Determination of incommensurate lattice modulations in La$_{0.4}$Sr$_{1.6}$MnO$_4$ by resonant r-ray scattering

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Abstract. Superlattice reflections, which appear below the semiconductor-insulator phase transition temperature in La$_{0.4}$Sr$_{1.6}$MnO$_4$, have been investigated by Resonant X-ray Scattering. We have observed two types of resonant reflections with modulation wave vectors $q_{h\pm\varepsilon}=(h\pm\varepsilon, h\pm\varepsilon, 0)$ and $q_{h\pm2\varepsilon}=(h\pm2\varepsilon, h\pm2\varepsilon, 0)$ ($h$-integer, $\varepsilon=0.2$) in the $I4/mmm$ setting. The energy dependence across the Mn K-edge, together with the azimuthal angle, polarization and temperature evolution have shown that reflections with $2\varepsilon$ periodicity only appear in the $\sigma$-$\sigma'$ channel, involving resonant and non-resonant scattering. On the other hand, reflections with $\varepsilon$ periodicity exclusively appear in the $\sigma$-$\pi'$ channel on resonance and the scattered intensity follows a $\pi$-periodicity with the azimuthal angle. We demonstrate that this different behaviour discards any possible Mn$^{3+}$/Mn$^{4+}$-like bimodal stripe ordering but it can be easily explained as due to oxygen displacements sinusoidal modulated along and perpendicular to the tetragonal [1, 1, 0] direction.

1. Introduction
Incommensurate structural phases in mixed valence transition metal oxides have been traditionally described as due to the ordering of the extra charges, giving rise to a sequence of stripes with rich and poor electronic density. This scenario has been considered of general relevance in the physics of nickelates, cobaltates and manganites [1-3]. Overdoped manganites show incommensurate structural ordering, where the periodicity of the modulations follows linearly the amount of extra charges [4]. Some authors interpret this fact as evidence for a stripe order with the Mn$^{4+}$ stripes aligned along the diagonal of the perovskite lattice [5], whereas recent electron and x-ray diffraction experiments [6] point to a continuous incommensurate structure. Resonant x-ray scattering (RXS) at the Mn K-edge allows to directly determine the charge and the anisotropic ordering of the Mn atoms. The specific atomic selectivity joined to the energy, azimuth and polarization dependences make this technique ideal to solve this controversy.

We present here a RXS study of the super-lattice reflections $(h\pm2\varepsilon, h\pm2\varepsilon, 0)$ (so-called CO reflections) and $(h\pm\varepsilon, h\pm\varepsilon, 0)$ (so-called OO reflections) with $\varepsilon=0.2$ that appear in the insulating phase of the La$_{0.4}$Sr$_{1.6}$MnO$_4$ manganite. The different polarization and azimuthal behaviour of the two types of resonant reflections has allowed us to discriminate between the stripe and the continuous incommensurate structural models. We demonstrate that both sets of reflections should show the same polarization and azimuthal behaviour in the bimodal stripe model. On the contrary, the experimental results are well described by a sinusoidal modulation of oxygen displacements.
2. Experimental Section

A single crystal of La$_{0.4}$Sr$_{1.6}$MnO$_4$ was grown by the floating-zone technique. Powder x-ray diffraction measurements on crushed crystals indicate that it is single phase and crystalizes in a tetragonal structure of space group $I4/mmm$ with room-temperature lattice constants $a=3.852$ Å and $c=12.4$ Å.

RXS experiments were performed at the ID20 beam line [7] at ESRF. The incident monochromatic beam, energy resolution being 1 eV at the Mn K edge, was linearly polarized (99%) with the polarization vector perpendicular to the scattering plane. The La$_{0.4}$Sr$_{1.6}$MnO$_4$ single crystal, cut and polished in the (1, 1, 0) plane in the tetragonal setting, was mounted in a four-circle vertical diffractometer equipped with a closed-cycle helium refrigerator. Energy scans of the scattered signal across the Mn K absorption edge and azimuth scans at the resonance energy were measured. The polarization of the scattered light was analysed using a Cu (2,2,0) crystal, which allows the measurement of the σ-σ’ and σ-π’ channels independently.

