# Complex Ordering in $La_{1-x}$ $Sr_xMnO_3$ ($x$~1/8) Investigated by Anisotropic Anomalous Scattering and High-energy X-ray Diffraction

Y. Su[1], D. Wermeille[2], J. Persson[1], K. Istomin[1], P. Meuffels[3], D. Prabhakaran[4], A.T. Boothroyd[4], P.D. Hatton[5], V. Kaiser[6] and Th. Brueckel[1]

[1]*Institute for Scattering Methods, IFF, Forschungszentrum Juelich, Germany*
[2]*MuCAT, Advanced Photon Source, Argonne National Lab., U.S.A.*
[3]*Institute for Electronic Materials, IFF, Forschungszentrum Juelich, Germany*
[4]*Department of Physics, University of Oxford, U.K.*
[5]*Department of Physics, University of Durham, U.K.*
[6]*Institut fuer Kristallographie, RWTH-Aachen, Germany*

## Introduction

Lightly doped $La_{1-x}Sr_xMnO_3$ ($x$~1/8) compound exhibits a very intriguing ferromagnetic insulating (FMI) phase at low temperatures. The exact nature of this FMI behavior is still being strongly debated in spite of intensive investigations carried out during last couple of years [1-4]. Nevertheless, the consensus on the importance of charge and orbital degrees of freedom has been reached. The central argument is now focused on how charge and orbital ordering take place. The latest suggestion is that the localized holes and surrounding $e_g$ orbitals in adjacent Mn cation sites are organized in the form of so-called orbital polarons. The ordering of such orbital polarons would lead to a FMI phase [2-3]. There are several alternative charge/orbital ordering models existing [4-5]. Therefore, this compound also represents an outstanding example to tackle complex ordering phenomena in highly correlated transition-metal oxides (TMO).

## Methods and Materials

In a real material, the charge and orbital ordering of valence electrons are often accompanied by significant lattice modulations due to strong electron-lattice interactions. This is usually signalized by the appearance of fractional superstructure reflections in a scattering experiment. To directly detect charge and orbital ordering is far from trivial due to their small perturbation to the average charge density of a lattice. The resonant X-ray scattering (RXS) technique has been tipped to have unique sensitivities to charge and orbital ordering due to its spectroscopic characteristics. In particular, RXS at the Mn K-edge via $1s \rightarrow 4p$ dipolar transitions has been widely applied to investigate orbital ordering in a number of manganites compounds [6]. However, the interpretation of the K-edge RXS has been intensively debated [6]. It is becoming increasingly clear that the RXS undertaken at the transition-metal K-edges is largely sensitive to the distortions of TM-$O_6$ octahedra instead of directly detecting the orbital ordering. Nevertheless, the sensitivity of this technique to the orbital ordering in the case of manganites can still be gained, since the orbital occupancy of single $e_g$ electron is always accompanied by a local Jahn-Teller distortion. This local anisotropic structure effects will lead to the occurrence of anisotropic anomalous scattering, also called Tempelton scattering. The anisotropic anomalous scattering always shows characteristic photon-polarization and azimuthal-angle dependence.

On the other hand, non-resonant scattering methods will provide accurate information on the charge-density distributions of core electrons. Therefore, they are sensitive to lattice modulations. Among various non-resonant scattering methods, high-energy X-ray diffraction is particularly suitable for quantitative measurements i.e. obtaining accurate structure factors or magnetic form factors, due to its small extinction effect, weak absorption by materials i.e. large penetration depth and its true bulk-probe character similar to that of neutron scattering. To disentangle complex ordering phenomena, an integral approach has to be chosen.

## Results and Discussions

Comprehensive RXS experiments on this compound have been undertaken at the MuCAT (Sector-6), Advanced Photon Source (APS). As shown in Fig. 1, significant resonant enhancements can be observed in the reciprocal space with $\boldsymbol{q}$ = ($H$,0,$L$/2) ($H$,$L$ ~ odd) below the so-called orbital ordering temperature (~ 140 K), when the photon energy is tuned to the Mn K-edge at ~ 6.554 KeV.

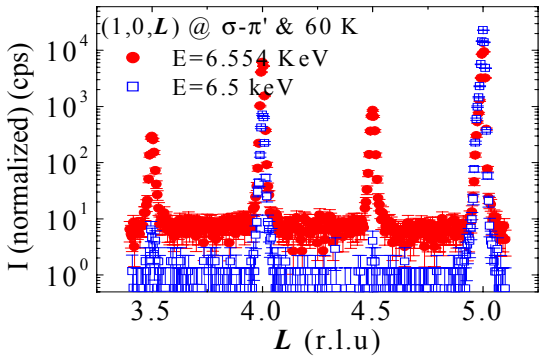


*Fig.1 Observation of significant resonant enhancements at (1,0,3.5) and (1,0,4.5) near the Mn K-edge, obtained at 60 K and with the σ→π' polarization set-up*

The energy dependence of several superstructure reflections with $\boldsymbol{q}$ = ($H$,0,$L$/2) ($H$,$L$ ~ odd) is shown in Fig. 2(a) and (b). The resonant enhancements can be observed in both the σ→π' and σ→σ' polarization set-up. All resonant reflections disappear when warming the sample above ~ 140 K. The temperature dependence of the resonant (1,0,4.5) reflections is shown in Fig. 2(c). The characteristic azimuthal-angle dependence has also

been confirmed, indicating that this resonant behavior is caused by the anisotropic effect i.e. orbital ordering, as shown in Fig. 3(d). A quantitative analysis is being carried out. The observation of this new set of resonant superstructure reflections will help us to finally resolve the issue concerning the exact nature of orbital ordering in this compound.

