Orbital Ordering and Resonant X-ray Scattering in Layered Manganites

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In layered manganites with orbital and charge orderings, the degeneracy of the Mn 4p orbitals as well as the 3d ones is lifted by the effects of the 4p bands and the local Coulomb interactions. We formulate the atomic scattering factor for the resonant x-ray scattering in the memory function method by taking into account these effects on an equal footing. It is shown that the polarization dependences of the scattering intensities at the orbital and charge superlattice reflections observed in LaSr$_2$Mn$_2$O$_7$ are caused by the local and itinerant characters of 4p electrons, respectively. We examine the type of the orbital ordered state.

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Orbital degree of freedom is one of the key factors to uncover the dramatic and fruitful phenomena in colossal magnetoresistive (CMR) manganites. However, since the experimental technique to detect the orbital structure has been limited for a long time [1], it was considered to be a hidden degree of freedom. The resonant x-ray scattering (RXS) has recently shed light on this issue. Murakami et al. have applied the scattering method to La$_{0.5}$Sr$_{1.5}$MnO$_4$ and observed the superlattice reflections near the Mn$^{3+}$ K-edge caused by the orbital ordering [2]. Immediately after the observation, this method was extensively studied in both the experimental and theoretical sides [3–8] and has been recognized to be a powerful tool to detect the orbital states through the application to several manganites.

Near the Mn$^{3+}$ K-edge, RXS is given by the electric dipole transition between Mn 1s and 4p orbitals. The anomalous part of the atomic scattering factor (ASF) is a tensor with respect to the polarization of x-ray and the anisotropy of the tensor elements brings about the scattering at the orbital superlattice reflections. It was shown that the Coulomb interactions between Mn 3d and Mn 4p electrons and between Mn 3d and O 2p orbitals are controlled by changing magnetic field [10–12]. The orbital states of 3d electrons and between Mn 3$^+$$d$ orbitals as well as 4$p$ orbitals explains the experimental results in LaSr$_2$Mn$_2$O$_7$. Being based on the calculated results, types of the orbital ordered state are discussed.

Let us first formulate ASF. On resonance, the relevant term in the diagonal part of ASF is given by

$$\Delta f_{\alpha} = \frac{m}{e^2} \sum_j \frac{\langle \alpha | j \alpha | \rho \rangle}{\varepsilon_0 - \varepsilon_j + \omega - i\Gamma},$$

(1)

where $|0\rangle$ ($|\rho\rangle$) denotes the initial (intermediate) electronic state with energy $\varepsilon_0$ ($\varepsilon_\rho$). $\omega$ is the energy of x-ray with polarization $\alpha$. $j_{\alpha}$ ($= \frac{\hbar}{m} \sum_\sigma P_{i\alpha\sigma} s_{i\sigma} + H.c.$) describes the 1s $\rightarrow$ 4p transition where $P_{i\alpha\sigma}$ and $s_{i\sigma}$ are the creation operator of Mn 4p electron at site $i$ with spin $\sigma$ and orbital $\alpha(=x,y,z)$ and the annihilation one of Mn 1s electron, respectively. $\Gamma$ denotes the damping of a core hole. Because the radius of the Mn 1s orbital is much smaller than the lattice constant, the 1s electron is excited to the 4p orbital at the same site. The relevant part of $\Delta f_{\alpha}$ is rewritten by using the Green’s function for the operator $J_{i\alpha\sigma} = P^\dagger_{i\alpha\sigma} s_{i\sigma}$ as follows,

$$\text{Im} \Delta f_{\alpha} = -\frac{e^2|A|^2}{m} \sum_\sigma \text{Im} G_{\alpha\sigma}(z) |_{z=\omega+i\Gamma},$$

(2)

where $G_{\alpha\sigma}(z)$ is the Fourier transform (FT) of the retarded Green’s function $G_{\alpha\sigma}(t) = \Theta(t) \int e^{-i\omega t} G_{\alpha\sigma}(\omega) d\omega$ defined by $G_{\alpha\sigma}(t) = \theta(t) \langle J_{i\alpha\sigma}(t), J_{i\alpha\sigma}(0) \rangle$.

