Soft X-ray resonant scattering study of single-crystal LaSr$_2$Mn$_2$O$_7$

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Soft X-ray resonant scattering studies at the Mn $L_{II,III}$ and the La $M_{IV}$ edges of single-crystal LaSr$_2$Mn$_2$O$_7$ are reported. At low temperatures, below $T_{K} \approx 160$ K, energy scans with a fixed momentum transfer at the $A$-type antiferromagnetic (0 0 1) reflection around the Mn $L_{II,III}$-edges with incident linear $\sigma$ and $\pi$ polarizations show strong resonant enhancements. The splitting of the energy spectra around the Mn $L_{II,III}$-edges may indicate the presence of a mixed valence state, e.g., Mn$^{3+}$/Mn$^{4+}$. The relative intensities of the resonance and the clear shoulder-feature as well as the strong incident $\sigma$ and $\pi$ polarization dependences strongly indicate its complex electronic origin. Unexpected enhancement of the charge Bragg (0 0 2) reflection at the La $M_{IV}$ edges with $\sigma$ polarization has been observed up to 300 K, with an anomaly appearing around the orbital-ordering transition temperature, $T_{\sigma\pi} \approx 220$ K, suggesting a strong coupling (competition) between them.

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INTRODUCTION

Strongly correlated electron systems such as 3$d$ transition-metal (TM) oxides present exciting fundamental properties, e.g., the superconducting behavior or the extraordinary colossal magnetoresistance effect. Their rich structural, magnetic and electronic properties are governed by the interplay of lattice, spin, charge and orbital degrees of freedom. Identification and precise characterization of the ordered phases is a prerequisite for understanding the physical properties and unusual phenomena. Among all possible experimental techniques, resonant X-ray scattering combined with its spectroscopic characteristics stands out due to its unique sensitivity to probe the charge/orbital ordering (CO/OO). With the application of resonant X-ray scattering in the hard X-ray regime [1], significant progress on the experimental quest of the orbital degree of freedom in 3$d$ TM compounds has been made. The resonant enhancement of the CO/OO super-reflections in LaSr$_2$Mn$_2$O$_7$ has been observed at the Mn $K$-edge [2]. However, the resonance at the $K$-edge of 3$d$ TMs is due to dipolar excitations from the 1$s$ to 4$p$ band and thus only indirectly reflects the 3$d$ electronic states. An alternative way is the resonant soft X-ray scattering. This is a powerful technique for directly probing the ordered phases individually. Utilizing this method, some studies [4-6] show strong resonant enhancements of the expected superlattice reflections around the Mn $L_{II,III}$-edges ($2p \rightarrow 3d$) which are known to be very sensitive to the details of the 3$d$ electronic states, supporting direct and definitive evidences for the ordering of charge, orbital and spin degrees of freedom in various manganites.

The compounds La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ consist of MnO$_2$ bilayers separated by the rock-salt-type (La, Sr)$_2$O$_2$ blocking bilayers. They are stacked vertically along the c axis ($I4/mmm, Z = 2$) as shown in Fig. [a] taking the half-doped LaSr$_2$Mn$_2$O$_7$ ($x = 0.5$) as an example. Though no structural transition was reported for LaSr$_2$Mn$_2$O$_7$ below room temperature [7], this compound undergoes a transition into the CE-type charge-orbital ordered state at $\sim$225 K [2]. This state starts melting around 170 K where the $A$-type antiferromagnetic (A-AFM) structure forms [Fig. [a]]. The (0 0 1) reflection corresponds to this long-range A-AFM ordering stacked along the crystallographic c axis. The CO/OO breaks down at $\sim$100 K but recovers again around 50 K. This reentrant behavior was discussed in terms of a polaron model [2]. In addition, the minor CE-AFM phase was reported to coexist with the major A-AFM one below $\sim$145 K and be drastically but not completely suppressed below $\sim$100 K. This phenomenon was viewed as an effective phase separation [8].

