Orbital and magnetic ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ studied by soft x-ray resonant scatteringU. Staub,¹ V. Scagnoli,¹ A. M. Mulders,¹ K. Katsumata,² Z. Honda,³ H. Grimmer,⁴ M. Horisberger,⁴ and J. M. Tonnerre⁵¹*Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*²*RIKEN Harima Institute, Mikazuki, Sayo, Hyogo 679-5148, Japan*³*Department of Functional Materials Science, Saitama University, Shimo-Ohkubo 255, Saitama, 338-8570, Japan*⁴*Laboratory for Neutron Scattering, ETH & PSI, CH-5232 Villigen PSI, Switzerland*⁵*Laboratoire de Cristallographie, CNRS, F-38042 Grenoble, France*

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Orbital and magnetic ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ have been studied with resonant soft x-ray scattering at the Mn $L_{2,3}$ edges and for the first time azimuthal angle scans and polarization analysis are presented. The azimuthal angle dependencies are well described by the occurrence of a quadrupole (orbital) ordering below T_{OO} and an additional dipole (magnetic) contribution below T_{N} . There are no indications that there is an enhanced Jahn-Teller distortion at T_{N} as reported in a previous study. Subsequently, it is shown that there is simultaneous ferro- and antiferromagnetic ordering along the c -direction.

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I. INTRODUCTION

Mixed valent perovskites are of current interest as they show a variety of electronic and magnetic properties such as high- T_c superconductivity, colossal-magneto resistance and/or temperature driven metal-insulator (MI) transitions. Recently, the ground state of the manganites $R_{1-x}A_x\text{MnO}_3$ and $R_{1-x}A_{1+x}\text{MnO}_4$ (R =rare earth, A =divalent metal ion and $x \sim 0.5$) have received much attention and various models have been proposed to describe the insulating state. In the past, it was generally accepted that the material shows a charge, magnetic and orbital order in its ground-state.¹ In this picture, the Mn ions are found at two distinct sites with charge states Mn^{3+} and Mn^{4+} . The Mn^{3+} ion resides in an octahedral environment with a doubly degenerate e_g ground state which allows orbital ordering connected with a Jahn-Teller (JT) distortion to occur, but it is unclear which of the two is the driving force. At elevated temperatures these materials show a single site with $\text{Mn}^{3.5+}$. Lowering the temperature a metal-insulator (MI) type transition occurs, which was interpreted as a charge order (CO) between Mn^{3+} and Mn^{4+} combined with an orbital ordering (OO) transition.¹ This simple charge ordering picture has been challenged recently by results obtained from magnetic neutron diffraction² introducing a model where these two Mn sites have equivalent charges and form a dimer, a Zener polaron. In addition, recent resonant x-ray scattering experiments at the Mn K -edge^{3,4} indicate that the effective spherical charge difference between the two sites is expected to be significantly smaller than one electron charge. The proposed ordering scheme is not consistent with the crystallographic structure proposed in the neutron study, but it is supported by the analysis of x-ray absorption data.⁵

Single layered manganite $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ exhibits a MI transition at $T_{\text{MI}}=T_{\text{CO}}=T_{\text{OO}} \approx 240$ K, which is followed by an antiferromagnetic transition at $T_{\text{N}} \approx 110$ K. The crystal structure at room temperature is tetragonal with space group $I4/mmm$ and lattice constants $a=3.86$ Å and $c=12.44$ Å. The MI transition causes an increase of the unit cell of type $\sqrt{2}a \times \sqrt{2}a \times c$, which results in two inequivalent Mn sites as

found by neutron diffraction.⁶ The magnetic structure shows a magnetic ordering wave vector of $(1/4, 1/4, 1/2)$, leading to a $2\sqrt{2}a \times 2\sqrt{2}a \times 2c$ magnetic unit cell. This is consistent with an orbital ordering with a unit cell of $\sqrt{2}a \times 2\sqrt{2}a \times c$. Further support for orbital ordering was obtained by resonant x-ray scattering at the Mn K -edge by the observation of $(h/4, h/4, 0)$ type reflections.⁷