3. Results and Discussion

The energy dependence of the scattered intensity across the Mn K edge for the (1, 1, 0) reflection in the σ-π’ channel at different azimuth angles (φ) are shown in figure 1a. We observe scattered intensity at energies below the Mn K absorption edge and a strong enhancement of the intensity at photon energies close to the Mn K edge. The overall intensity at the maxima shows moderate marked azimuthal angle dependence. The scans corresponding to the two polarization channels at resonance (6556 eV) are shown in the inset of figure 1a. It is clear that this reflection is not observed in the σ-π channel. Figure 1b shows the energy dependence spectra of the (1.8, 1.8, 0) reflection, where a strong resonance is observed in the σ-π’ channel at the Mn K edge. The absence of Bragg diffraction in the σ-σ’ channel, as shown in the inset of figure 1b on resonance for example, indicates that these reflections are forbidden by symmetry [8]. The shape of the energy spectrum is the same regardless of the azimuth angle but it shows a strong azimuthal angle dependence of π period (figure 1b). The intensity of both type of reflections, ($h$=0.2, $h$=0.2, 0) and ($h$=0.4, $h$=0.4, 0), decreases with increasing temperature. These reflections vanish at T$_{CO}$~240 K, which agrees with the change in the electrical resistivity.

![Figure 1](image_url)

**Figure 1.** (a) Energy dependence of (1.6, 1.6, 0) reflection at T=80 K close to the Mn K-edge in the σ-σ’ channel for three different azimuthal angles. Inset: The signal collected at the Mn K-edge in the π’ and π detection channels. (b) Energy dependence of (1.8, 1.8, 0) reflection at T=80 K close to the Mn K-edge in the σ-π’ channel for three different azimuthal angles. Inset: The signal collected at the Mn K-edge in the σ’ and π detection channels.

We have simulated the intensity of the reported superlattice reflections considering two models, the bimodal stripe pattern and the sinusoidal modulated one. In the first case, we make use of the anomalous atomic scattering tensors (AAST) of anisotropic Mn$^{3+}$ ions ($f^{aa}_{\text{Mn}^{3+}}$) and isotropic Mn$^{4+}$ ions ($f^{aa}_{\text{Mn}^{4+}}$) that are ordered forming stripes. In the sinusoidal case, the terms $f^{aa}$ of the AAST will follow a dependence $f^{aa} = f^{aa}_0 + \Delta f^{aa} \cos (2\pi q r + \gamma)$, where $\Delta f^{aa}$ is the amplitude of the sinusoidal
modulation, $\mathbf{q}$ is the modulation vector, $\mathbf{r}_i$ is the Mn position in the supercell and $\gamma$ is the phase. Figure 2 shows a sketch of the orthorhombic supercell projected in the $\mathbf{a}_0\mathbf{b}_0$ plane. In our case, the incommensurate periodicity matches with the lattice in the [1, 1, 0] direction for five unit cells and we can identify five distinct Mn sites. The two possible stripe arrangements with sequences Mn$^{3+}$-Mn$^{3+}$-Mn$^{3+}$-Mn$^{4+}$ and Mn$^{4+}$-Mn$^{3+}$-Mn$^{4+}$-Mn$^{3+}$-Mn$^{4+}$, together with the sinusoidal modulated one are indicated in figure 2.

Figure 2. Schematic picture of the proposed superstructural orders in the $\mathbf{a}_0\mathbf{b}_0$ plane showing (lower panel) longitudinal and transverse atomic displacements for the five non-equivalent MnO$_6$ octahedra in the sinusoidal modulated model and (upper panel) bimodal charge stripe models.

We first discuss the stripe models. The real and imaginary parts of the diagonal terms of the AAST differ on the energy chemical shift, i.e. $f^{(\alpha\alpha}_{Mn^{3+}}(E) = f^{(\alpha\alpha}_{Mn^{4+}}(E-\Delta E)$, where $\Delta E$ is the difference of the absorption edge energy. The anisotropic $f^{\alpha\beta}$ term is zero for the isotropic Mn$^{4+}$ site whereas it is equal to that calculated for the anisotropic Mn$^{3+}$ site in ref. 9. Figure 3 (left panel) shows the simulated energy dependence of the superlattice reflections for the two stripe models compared with the experimental spectra. We obtain a good agreement with the experimental data for the $(h\pm0.4, h\pm0.4, 0)$ reflections in the $\sigma$-$\sigma$' channel and the $(h\pm0.2, h\pm0.2, 0)$ reflections in the $\sigma$-$\pi$' channel. However, important $\sigma$-$\sigma'$ and $\sigma$-$\pi'$ contributions are also obtained for the $(h\pm0.2, h\pm0.2, 0)$ and $(h\pm0.4, h\pm0.4, 0)$ reflections, respectively that are not experimentally observed. Therefore, the bimodal stripe ordering can be completely discarded.