We consider a MnO$_6$ cluster where x-ray is absorbed. The electrons in the cluster couple to the 4p bands. The Hamiltonian is given by $H = H_0 + H_{4p}$, with

$$H_0 = \varepsilon_d \sum_{\gamma\sigma} d^\dagger_{\gamma\sigma} d_{\gamma\sigma} + \varepsilon_p \sum_{\gamma\sigma} P^\dagger_{\gamma\sigma} P_{\gamma\sigma} + \varepsilon_s \sum_{\sigma} s^\dagger_{\sigma} s_{\sigma}$$

$$+ t_{pd} \sum_{\gamma\sigma} (d^\dagger_{\gamma\sigma} p_{\gamma\sigma} + P_{\gamma\sigma} d_{\gamma\sigma})$$

$$+ U \sum_{\gamma} n^d_{\gamma\uparrow} n^d_{\gamma\downarrow} + U' \sum_{\sigma\sigma'} n^d_{i\alpha\sigma} n^d_{i\beta\sigma'},$$

where $d_{\gamma\sigma}$ and $p_{\gamma\sigma}$ are the creation operators of 4p and Mn 3p electrons, respectively. $\varepsilon_d$ and $\varepsilon_p$ are the energy levels of 4p and Mn 3p orbitals, respectively. $U$ and $U'$ are the Coulomb interactions between 4p and 3p electrons. $t_{pd}$ is the hopping integral between 4p and 3p orbitals.

