ESRF	**Experiment title:** Resonant X-ray scattering study on the charge-ordered state of Mn and Fe perovskites with doping level x far from 0.5	**Experiment number**: HE-2413
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Report:

In order to better understand the electronic, magnetic and structural configuration in the so called charge-ordered (CO) phases in transition metal oxide perovskites we have studied single crystalline samples of the $Bi_{0.67}Sr_{0.33}MnO_3$ and $Nd_{0.33}Sr_{0.67}FeO_3$ mixed valence systems by means of resonant X-ray scattering (RXS). The measurements have been taken at the ID20 beamline at energies close to the K absorption edge of Mn and Fe and in a wide range of temperatures from 210 K down to 10 K.

$Bi_{0.67}Sr_{0.33}MnO_3$ is described as an orthorrombic (space group Ibmm) compound at room temperature, where it shows an electrical insulating behaviour. In fact, it suffers a metal to insulator phase transition, linked to the developing of a CO state, at about 550 K [1]. In the experiment, strong resonances have been observed as the energy was tuned through the Mn K-edge for several weak superstructures of the CO phase. We have seen that the energy, polarization and azimuth dependences (Fig. 1) at room temperature agree with a checkerboard ordering of two types of manganese atoms in terms of their different local geometrical structures. One of these sites is anisotropic, a tetragonal distorted oxygen octahedron and the other is nearly isotropic, structurally octahedral, as observed in $Bi_{0.5}Sr_{0.5}MnO_3$ and other half-doped manganites. This result indicates that the checkerboard pattern is strongly stable and extends into doping concentrations $x < 0.5$. Moreover, intermediate valence states lower than 3.5 according to fractional charge segregation have been deduced for the two non-equivalent Mn atoms, i.e. $Mn^{3.23+}$ and $Mn^{3.37+}$ [2].

In the case of $Nd_{0.33}Sr_{0.67}FeO_3$, the structure at room temperature is pseudo-cubic, with a slight rhombohedral distortion along the [111] direction, which makes this ferrite often be described in the R-3c space group [3]. Below $T_{CO}=T_N\sim180$ K, superlattice peaks of the type $\mathbf{q}=\mathbf{a}^*(1/3, 1/3, 1/3)$, $\mathbf{q}=\mathbf{a}^*(1/2, 1/2, 1/2)$ and $\mathbf{q}=\mathbf{a}^*(1/6, 1/6, 1/6)$ become visible, being $\mathbf{a}^*$ the reciprocal lattice vector in the cubic notation. Whilst the first kind ones are usually ascribed to an integer charge disproportionation between equivalent Fe sites following a +3, +3, +5, +3, +3, +5, +3, +3, +5… sequence, the half integer index and latter ones seem to be a consequence of the AFM ordering [4]. Our study of the energy, polarization and azimuthal dependence of representative superlattice peaks of these categories has revealed that a real charge disproportionation between Fe sites takes place, though our analysis indicates that this is far from being integer. Moreover, the presence of a non-

resonant Thomson scattering weak background in these reflections implicates a small displacement of the Fe, Nd(Sr) or O atoms from their Rietveld refined positions in the R-3c group. We have seen what seems to be a non periodical small azimuthal evolution that we expect to refine soon during a subsequent experiment. In any case, the resonant peaks are visible at every azimuthal angle, fingerprint of a real (though small) CO. A very interesting feature we also want to check by further measurements is the observed disappearance of the CO reflections at temperatures lower than 25 K (Fig. 2). This is a very unusual behaviour in these kind of compounds and its causes are not clear at the moment. The intensity and periodicity of the magnetic reflections appear to be insensitive to these evolution but the confirmation requires new measurements with higher resolution in temperature and more integration time.

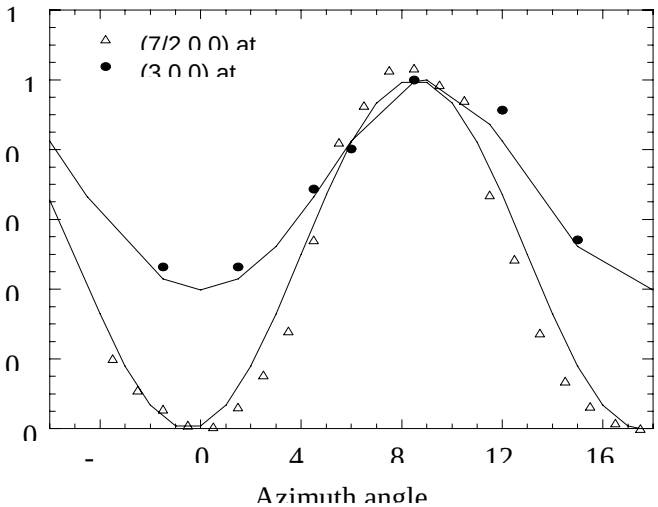

Figure 1. Azimuthal dependence of the $(3,0,0)_{\sigma-\sigma'}$ and $(7/2,0,0)_{\sigma-\pi'}$ integrated intensities at the energy of the maximum of the resonance in $Bi_{0.67}Sr_{0.33}MnO_3$. Intensities are normalized at the maximum for the sake of comparison. Solid lines are the best-fit curves from the structural checkerboard model

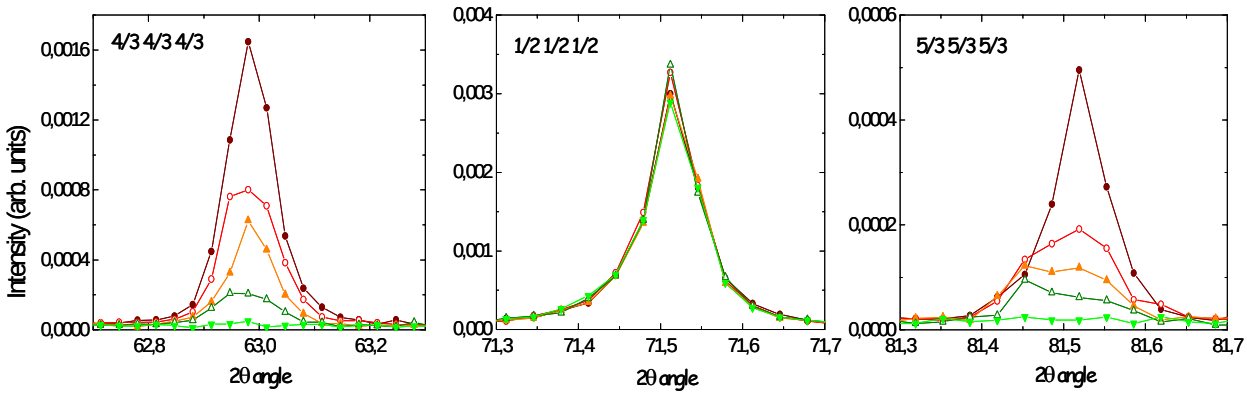

Figure 2. Rocking curves of different superstructure reflections in $Nd_{0.33}Sr_{0.67}FeO_3$ as a function of temperature (by lowering) in the σ-σ' channel from 32 K (solid circles) to 24 K (inverted filled triangles). Intermediate measurements are taken at 30 K (empty circles), 28 K (filled traingles) and 26 K (empty triangles).

References:

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[3]: P. D. Battle et al., J. Solid State Chem. **84**, 271 (1990)
[4]: R. Kajimoto et al., J. Phys. Chem. Solids **62**, 321 (2001)