X-ray resonant scattering study of the incommensurate charge-orbital density wave in La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ ($x = 0.7$)

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Abstract.

Orbital order has been proposed theoretically for more than half a century, and has subsequently been observed in a huge range of materials. Charge ordering is generally accompanied by a transition from a metal to an insulator. In manganites, colossal magnetoresistance (CMR) is associated with competition between charge and orbital antiferromagnetic insulating phases and ferromagnetic metallic phases. Initial models of charge and orbital order in the manganites concentrated on the chequerboard charge order structure, observed in many half doped systems. Incommensurate charge ordering and structural distortions have been identified in La$_{0.6}$Sr$_{2.4}$Mn$_2$O$_7$ through the observation of superlattice reflections using resonant x-ray scattering. Such structural distortions are indicative of concomitant orbital order, leading to our proposal of an incommensurate charge-orbital density wave. Superlattice structural distortion reflections were observed with a modulation vector (0.178, 0.178, 0), and charge order reflections with a modulation vector (0.356, 0.356, 0). Low temperature charge order melting, observed in the half doped bilayer manganite, is not present due to the absence of long range magnetic order.

1. Introduction

Transition metal oxides have been extensively studied due to the complex interactions between the different order parameters. The layered manganites have shown long-range magnetic, charge, orbital and correlated structural distortions. Such order parameters in the Ruddleston-Popper group, (La,Sr)$_{n+1}$Mn$_n$O$_{3n+1}$ have been studied with a variety of techniques[1, 2, 3]. In this paper we present resonant x-ray scattering results for the bilayer $n = 2$ member with $x = 0.7$ (Fig. 1). This overdoped system has a hole density provided by the doped strontium ions sufficient for the usual half doped CE chequerboard to become unstable. Indeed, this breakdown of the 1:1 chequerboard pattern and associated herringbone orbital order has been observed to collapse with $x \geq 0.575[4]$. Further investigations have suggested that the orbital and charge order are caused to melt through the onset of antiferromagnetic order[5]; in contrast no such long range magnetic order has been observed in La$_{0.6}$Sr$_{2.4}$Mn$_2$O$_7[6]$. 

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Figure 1. The crystal structure of La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$. The shaded $ab$ plane indicates the plane in which the charge-orbital density wave propagates.

Figure 2. Phase diagram for the bilayer manganite series La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ ($0.35 < x < 0.75$). Data points marked by $\times$ show the onset of charge order (and JT) through the appearance of superlattice reflections, $+$ data points mark the maxima in the intensity of the CO (or JT) reflections, interpreted as the onset of A-type AFM order. The data points marked by symbols are taken from this and previous publications[5, 4], and the areas of the phase diagram not marked by data symbols are generated from previous phase diagrams[7, 6].

Figure 2 displays the phase diagram for the bilayer manganites, showing a general transition from a ferromagnetic phase in the underdoped system, to an antiferromagnetic phase around half doping, to a paramagnetic overdoped system as a function of increasing doping. Charge order and co-operative Jahn-Teller distortions are observed in the half doped and overdoped systems. We have previously shown that the CE chequer-board charge order breaks down at $x \geq 0.575$[4], and through resonant x-ray diffraction we now extend this study and suggest the formation of a charge density wave and associated orbital density wave in the $x = 0.7$ system.
2. Experimental Details

High quality single crystals of La$_{0.6}$Sr$_{2.4}$Mn$_2$O$_7$ were grown at the University of Oxford using the floating zone method[8, 9]. Due to the large $c/a$ lattice parameter ratio, the samples naturally cleave in the $ab$ plane, providing a suitable scattering surface. A selection of crystals were pre-aligned using a rotating anode diffractometer, with a single domain crystal of approximately $3 \times 4 \times 0.5$ mm selected for experiments using synchrotron radiation.

Resonant x-ray diffraction experiments were performed on BM28 at the ESRF[10]. The beamline is situated on a bending magnet, providing a focussed monochromatic x-ray beam in the energy range 2.4 - 15 keV. For this experiment, the sample was illuminated by an x-ray beam with an incident energy of 6.555 keV, provided by a double bounce Si (111) monochromator with the higher energy x-ray harmonics rejected by a set of rhodium coated mirrors. The sample was mounted on a copper puck in a closed cycle cryostat held in an Eulerian cradle, with the cleaved ($ab$) plane perpendicular to the scattering plane. Polarisation analysis of the scattered beam was undertaken using a copper (220) polarisation analyser (PA) crystal (Fig. 3). At the manganese $K$-edge the (220) Bragg reflection of copper gives a leakthrough between the channels of less than 3%.