More recently, resonant soft x-ray scattering at the Mn $L_{2,3}$ edges has been used to investigate the orbital order reflection $(1/4, 1/4, 0)$.⁸⁻¹⁰ First principle calculations¹¹ predict a different photon energy dependency of the scattered intensity for a situation where OO (direct $3d$ states splitting) takes place and a situation where JT distortion ($2p$ - $3d$ hybridization) ordering is dominant. Therefore, experiments performed at the $L_{2,3}$ edge allows us to probe directly the $3d$ states and the associated OO. This is in contrast to the Mn K -edge experiments for which theoretical calculations indicate^{12,13} that the scattered intensity is dominated by the JT contribution. Note that the most direct access to orbital ordering is nonresonant x-ray scattering as it probes the ground-state of the material, but this has only recently been successful for the case of CeB_6 .¹⁴

The theoretical predictions for the Mn $L_{2,3}$ edges¹¹ have been compared with recent soft x-ray experiments,⁹ but the interpretation is not fully convincing, as the calculations do not well describe the experiments. In addition, the different features of the spectra undergo different intensity changes when passing through the magnetic ordering temperature T_{N} , which was interpreted in terms of an enhancement of the JT distortion caused by the magnetic ordering. In view of the controversy about the charge order^{3,4} it is not clear which electronic states have to be used for the two Mn sites in the theoretical calculations. Therefore, the interpretation of these pioneering energy scans at the Mn $L_{2,3}$ edges is uncertain. Moreover, no azimuthal angle (Ψ) dependencies and polarization analysis were recorded, which does not allow to fully identify the origin of the different contributions to the scattering.

We present soft x-ray resonant scattering data including for the first time an energy dependent polarization analysis

FIG. 1. Experimental geometry of the scattering experiment. The polarization of the linear incoming light can be rotated from σ to π and with the analyzer σ' polarization is collected.

performed on the scattered beam. Additionally, we have performed azimuthal scans on selected peaks in the energy spectra. Below T_N , an additional component is observed in the spectra, which is shown to be of magnetic origin. This is in contrast with earlier interpretations, which claim an enhancement of the JT distortion at T_N .⁹

II. EXPERIMENT

To obtain a single crystal of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, powder samples were synthesized by a conventional ceramic technique. Stoichiometric amounts of La_2O_3 , SrCO_3 , and Mn_3O_4 were fired at 1373 K in air for 48 h with intermediate grinding. This powder sample was pressed into rods and sintered at 1373 K for 12 h. The single crystal samples were melt grown with a floating zone method in an atmosphere of 2 bar of oxygen gas. Susceptibility measurements have been performed with a Quantum Design SQUID magnetometer indicating that $T_{\text{OO}}=240$ K and $T_N=120$ K. Below T_N a small ferromagnetic component (difference between field cooled and zero-field cooled) is observed. The soft x-ray scattering experiments were performed at the SIM beamline of the Swiss Light Source at the Paul Scherrer Institut using the RESOXS endstation.¹⁵ Polarization analysis was performed using a W/C multilayer in a newly developed analyzer stage mounted on the two-theta arm. For the azimuthal scans (rotation around the Bragg scattering wave vector) the sample transfer line was used to rotate the sample holder. With pins attached in a threefold symmetry on the sample holder, an accuracy of approximately 5 deg was obtained. A continuous helium-flow cryostat allows measurements between 40 and 300 K. The experimental scattering geometry is such that the linear polarization of the incoming beam can be rotated from horizontal (π) to vertical (σ), see also Fig. 1.

