure (a tetragonal distorted and a nearly regular MnO_6 octahedral environments, respectively) without taking into account any real-space charge and orbital ordering. A fractional charge segregation $Mn^{+3.37}$ – $Mn^{+3.63}$ has been deduced. The present experiment discards both, the double-stripe and the Zener-polaron, patterns for the description of the so-called charge-ordered phase in $Bi_{0.5}Sr_{0.5}MnO_3$.

We have also carried out a preliminary study of the charge-orbital ordered phase (T_{CO}~600 K) of a underdoped $Bi_{0.7}Sr_{0.3}MnO_3$ single-crystal with [001] surface normal. Both, (300) and (5/200) superlattice reflections were detected at RT with identical azimuthal and polarization dependence as for the half-doped sample. However, $Bi_{0.5}Sr_{0.5}MnO_3$ and $Bi_{0.7}Sr_{0.3}MnO_3$ samples has been reported to show different charge-ordering phases. The x=0.3 sample also doubles the c-axis and apparently ferromagnetism seems to coexist with the charge order phase. A more detail study of this new periodicity and the dependence of the superlattice reflections on the applied magnetic field is needed to make a complete characterization.

[1] M. Hervieu et al., *Chem. Mater*. **13**, 1356 (2001)
[2]A. Daoud-Aladine et al., *Phys. Rev. Lett*. **89**, 097205 (2002)
[3] J. García et al., *J. Phys.:Conden. Matter* **13**, 3243 (2001); J. Herrero-Martin, *Phys. Rev. B* **70**, 024408 (2004)