In this article, we report a resonant soft X-ray scattering study of the AFM (0 0 1) and the charge Bragg (0 0 2) reflections in LaSr$_2$Mn$_2$O$_7$, varying incident photon polarizations. The detailed energy and temperature dependencies were monitored. Our study confirms that the energy spectra of the AFM (0 0 1) over the Mn $L_{II,III}$-edges consist of six clear features. In addition, we found a huge resonant enhancement of the charge Bragg (0 0 2) reflection at the La $M_{IV}$, $\sigma$-edges.

EXPERIMENTAL DETAILS

Most available soft X-ray scattering hosts room-temperature two-circle diffractometers. This geometry leads to severe restrictions for sample rotating around the surface normal (ψ-circle) and sample tilting (χ-circle) [Fig. [a]], which are both essential degrees of freedom for single-crystal resonant soft X-ray scattering studies. Therefore,
FIG. 1: (color online) (a) Structural (I4/mmm, Z = 2) unit-cell of \(\text{La}_2\text{Sr}_2\text{Mn}_2\text{O}_7\) and arrangement of A-AFM spins of Mn ions. Structural parameters were taken from [7]. (b) An octahedron of MnO₆ along the \(c\) axis and its distortion mode. (c) Local crystal environments for the La1 and La2 sites.

FIG. 2: (color online) (a) Miniature goniometer utilized in this study for rotating and tilting the \(\text{La}_2\text{Sr}_2\text{Mn}_2\text{O}_7\) sample in \(\psi\) and \(\chi\) angles, respectively. (b) Basic notations for the resonant soft X-ray scattering set-up at the UHV ALICE diffractometer at Berliner Elektronen-Speicherring Gesellschaft für Synchrotronstrahlung (BESSY).

RESULTS AND DISCUSSION

Fig. 3(a) shows the energy dependence of the integrated intensity of the AFM (0 0 1) through the Mn \(L_{\text{II}, \text{III}}\)-edges at 15 K. A similar observation on this compound was previously reported [11] where only observed intensity without polarization analysis was recorded at 20 K. Clearly, the present study is more detailed. The spectra show a very strong polarization dependence and are dominated by scattering at the Mn \(L_{\text{III}}\)-edge. Six clear features are present: four peaks (2, 4, 5 and 6) and two shoulders (1 and 3). The intensity ratio between the two main features 2 and 4 is reversed with the different polarizations. The splitting of the energy spectra with \(\sigma\) and \(\pi\) polarizations around the Mn \(L_{\text{II}, \text{III}}\)-edges is probably ascribed to the existence of a mixed valence state, e.g., \(\text{Mn}^{3+}/\text{Mn}^{4+}\) type. The contrast intensity between both
The resonance of the charge Bragg (0 0 2) reflection at and off their strongest resonant energies respectively, at and off their strongest resonant energies ~634.0 eV (Mn $L_{III}$-edge) and ~834.2 eV (La $M_{IV}$-edge).

FIG. 3: (color online) Energy dependence of (a) AFM (0 0 1) recorded over the Mn $L_{III, II}$-edges and (b) charge Bragg (0 0 2) reflection over the La $M_{IV}$, $\nu$-edges with incident linear $\sigma$ and $\pi$ polarizations at 15 K. The intensity was integrated from longitudinal scans at each energy point. (c) and (d) longitudinal scans of the (0 0 1) and (0 0 2) reflections, respectively, at and off their strongest resonant energies ~634.0 eV (Mn $L_{III}$-edge) and ~834.2 eV (La $M_{IV}$-edge).