III. RESULTS

Resonant soft x-ray scattering data of the $(1/4, 1/4, 0)$ reflection with photon energies in the vicinity of the Mn $L_{2,3}$

FIG. 2. Photon energy dependences of the intensity of the $(1/4, 1/4, 0)$ reflection of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ taken at $T < T_N$ (40 K) and $T_N < T < T_{\text{CO}}$ (160 K) are compared with two different azimuthal angles with incident π polarization.

edge are shown in Fig. 2 taken at $\Psi=0^\circ$ ($[001]$ is perpendicular to the scattering plane) and $\Psi=90^\circ$ azimuthal angles and at temperatures $T_N < T < T_{\text{CO}}$ and $T < T_N$. The weak fluorescence contribution has been collected at ambient temperatures and subtracted from these data. The data taken at $\Psi=90^\circ$ are similar to those found in Refs. 8 and 9. At $T < T_N$ the energy dependence of the spectra at $\Psi=0^\circ$ and $\Psi=90^\circ$ are very different, indicating that the scattering is, at least partly, of different origin. This contribution may originate from a magnetic contribution or from a change of the orbital ordering below T_N . A less resolved and weak signal is found for $\Psi=0^\circ$ and $T_N > T > T_{\text{CO}}$ with detectable intensity only at the L_3 edge. Such a small intensity maybe related to a small misalignment of Ψ , due to a small crystal distortion, lowering the Mn symmetry below $2/m$, or more likely due to weak diffuse magnetic scattering indicating magnetic short range correlations above T_N . In an earlier study⁹ the strong enhancement of several features at the L_3 edge in the spectra have been attributed mainly to an increase in the JT distortion, with a smaller effect on the OO. The temperature dependence of the peak at 645.2 eV for $\Psi=0^\circ$ and $\Psi=90^\circ$ are shown in Fig. 3, indicating that the contributions are directly related to the occurrence of the orbital order ($T_{\text{OO}} \approx 240$ K) and magnetic order ($T_N \approx 120$ K), respectively. Careful inspection of the $\Psi=90^\circ$ signal in Fig. 3 shows a change of slope at T_N indicating an additional contribution below this temperature as observed previously.⁹ The azimuthal angle dependence of selected peak features of the energy scans taken with π incident radiation are shown in Fig. 4. An azimuthal angle dependency, consistent with twofold symmetry is observed for all features at $T_N < T < T_{\text{CO}}$ [Fig. 3(a)]. This dependence was also observed at the Mn K -edge⁷ and is in agreement with the proposed orbital ordering and Jahn-Teller distortion. The pioneering work in the hard x-ray regime by Murakami *et al.*⁷ shows that the diffracted intensity of rotated polarization $\pi\sigma'$ is proportional to $|\sin(\Psi)|^2$ indicating a tensorial component of second rank responsible for the scattering.

FIG. 3. Temperature dependence of the intensity of the $(1/4, 1/4, 0)$ reflection of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ taken with incident π polarization at $E=645.2$ eV at two azimuthal angles Ψ , whereas T_{OO} (T_{CO}) is clearly observed at $\Psi=90^\circ$, $\Psi=0^\circ$ is mainly sensitive to T_N .

Below T_N the azimuthal evolution strongly depends on the energy, giving clear evidence that two contributions to the structure factor have different azimuthal angle dependencies. The intensity at $\Psi=0^\circ$ and $\Psi=180^\circ$ is different (not shown) and the intensity of the features at 643.4 eV and 645 eV is four times larger at $\Psi=0^\circ$ than at $\Psi=180^\circ$. This difference shows that the azimuthal angle dependence of the additional component is neither two- nor fourfold. Another observation is that the intensity at 658.2 eV no longer increases between 160 K and 40 K, whereas the other peak features do. This is consistent with Ref. 8, where different temperature dependencies of different peak features were observed above T_N , but in contrast to the observations in Ref. 9. Setting this aside, the different temperature dependence of individual peak features has been interpreted as due to the different behavior of Jahn-Teller distortion and orbital ordering. Here we show that the situation is more complex.

IV. DISCUSSION

The additional contribution observed in our spectra below T_N can have two origins, structural, maybe caused by a rearrangement of the orbitals, or magnetic, as it is coupled to T_N . First, let us assume that the additional contribution is due to a (re)orientation of orbitals and/or a further structural transition induced by the magnetic ordering or vice versa. An increase of the JT distortion only, without symmetry lowering, can be excluded due to the observed differences of the azimuthal dependencies. Because the additional component does not have a two or fourfold symmetry, a small reorientation is very unlikely to cause this contribution. If the Mn^{4+} sites contribute to the OO, this leads to a contribution with at least a twofold axis. A more complicated scenario is of course possible.

