# The Checkerboard Pattern of the Charge-Ordered Phases in $Bi_{1-x}Sr_xMnO_3$ ($x \leq 0.5$) Studied by Resonant X-Ray Scattering at the Mn K Edge

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**Abstract.** We report here resonant x-ray scattering (RXS) experiments carried out at the Mn K edge in $Bi_{1-x}Sr_xMnO_3$ (x=0.3, 0.5) single-crystals at room temperature. These compounds show a so-called charge ordered (CO) state at room temperature. Strong resonances were observed as the photon energy is tuned through the Mn K-edge for several weak superstructure (h 0 0) and (0 k 0) and forbidden (h/2 0 0) and (0 k/2 0) reflections with h, k odd within the *a-b* plane (*Ibmm* setting) in the x=0.3 and x=0.5 compounds, respectively. The reported azimuth angle and polarization dependences of the resonant intensity for the complete set of reflections point out to a structural transition at $T_{CO}$ that stabilizes a checkerboard ordering of two non-equivalent Mn atoms with different local geometrical structures. We conclude that the checkerboard ordered phase is a common ground state in the so-called CO manganites, $A_{1-x}B_xMnO_3$, independently of the nature of the A and B atoms and for compositions x even far from 0.5. Moreover, the quantitative analysis of the resonant reflections shows that the electronic states of the two non-equivalent Mn atoms are far from the ionic (+3 and +4) species.

**Keywords:** X-ray resonant scattering, Mn K-edge, manganites, charge ordering
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## INTRODUCTION

A great interest was lastly focused on mixed valence manganese perovskites due to the discovery of colossal magnetoresistance [1]. Near half-doping, the formal valence of Mn atoms is +3.5 and most of these manganites undergo a structural phase transition, which is accompanied by the appearance of charge and orbital modulations, the so-called charge and orbital ordering (CO and OO) transitions [2]. Resonant x-ray scattering (RXS) is the most suitable technique for unraveling CO and OO because of the combined element and site selectivity it provides. Resonant superlattice reflections appear in the vicinity of Mn K absorption edge because of differences in the anomalous atomic scattering factors of symmetry related Mn atoms in the unit cell. At Mn K-edge RXS, the anomalous atomic scattering factor is a symmetric tensor of second rank for dipole transitions. Resonance can be originated either because the tensors describing each of the Mn atoms are different, generally denoted as CO reflections, or due to the fact that the orientations of the tensor anisotropy axes are different for distinct Mn atoms, generally the literature refers to it as OO reflections. These last reflections are also known as Anisotropy of the Tensor of Susceptibility or ATS reflections [3] and they appear in crystallographic forbidden reflections, i.e. the Thomson scattering is zero.

Bismuth based manganites have received great attention [4] because of the strong enhancement of their CO temperature ($T_{CO}$). In the whole series, CO occurs at temperatures well above room temperature. $Bi_{0.5}Sr_{0.5}MnO_3$ suffers a metal-insulator phase transition at $T_{CO}$~500 K [5] while for $Bi_{0.7}Sr_{0.3}MnO_3$ $T_{CO}$~ 600 K [6]. Several CO models have been proposed for $Bi_{0.5}Sr_{0.5}MnO_3$, including the bi-stripe [7], the Zener polaron [8] and the checkerboard model [2]. We have recently shown by means of Mn K-edge RXS that the ordering for the half-doped bismutate is the checkerboard arrangement of tetragonal distorted and nearly undistorted $MnO_6$ [9]. The occurrence of

this bimodal ordering in half-doped manganites could be easily described as an ordering of $Mn^{3+}$ and $Mn^{4+}$ ions but the estimated charge segregation is far from one electron [9,10]. In this paper, we present a RXS study of the $Bi_{0.7}Sr_{0.3}MnO_3$ sample compared to the half-doped compound. We will show that the ordering pattern is also the checkerboard one despite the doping being far from x=0.5. This indicates that the charge segregation is not directly correlated with the doping level. This result casts serious doubts on the several ordering models proposed for bismutates with similar doping level [7,8,11].