3. Results and Discussion

Superlattice reflections were observed below 330 K at (0.178, 0.178, 10) and (0.356, 0.356, 10) wavevectors (Fig. 4). Both these reflections showed a resonant enhancement at the manganese $K$ edge, with the (0.178, 0.178, 10) reflection observed in both polarisation channels and the (0.356, 0.356, 10) reflection only present in the unrotated $\sigma - \sigma$ polarisation channel. In addition, further reflections were observed around the (005) Bragg reflection, at (1.178, 0.178, 5). These reflections displayed no resonant enhancement, and reduced in intensity through the absorption edge congruent to the Bragg reflection.

The manganese $K$ edge probes the 4p electron band through the 1s-4p virtual transition, and is thus only sensitive to the symmetry of the 4p band and not directly sensitive to the orbital occupation of the 3d electron orbital occupation. However we are able to observe reflections arising from the anisotropic tensor of susceptibility (ATS)[11]. These ATS reflections arise through the anisotropic charge density in the crystal probed in the resonant condition. In this system the anisotropy of the Jahn-Teller distortion, allows the ATS reflections that we observe at (0.178, 0.178, 10).

In the bilayer manganite systems the orbital order is concomitant and possesses the same symmetry as the Jahn-Teller distortions, and thus by determining the nature of the Jahn-Teller distortion we can deduce that of the orbital order. In contrast to the ATS scattering, the charge order satellites are observed with finite intensity away from the resonant condition, however there is an enhancement in the signal through the absorption edge. This enhancement is caused by the charge order existing primarily on the manganese ions, which is selectively enhanced by

**Figure 3.** Schematic of the experimental setup, showing the two linear polarisation channels. Polarisation analysis is enabled through the rotation of the PA crystal ($\eta$), here shown at $\eta = 90^\circ$. 

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Figure 4. (a) [110] scan in reciprocal space away from the (0,0,10) Bragg peak at 10 K. Two superlattice reflections are observed in the $\sigma \rightarrow \sigma$ polarisation channel corresponding to the JT-ATS reflection (0.178, 0.178, 10) and charge order reflection (0.356, 0.356, 10). Energy scans at fixed $\vec{Q}$ of the ATS reflection are shown in the unrotated (b) and rotated (c) polarisation channels. Energy scans at fixed $\vec{Q}$ of the charge order reflection show resonance in the unrotated channel (d). A scan along [110] through the charge order reflection in the rotated channel shows no scattered intensity(e).

Figure 5. Schematic of the incommensurate Jahn-Teller distortions in La$_{0.6}$Sr$_{2.4}$Mn$_2$O$_7$. The shading represents the charge ordering, with heavily shaded MnO$_6$ octahedra representing those with more electron density (i.e. nearer to Mn$^{3+}$), and consequently show a bigger distortion. The light MnO$_6$ represent Mn$^{4+}$ with no distortion.
shown in this figure represents the most compelling model, with this data we are unable to
distinguish between this and an incommensurate square-wave modulation. A sinusoidal charge-
orbital density wave has been proposed in the single layered manganites Nd$_{1-x}$Ca$_{1+x}$MnO$_4$ and
Nd$_{1-x}$Sr$_{1+x}$MnO$_4$, supported by high resolution electron microscopy data[13, 14], and also in
cubic La$_{1-x}$Ca$_x$MnO$_3$[15]. The surprising aspect of the CDW in the cubic manganite is that
this incommensurate wave is observed with a doping of $x = 0.52$, unlike the bilayer manganite
series where the charge order is locked into the chequer-board pattern below $x = 0.575$.

4. Conclusion
Resonant x-ray scattering measurements at the manganese $K$ edge in La$_{0.6}$Sr$_{2.4}$MnO$_7$ show
evidence of charge order and Jahn-Teller distortions with the observation of superlattice
reflections. Multiple superlattice reflections corresponding to charge order, Jahn-Teller
distortions, and reflections arising from the anisotropic tensor of susceptibility were observed.
These show an incommensurate order, that we have suggested form a charge-orbital density
wave. Such a wave occurs when the doping level in the bilayer manganite is greater than
$x = 0.575$, however it is more stable as $x \to 0.7$.

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