Second, let us assume that the additional contribution is of magnetic origin. This assumption is supported by the energy dependence observed below T_N which is similar to the ones observed for the magnetic reflections found in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ (Ref. 16) and $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$.¹⁷ This contribution would then correspond to a magnetic ordering wave vector $(1/4, 1/4, 0)$ with the same in-plane magnetic

FIG. 4. (Color online) Azimuthal angle dependence of the intensity of $(1/4, 1/4, 0)$ reflection taken at various photon energies and π incident polarization for (a) 160 K and (b) 40 K. (c) The azimuthal angle dependence of the two features at 40 K which no longer show a two-fold symmetry, compared to calculations based on an orbital (or JT) and a magnetic contribution with $\alpha=35^\circ$.

structure as proposed by neutron diffraction.⁶ In this neutron study⁶ an ordering wave vector $(1/4, 1/4, 1/2)$ has been observed with also a small intensity at $(h/4, h/4, 0)$ type positions interpreted as a minority stacking. In layered materials (a, b -plane) it is not uncommon to have ferro- and antiferromagnetic coupling along the c direction, as exemplified for $\text{Pb}_2\text{Sr}_2\text{TbCu}_3\text{O}_8$.¹⁸ The in-plane magnetic moment is described by $\vec{m}=m\sqrt{2}/2(\cos\alpha-\sin\alpha, \sin\alpha+\cos\alpha, 0)$. An $\alpha\approx 45^\circ$ corresponds to the moments being parallel $[010]$ and $\alpha=0^\circ$ corresponds to the moments being parallel $[110]$ using the $2\sqrt{2}a\times 2\sqrt{2}a\times 2c$ cell. The resonant magnetic scattering factor is expressed for the dipole transition as

$$f = F^{(0)}A(\theta) - iF^{(1)}B(\theta) + F^{(2)}C(\theta) \quad (\text{Ref. 19}). \quad (1)$$

For a collinear antiferromagnetic structure and our experimental geometry, the first and third term are zero and

$$B(\theta) = 0; \quad \sigma\sigma',$$

$$\begin{aligned}
B(\theta) &= z_3 \sin(\theta) + z_1 \cos(\theta); & \pi\sigma', \\
B(\theta) &= z_3 \sin(\theta) - z_1 \cos(\theta); & \sigma\pi', \\
B(\theta) &= -z_2 \sin(2\theta); & \pi\pi'
\end{aligned} \tag{2}$$

(Ref. 19) with θ the Bragg angle. The $\mathbf{z}$ components are proportional to the magnetic moment contributions parallel to the corresponding unit directions as shown in Fig. 1. Therefore, rotation about the Bragg wave vector (azimuthal scan) depends strongly on the magnetic moment direction and the polarization of the incoming and scattered radiation. The intensities for the different polarization channels are calculated and are proportional to $(\pi\pi')$: $|\sin 2\theta \sin \Psi \cos \alpha|^2$, $(\pi\sigma')$: $|\cos \theta \cos \Psi \cos \alpha + \sin \theta \sin \alpha|^2$, $(\sigma\pi')$: $|\cos \theta \cos \Psi \cos \alpha + \sin \theta \sin \alpha|^2$, and $(\sigma\sigma') := 0$. Therefore, for $\alpha \approx 45^\circ$ and π incident radiation there is a magnetic contribution in $\pi\sigma'$ peaking at $\Psi=0^\circ$ and minimum at $\Psi=180^\circ$, where the signal is expected to be of pure magnetic origin. There is an additional contribution in the $\pi\pi'$ channel with maxima at $\Psi=90^\circ$ and $\Psi=270^\circ$.