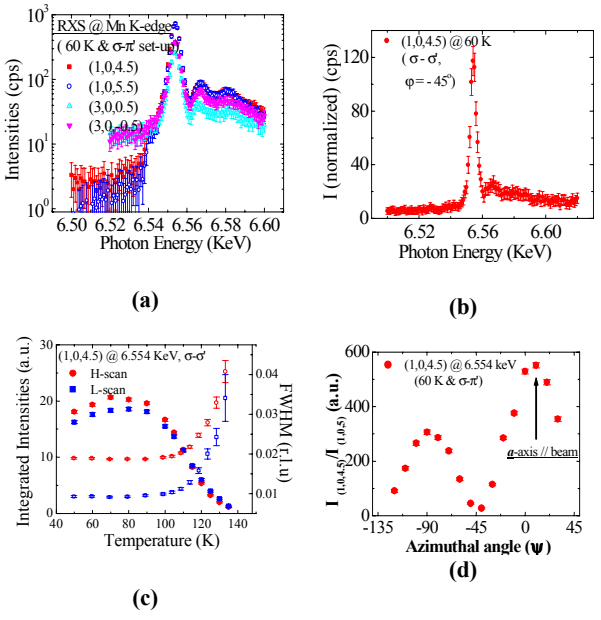


*Fig. 2 Anisotropic resonant X-ray scattering at the Mn K-edge, (a) the energy dependence of several superstructure reflections measured with the σ→π' polarization set-up; (b) the energy dependence of (1,0,4.5) with the σ→σ' polarization set-up; (c) the temperature dependence of resonant (1,0,4.5); (d) the Azimuthal-angle dependence of resonant (1,0,4.5) at the σ→π' set-up*

It has been known that $La_{1-x}Sr_xMnO_3$ ($x$~1/8) undergoes several complex lattice modulations and structural phase transitions in the FMI regime. However, the nature of these structural modulations has not been well established. Therefore, high-energy X-ray diffraction experiments were undertaken at the 6-ID-D undulator beamline of MuCAT, APS to investigate the complex lattice modulations with photon energy chosen around 100 keV. As shown in Fig. 3(a), the superstructure lattice modulation with $\boldsymbol{q}$ = ($H$/2,$H$/2,$H$) ($H$ ~ odd) can be observed up to reciprocal positions with very high $\boldsymbol{q}$ e.g. at (10.5,10.5,21) below ~ 140 K. It can be found that all of superstructure reflections are single-peak, but on the other hand, the neighboring Bragg reflections are all split due to the presence of a triclinic symmetry in the FMI phase as shown in the lower part of Fig. 3(a). This observation leads us to suspect that $\boldsymbol{q}$ = ($H$/2,$H$/2,$H$) ($H$ ~ odd) represents a coherent strain wave modulation. The strain wave modulation will help to stabilize a certain kind of orbital ordering model through elastic interactions. As shown in Fig. 3(b), the temperature dependence of the integrated intensities of (5.5,5.5,11) is obtained, displaying a profound hysterisis feature during the cooling – warming loop. To identify the origin of this lattice modulation, a large number of reflections with $\boldsymbol{q}$ = ($H$/2,$H$/2,$H$) ($H$ ~ odd) were measured, the corresponding structure factors have been accurately obtained. The preliminary analysis of the $\boldsymbol{q}$-dependence of obtained structure factors indicates that this modulation is in resemblance to a sinusoid charge-density wave propagating along the [1,1,2] direction. In addition, a weak transverse lattice modulation with $\boldsymbol{q}$ = ($H$/4,$H$/4,$H$/2) ($H$ ~ odd) is observed. It appears that the complexity of lattice modulations in this compound is far beyond our initial estimation. Further experiments are certainly necessary.

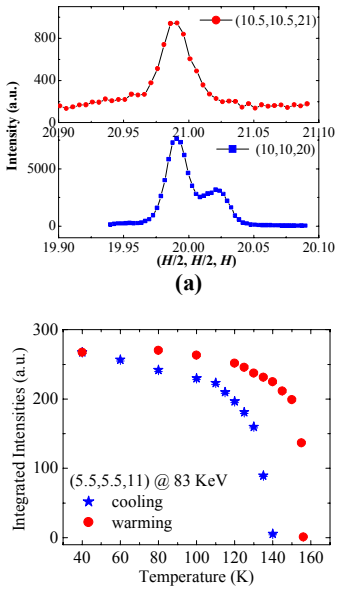


*Fig.3 Investigation of complex lattice modulations by high-energy X-ray diffraction*

In summary, comprehensive synchrotron X-ray scattering experiments on one of the most challenging and complex correlated electron systems – lightly doped $La_{1-x}Sr_xMnO_3$ ($x$~1/8) have been undertaken, which enable us to obtain the new insights on the orbital ordering and unusual lattice modulations.

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