The resonance of the charge Bragg (0 0 2) reflection at the La $M_{IV}$, $\nu$-edges with $\sigma$ polarization [(Fig. 3b)] was unexpectedly observed at 15 K. This resonant enhancement is extremely large with dramatic polarization dependence at the La $M_{IV}$, $\nu$-edges as shown in Fig. 3d where the resonance with the incident $\pi$ polarization is very small. Figures 3c and d comparatively show the longitudinal scans of the AFM (0 0 1) and the charge Bragg (0 0 2) reflections, respectively, at and off their strongest resonant energies ~634.0 eV (Mn $L_{III}$-edge) and ~834.2 eV (La $M_{IV}$-edge).

The temperature dependences of the AFM (0 0 1) reflection at the six energies corresponding to the six features 1, 2, 3, 4, 5 and 6 [Fig. 3(a)] and the charge Bragg (0 0 2) reflection at the La $M_{IV}$-edge with $\sigma$ polarization upon warming were shown in Fig. 4. The integrated intensities of the AFM (0 0 1) decrease gradually as increasing temperature to $T_N$ ~160 K and then disappear simultaneously [Fig. 4(b)]. The intensity of the charge Bragg (0 0 2) reflection persists up to 300 K and exhibits a broad peak around 220 K [Fig. 4(a)]. The recorded intensity of the charge Bragg (0 0 2) reflection over the Mn $L_{II, III}$- and the La $M_{IV}$, $\nu$-edges at 300 K was shown in Fig. 4(a). The corresponding longitudinal scans at the Mn $L_{III}$- and the La $M_{IV}$-edges were shown in Fig. 4(b). The intensity ratio between the two main peaks at the Mn $L_{III}$-edge keeps the numerical relationship with $\sigma$ and $\pi$ polarizations. Compared to Ref. 4 where the La$_{0.05}$Sr$_{0.95}$Mn$_2$O$_7$ sample was investigated, the resonance observed here has a different spectral shape and much clearer features, i.e., an obvious peak splitting at 15 K. The intensity was integrated from longitudinal scans at each energy point. (c) and (d) longitudinal scans of the (0 0 1) and (0 0 2) reflections, respectively, at and off their strongest resonant energies ~634.0 eV (Mn $L_{III}$-edge) and ~834.2 eV (La $M_{IV}$-edge).

FIG. 4: (color online) Temperature dependent integrated intensity (measured in the longitudinal direction) of (a) charge Bragg (0 0 2) reflection at the La $M_{IV}$-edges, and (b) AFM (0 0 1) reflection recorded at the six energies corresponding to the six features 1, 2, 3, 4, 5 and 6 as labeled in Fig. 3(a).