## EXPERIMENTAL

Single crystals of $Bi_{0.5}Sr_{0.5}MnO_3$ and $Bi_{0.7}Sr_{0.3}MnO_3$ were grown by the conventional flux method. Characterization of the crystals was made by means of x-ray powder diffraction and energy dispersive spectroscopy (EDS). The chemical composition was verified by electron microanalysis being the composition close to the nominal one. At room temperature, the average structure is well described by using a Ibmm cell with a=5.539 Å, b=5.530 Å and c=7.587 Å for $Bi_{0.5}Sr_{0.5}MnO_3$ and a=5.54 Å, b=5.50 Å and c=7.77 Å for $Bi_{0.7}Sr_{0.3}MnO_3$. The CO superstructures result from the doubling of the b and a axis for $Bi_{0.5}Sr_{0.5}MnO_3$ and $Bi_{0.7}Sr_{0.3}MnO_3$ crystals, respectively. A polished $(110)_{cubic}$ surface was used for the RXS study. The twinned crystal has (100) and (010) oriented domains at the same sample surface. The basic transport and magnetic properties for the two samples were described elsewhere [5,6].

The RXS experiments were performed at the magnetic scattering undulator beamline ID20 at the European Synchrotron Radiation Facility (ESRF, Grenoble-France). A double crystal Si(111) monochromator was used. The energy resolution was about 1 eV and the incoming beam was linearly polarized (σ). The energy dependence of the diffracted intensity was recorded through the Mn K-absorption edge at the (0 3 0), (0 5 0), (0 5/2 0) and (0 7/2 0) reflections in the $Bi_{0.5}Sr_{0.5}MnO_3$ crystal and (3 0 0), (5 0 0), (5/2 0 0) and (7/2 0 0) reflections in the $Bi_{0.7}Sr_{0.3}MnO_3$ crystal. Azimuth evolution was also measured by rotating the sample around the diffraction vector. The polarization analysis was performed using a Cu(220) analyzer, so the scattered beam was resolved into the respective σ-σ' and σ-π' polarization channels.

The temperature evolution of the studied reflections was also measured. The reflections disappear at around $T_{CO}$ for both samples showing that the characteristic structural modulations occur at the onset of the CO-OO transition.

## RESULTS AND DISCUSSION

Figure 1 shows the energy dependence of the σ-σ' polarized intensity of the (030) reflection for $Bi_{0.5}Sr_{0.5}MnO_3$ and the (300) reflection for $Bi_{0.7}Sr_{0.3}MnO_3$ at the azimuth angle where the resonance is maximum. A similar line shape versus incident photon energy is observed in the two crystals consisting of a non-resonant Thomson scattering below the absorption edge and a broad peak at the Mn K edge. The spectra taken at different azimuth angles are also very similar for the two samples showing a π periodicity (not shown). It is noteworthy that the intensity approaches the non-resonant contribution at the azimuth angle correspondent to the minimum intensity, in contrast with the constant evolution expected for a pure CO reflection [12].

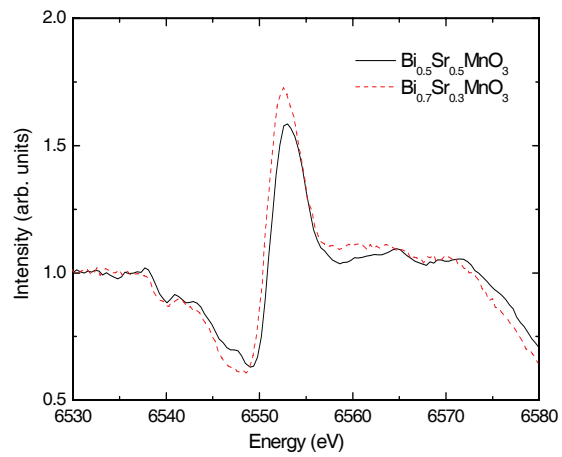


**FIGURE 1.** Normalized intensity versus photon energy of the (030) reflection in $Bi_{0.5}Sr_{0.5}MnO_3$ and the (300) one in $Bi_{0.7}Sr_{0.3}MnO_3$ near the Mn K-edge at room temperature in the σ-σ' channel .

Figure 2 compares the energy dependence of the (07/20) and (7/200) reflections across the Mn K-edge in the σ-π' channel for the x=0.5 and 0.3 samples, respectively. No intensity was observed below the absorption edge showing that these reflections are forbidden. The scattered intensity is purely resonant and π' polarized. The energy dependence for both resonances is nearly identical except for a slight energy shift. As it is shown in the inset of Fig. 2, the reported chemical shift between the two absorption spectra comes from the different intermediate valence state of the Mn atom. The formal valence state for x=0.3 is +3.3 whereas it is +3.5 for the x=0.5 sample, which agrees with a shift of the absorption edge to higher energies in the latter.