In the following, we show that the sinusoidal modulation of the AAST for the Mn atoms gives the appropriate uncorrelated reflections. Since the Mn AAST mainly depends on the local structure around the scattered atom, a modulation in the atomic position of the nearest neighbour oxygen atoms will induce the same kind of modulation as for the Mn AAST. A uniform compression/expansion of the bond lengths will originate changes in the diagonal AATS terms (monopoles) whereas a deformation maintaining the average bond-distances induces a change in the out of diagonal terms (quadrupoles). We have built a model where oxygen motions either in the $\mathbf{a}_0\mathbf{b}_0$ plane or along the $\mathbf{c}_0$ axis are longitudinal modulated with an amplitude $\Delta x(\Delta z)=\Delta x_0 (\Delta z_0)\cos (2\pi \cdot n \cdot 0.4)$, being $n$ the position of the oxygen atom in the supercell (figure 2). The transverse modulation for the quadrupole mode will follow the expression $\Delta y=\Delta y_0 [\cos(2\pi \cdot n \cdot \epsilon) + \sin(2\pi \cdot n \cdot \epsilon)]$. The same kind of displacements yield a checkerboard sequence of expanded-distorted and compressed-undistorted MnO$_6$ octahedra for La$_{0.5}$Sr$_{1.5}$MnO$_4$ ($2\epsilon=0.5$). The AAST for each of the five distinct Mn atoms were calculated using the FDMNES code [10]. We have got that the structure factor for the $(h\pm0.4, h\pm0.4, 0)$ reflections is $F(h\pm0.4, h\pm0.4, 0) = \Delta F_{yy} \cos^2 \phi + \Delta F_{zz} \sin^2 \phi$ in the $\sigma$-$\sigma'$ channel, whereas it is given by $F(h\pm0.2, h\pm0.2, 0) = \Delta F_{xy} \cos \theta \cos \phi$ for the $(h\pm0.2, h\pm0.2, 0)$ reflections in the $\sigma$-$\pi'$ channel.
Similar $\Delta F_{yy}$ and $\Delta F_{zz}$ amplitudes do barely produce any significant intensity variation of $(h \pm 0.4, h \pm 0.4, 0)$ reflections as a function of $\varphi$ whereas $(h \pm 0.2, h \pm 0.2, 0)$ reflections show a pronounced $\cos^2 \varphi$ dependence as experimentally observed. Moreover, $F(h \pm 0.2, h \pm 0.2, 0)^{\sigma-\sigma}=0$ and $F(h \pm 0.4, h \pm 0.4, 0)^{\sigma-\sigma}=0$. Figure 3 (right panel) compares calculated and experimental spectra for representative reflections of La$_{0.4}$Sr$_{1.6}$MnO$_4$. We obtained a satisfactory agreement with $\Delta v_0=0.0024 \, \text{Å}$; $\Delta v_0=0.014 \, \text{Å}$ and $\Delta z_0=0.0012 \, \text{Å}$, the values of the refined distortions for the longitudinal, transverse and apical modulations. For the $(h \pm 0.4, h \pm 0.4, 0)$ reflections, $\Delta F_{yy}$ and $\Delta F_{zz}$ can be related to the chemical shift arising from a charge disproportionation among the different Mn atoms. We obtain a chemical shift of $-0.1$ eV, which corresponds to a charge disproportionation of $0.04$ electron.

This RXS study demonstrates that the occurrence of $(h \pm 0.4, h \pm 0.4, 0)$ and $(h \pm 0.2, h \pm 0.2, 0)$ reflections in La$_{0.4}$Sr$_{1.6}$MnO$_4$ is originated by sinusoidal oxygen motions, longitudinal and transverse to the modulation direction (orthorhombic $a_y$-vector). Reflections that arise from the transverse modulation are forbidden for Thomson scattering and they are only detected in the $\sigma-\pi$-polarisation channel. Thus, our results confirms that the two modulations with $\varepsilon=0.2$ and $2\varepsilon=0.4$ have different origin, i.e. the modulation with $2\varepsilon=0.4$ does not correspond to the second harmonic of the modulation with $\varepsilon=0.2$. In conclusion, we show that a continuous charge-orbital density wave model better describes the low temperature incommensurate-ordered phases in overdoped manganites.

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