Superlattice reflections corresponding to the propagation vector $\mathbf{Q} = (1/3, 1/3, 1/3)$ in LaSr$_2$Mn$_2$O$_7$ were believed to be relevant to the 3d OO $(3x^2 - r^2/3y^2 - r^2)$ of Mn$^{3+}$ ions, which is accompanied by the CO of 1:1 Mn$^{3+}$/Mn$^{4+}$ species [12]. X-ray, neutron and electron diffraction studies [2, 12] indicate that the coupled CO/OO developed
It is interesting to explore the reasons for the huge resonant enhancement of the charge Bragg (0 0 2) reflection at the La Mn\textsubscript{IV} \textit{\gamma}-edges. This peak is allowed for the tetragonal structure of this compound. The observed intensity in resonant soft X-ray scattering is mainly determined by the anomalous atomic scattering factor of the resonant atoms. This factor is a function of the incident photon energy \(E\) and can be expressed as \(f(E) = f_1(E) + if_2(E)\), where the imaginary part \(f_2(E)\) is related to the absorption coefficient and the real part \(f_1(E)\) can be deduced from \(f_2(E)\) through the mutual Kramers-Kronig relation \([13]\). The X-ray absorption spectrum of this compound at the La Mn\textsubscript{IV}, \textit{\gamma}-edges needs to be measured for a quantitative calculation of the anomalous scattering factor. The anomalous atomic scattering factor shows a tensorial character and its anisotropy is mainly related to the distortion of the local environment. During the resonant soft X-ray scattering process, in principle, the excited electron is sensitive to any anisotropy around the absorbing ions, e.g., the anisotropy of charge, orbital, spin or lattice. There are two types of distortion related to the MnO\textsubscript{6} octahedra in manganites: (i) one is the Jahn-Teller (JT) distortion that is inherent to the high-spin \((S = 2)\) Mn\textsuperscript{3+} ions, resulting in different Mn-O bond lengths, which is accompanied by the OO of occupied Mn 3d orbitals; (ii) another is the cooperative rotation corresponding to the Mn-O-Mn bond angle and tolerance factor, leading to lattice modulations and forming the octahedral tilt-ordering (TO). An octahedral TO of Pr\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3} and LaMnO\textsubscript{3} \([14]\) was observed by tuning the incident X-ray energy to the \(L_1\), \(L_1\), and \(L_{III}\) absorption edges of Pr and La, respectively. The structural data of LaSr\textsubscript{2}Mn\textsubscript{2}O\textsubscript{7} as a function of temperature was not completed \([15]\) and the existing structural parameters were strongly challenged by the single-crystal study \([16]\). The tetragonal symmetry \((I4/mmm)\) of LaSr\textsubscript{2}Mn\textsubscript{2}O\textsubscript{7} determines that the out-of-plane Mn-O-Mn bond angle along the \(c\) axis is \(180^\circ\) and the JT distortion size which is defined as the ratio of the averaged apical and the equatorial Mn-O bond lengths is close to unity down to 10 K [Fig. 4(c)]. Thus no octahedral TO exists in LaSr\textsubscript{2}Mn\textsubscript{2}O\textsubscript{7}. However, the distortion mode developed for the MnO\textsubscript{6} octahedra based on the Mn-O bond lengths indeed exists [Fig. 4(b)], which was confirmed by a Raman spectroscopy study \([17]\). Raman spectroscopy is a very sensitive probe of the local and dynamical structural changes. This scattering method can be used to study the complex interplay of lattice dynamics with ordering parameters in manganites. In \([17]\), the major intensity of out-of-plane spectra was assigned to this stretching mode [Fig. 4(b)] and is independent of temperature. In addition, two tiny intensities in out-of-plane spectra were attributed to the Raman allowed modes in the original structure: atomic motion of La/Sr ions along the \(c\) direction. Moreover, the rest appreciable intensities were thought to be from the
activated modes, i.e., the coupling between lattice distortion and CO/OO. This octahedral distortion mode has little effect on the local crystal environment of La1 sites that locate at the center of four double-MnO$_6$ octahedra [Fig. 1(c)], while it has a profound effect on that of the La2 sites due to the asymmetric action. Indeed, based on the reported structural parameters at room temperature [7], the calculated local distortion sizes of La1 and La2 sites by Fullprof suite [18] are $3.2 \times 10^{-5}$ and $1.4 \times 10^{-3}$, respectively. The strongly produced anisotropy of La2 sites may lead to the resonant enhancement of the charge Bragg (0 0 2) reflection at the La $M_{IV, V}$-edges.

In addition, the observed competition between OO and temperature dependent integrated intensity of the charge Bragg (0 0 2) reflection is in agreement with Ref. [17].

To summarize, a systematic resonant soft X-ray scattering study at the La $M_{IV, V}$-edges on the possible lattice modulations and at the Mn $L_{III, III}$-edges on the A-AFM structure in LaSr$_2$Mn$_2$O$_7$ has been accomplished. At 15 K, well below $T_k \sim 160$ K, dramatic enhancements of the charge Bragg (0 0 2) and the AFM (0 0 1) reflections at the La $M_{IV, V}$- and the Mn $L_{III}$- edges were observed, respectively. The temperature dependences of the AFM (0 0 1) resonance at the six featured energies show a similar trend and disappear simultaneously above $T_N$. The resonant intensity of the charge Bragg (0 0 2) reflection persists from 15 K to 300 K and was strongly strived by the OO around 220 K.

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