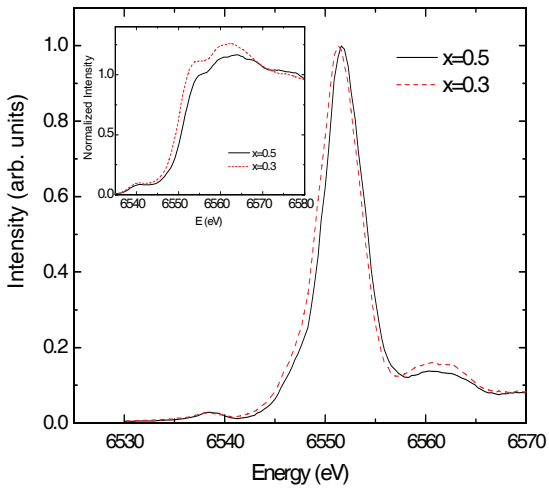


**FIGURE 2.** Normalized intensity versus energy of the (0 7/2 0)σ-π' [$Bi_{0.5}Sr_{0.5}MnO_3$] and (7/2 0 0)σ-π' [$Bi_{0.7}Sr_{0.3}MnO_3$] reflections at room temperature. **Inset**: Fluorescence spectra for the x=0.3 and 0.5 samples, as an energy reference.

Figure 3 shows the azimuthal dependence of the intensity at the maximum of the respective resonances for the two semi-integer reflections. We observe a π periodicity being the scattered intensity zero at the minimum position. We note that RXS experiments for the two samples are coincident pointing out to the same kind of CO and OO ordering model.

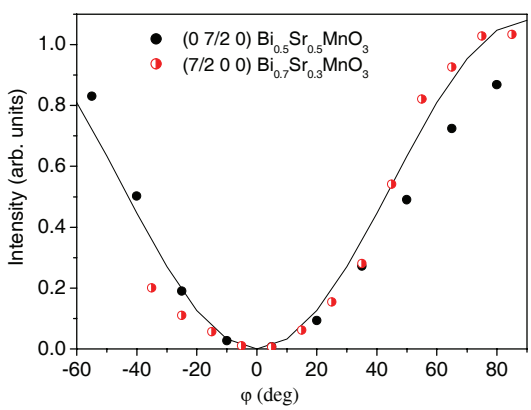


**FIGURE 3.** Azimuthal dependence of the σ-π intensity of the semi-integer OO reflections of [$Bi_{1-x}Sr_xMnO_3$] with x= 0.3 and 0.5 at the maximum of their respective Mn K edge resonances.

RXS experiments in half-doped lanthanide manganites have been described by a checkerboard ordering of anisotropic Mn atoms (in the ionic description assigned to $Mn^{3+}$) and isotropic Mn atoms (assigned to $Mn^{4+}$) [1,2]. Therefore we can deduce the same kind of ordering in bismutates as for half-doped lanthanide manganites in contrast with other proposed orderings, including a 3-fold periodicity. Using a semiempirical model, the diagonal components of the atomic anomalous scattering factor tensors can be estimated in terms of a chemical shift (energy shift between the atomic scattering factors of isotropic and anisotropic Mn atoms) and the anisotropic shift (energy shift between the parallel and the perpendicular components of the atomic scattering factor for the anisotropic Mn atoms). Thus, the charge disproportion for the half-doped bismutate was determined to be δ=0.14 electrons. For the sake of comparison, the charge segregation found for $Nd_{0.5}Sr_{0.5}MnO_3$ [10] was δ=0.16 electrons.

Summarizing, we can get two important conclusions. On one hand, the observation of the checkerboard ordering in $Bi_{0.7}Sr_{0.3}MnO_3$ shows that this ordering is not exclusive of half-doped manganites. Two electronically different Mn atoms are observed. This contrasts with the type of ordering of $Mn^{3+}$ and $Mn^{4+}$ ions expected for this composition within the ionic picture, where a higher periodicity than two should be observed. On the other hand, the small charge segregation observed in the CO phase seems to be a common feature even for disproportionations far from the half-doped state. As it was previously claimed, the CO-OO phase transition can be considered as a structural one, which distinguishes different transition-metal atoms by modifying their local electronic state.

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