For a comparison of the azimuthal scans with these calculations, the structure factor from both contributions has to be considered. The OO contribution has a purely imaginary structure factor whereas the magnetic structure factor is real, but the $F^{(1)}$ contribution is complex and only the Mn^{3+} sites contribute. However, because the energy dependencies of the magnetic and orbital term is not the same, the real situation is even more complex. Here it is important to note that at $\Psi=0^\circ$ $\Psi=180^\circ$, we do not expect interference because the OO signal is negligible. Therefore, we take the most simple model and add the intensities without any interference, which of course may not be correct. This model describes the observations reasonably well [see Fig. 4(c)], it especially accounts for the increase of intensity at $\Psi=0^\circ$ and the intensity ratio between $\Psi=0^\circ$ and $\Psi=180^\circ$. It strengthens the interpretation that this contribution is of magnetic origin and not due to different contributions of JT and OO.⁹ Moreover, it allows us to determine the in plane angle of the magnetic moment (from the intensities of $\Psi=0^\circ$ and $\Psi=180^\circ$), which is in the order of $35 \pm 5^\circ$. This means that the angle deviates from the $[100]$ or $[010]$ as the material is tetragonal) by roughly $10 \pm 5^\circ$, significantly less than proposed by neutron diffraction.⁶

Further support for a magnetic origin comes from the energy dependent polarization analysis, which shows that the signal at $\Psi=90^\circ$ appears only in $\pi\sigma'$ and no signal in $\sigma\sigma'$ [Fig. 5(a)]. To our knowledge this is the first polarization analysis on a diffracted peak in the soft x-ray regime. Although the signal is weak, it supports our interpretation that all the features in the spectra arise from the two contributions, even though the comparison with theoretical calculations¹¹ is not satisfactory. A significant deviation from twofold site symmetry is unlikely because it would introduce a contribution in the $\sigma\sigma'$ channel. At $\Psi=90^\circ$ the magnetic model can be tested further by taking the difference of the scattered signals for π and σ incident radiation, without polarization analysis of the scattered radiation. This difference is shown in Fig. 5(b). and strongly resembles the contribu-

FIG. 5. (a) Energy dependence of the intensity of the $(1/4, 1/4, 0)$ reflection taken at $\Psi=90^\circ$ and $T=40$ K using polarization analysis. (b) The difference between π and σ incident radiation without polarization analysis, expected to be $(\pi\pi')$ like.

tion observed at $\Psi=0^\circ$. The intensity is one third of that observed at $\Psi=0^\circ$ and is in good agreement with the calculated azimuthal angle dependence of the proposed magnetic contribution. This magnetic difference is expected to appear only in the $\pi\pi'$ channel. Note that there is a magnetic signal of the same magnitude expected also in the $\pi\sigma'$ and $\sigma\pi'$ channels, which cancels in the difference presented in Fig. 5. Recently, magnetic and orbital contributions have been observed for the three-dimensional manganite $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$.¹⁷ In this study a general energy shift of approximately 3 eV between magnetic and OO scattering was found, which has been used to argue against a classical picture of charge ordering. The situation for the layered $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ investigated here is different in this respect, as there is no general energy shift observed between the magnetic and OO signals.

V. CONCLUSION

We have performed resonant soft x-ray scattering experiments at the Mn $L_{2,3}$ edges, including for the first time azimuthal scans and polarization analysis. The $(1/4, 1/4, 0)$ reflection shows a single tensorial contribution between $T_{\text{OO}} > T > T_N$ reflecting the quadrupole of the $3d$ shell and an additional contribution below T_N . The latter is of magnetic origin and is not an indication of an enhanced Jahn-Teller distortion. From the intensities observed at $\Psi=0^\circ$ and $\Psi=180^\circ$, we estimated an in-plane angle of the magnetic moments deviating from the $[100]$ of $10 \pm 5^\circ$. The magnetic ordering contains two ordering wave vectors of $(1/4, 1/4, 1/2)$ and $(1/4, 1/4, 0)$ anti- and ferromagnetic coupling along the c axis, the second with a smaller volume or moment contribution.

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