The energy levels of the three 4p orbitals are nearly degenerate in the local sense. On the other hand, the layered structure provides the quasi-two-dimensional character of the 4p band and lifts the degeneracy. We formulate ASF in the memory function method by taking into account the effects of the 4p band and the local Coulomb interactions on an equal footing. The anisotropy of ASF reflected from the local and itinerant characters of the 4p electrons explains the experimental results in LaSr$_2$Mn$_2$O$_7$.
\[ + I \sum_{\alpha} d_{i\alpha}^\dagger \Sigma_{i\alpha} d_{i\alpha} - J_H \hat{S}_i \cdot \hat{S}_i \]
\[ + n_{ih} \sum_{\gamma \sigma} (V_{sd} n_{i\gamma}^d + V_{sp} n_{i\alpha}^p) + \sum_{\alpha \gamma \sigma \sigma'} V_{\gamma \alpha} n_{i\gamma}^d n_{i\alpha}^p, \]
\[ \text{and} \]
\[ H_{4p} = \varepsilon_p \sum_{j \alpha} P_{j \alpha}^\dagger P_{j \alpha} + \sum_{j \beta \sigma} i \alpha \beta \sigma P_{j \alpha}^\dagger P_{j+\delta \sigma \alpha} \],
\[ \text{where} \ H_0 \text{ and } H_{4p} \text{ describe the electronic states in the MnO}_6 \text{ cluster and in the } 4p \text{ band, respectively.} \]
\[ \text{i indicates the site where } x \text{-ray is absorbed.} \]
\[ \text{d}_{i\gamma \sigma} \text{ is the annihilation operator of Mn } 3d \text{ electron with spin } \sigma \text{ and orbital } \gamma \text{ and is defined by } \theta_{i\gamma \sigma} = \cos(\theta_i/2) \left[ \text{direction of } i \text{ bond in the orbital space } \gamma \right] \text{ and } \sin(\theta_i/2) \left[ \text{direction of } i \text{ bond in the orbital space } \gamma \right]. \]
\[ n_{il} \text{ is neglected, since it is experimentally confirmed to be small in the layered manorites around } x = 0.5 \text{ [6]. Thus, } \varepsilon_{d(4p)} \text{ and } \varepsilon_\sigma \text{ are chosen to be independent of } \gamma \text{ and } \alpha, \text{ respectively.} \]
\[ \text{The inter-site Coulomb interaction between } \text{Mn } 4p \text{ and O } 2p \text{ electrons is not included, because the interaction brings about the anisotropy of ASF in the same way as } V_{\gamma \alpha} \text{ [4].} \]
\[ \text{The memory function method (the composite operator method) in the Green’s function formalism is adopted in the calculation of ASF. This method is suitable to describe the excitation in the highly correlated systems [7,13] and treats the local Coulomb interactions and the } 4p \text{ band on an equal footing. We introduce the relaxation function defined by } C_{\alpha \sigma}(t) = \theta(t) \beta^{-1} \int_0^\beta d\lambda \langle J_{i\alpha \sigma}(t) J_{i\alpha \sigma}(i\lambda) \rangle \equiv \theta(t) \langle J_{i\alpha \sigma}(t) J_{i\alpha \sigma}(0) \rangle \lambda \text{ with } \beta = 1/T. \]
\[ \text{We have } \text{Im} C_{\alpha \sigma}(\omega) = \text{Im} C_{\alpha \sigma}(\omega)/\beta(\omega), \text{ } C_{\alpha \sigma}(\omega) \text{ being FT of } C_{\alpha \sigma}(t). \text{ At the end of the calculation, we take } T = 0. \text{ The final form of } C_{\alpha \sigma}(\omega) \equiv \delta M_{\alpha \sigma}^{(0)}(\omega) \text{ is given by the continued fraction [18]:} \]
\[ \frac{\delta M_{\alpha \sigma}^{(n-1)}(\omega)}{\omega - (M_0^{(n)} + \delta M^{(n)}(\omega)) I^{(n-1)}} = \frac{I^{(n)}}{\omega - (M_0^{(n)} + \delta M^{(n)}(\omega)) I^{(n-1)}}, \]
\[ \text{with } \delta M^{(n)}(\omega) = \delta M^{(n)}(\omega) + \delta M_{\beta \alpha}^{(n)}(\omega) \text{ for } n > 1. \]
\[ \delta M_{\beta \alpha}^{(n-1)}(\omega) \text{ is given by FT of } \delta M_{\beta \alpha}^{(n-1)}(t) = \theta(t) \langle \psi_{n}(t) \psi_{n}(0) \rangle \lambda. \]
\[ \delta M^{(3)}(\omega) \text{ is taken to be zero and the continued fraction is truncated at } n = 3. \text{ Here, } \psi_n \text{ is the composite operator represented by an operator product [19]. } \]
\[ \text{This calculation will be presented elsewhere. Advantages of this method in the present issue are the following: 1) The many body excitations originating from the local Coulomb interactions are treated by the composite operators. For example, } P_{i\alpha \sigma}^\dagger S_{i\alpha \sigma} P_{i\alpha \sigma}^\dagger \text{ describes the dipole transition associated with the charge transfer between Mn } 3d \text{ and O } 2p \text{ orbitals. By treating } \psi_n \text{ as a single quantum variable, the many body excitations and the interactions between them, i.e. so-called the configuration interactions, are taken into account in } \delta M_{\alpha \sigma}^{(n)}(\omega) \text{ and } M_0^{(n)}. \text{ This kind of the excitation is not treated by the independent single-particle scheme with an averaged potential. 2) The band effects of the } 4p \text{ electrons are included in } \delta M_{\beta \alpha}^{(n)}(\omega). \text{ By adopting the loop approximation in the diagram technique, where the } 4p \text{ state is treated as the single-particle state described by } H_{4p}, \text{ the itinerant character of the excitation is introduced. This kind of excitation plays a crucial role on ASF in the present case where the layered structure lifts the orbital degeneracy and is not described by the calculation in a small cluster.} \]
\[ \text{The calculated ASF is presented in Fig. 1(a), where the } d_{3z^2-r^2} \text{ orbital is occupied. The } [d_{3z^2-r^2}/d_{3p2^2-r^2}] \text{-type orbital ordered states, where the two orbitals are alternately aligned in the } xy \text{ plane, is assumed. The anisotropy of the } 4p \text{ band is characterized by } t_{xy}^\|/t_{xy}^\perp = 4 \text{ and } t_{\sigma}^\parallel/t_{\sigma}^\perp = t_{\parallel}^\perp/t_{\perp}^\parallel = 4 [24]. \text{ A continuous spectrum in } \text{Im} \Delta f_{z}(\omega) \text{ spreads over a wide region of } \omega. \text{ The weight near the } K \text{-edge is dominated by } \text{Im} \Delta f_{z}(\omega), \text{ because the } 4p_{\pi}(\omega) \text{ band is wider than the } 4p_{\sigma} \text{ band; the quasi-two-dimensional band of the } 4p \text{ electrons causes the anisotropy between } \Delta f_{z}(\omega) \text{ and } \Delta f_{\parallel}. \text{ However, it is worth to note that } \text{Im} \Delta f_{\parallel} \text{ is not the density of states itself. There are several peak structures in } \text{Im} \Delta f_{\parallel} \text{ caused by the local excitations in the } \text{MnO}_6 \text{ cluster. Near the edge, the clear anisotropy between } \text{Im} \Delta f_{\parallel} \text{ and } \text{Im} \Delta f_{\parallel} \text{ appears and } \text{Im} \Delta f_{\perp} \text{ governs the intensity. This anisotropy is caused by the Coulomb interaction between } 3d \text{ and } 4p \text{ electrons. The core hole potential makes the anisotropy remarkable, since the potential reduces the energy of the dipole transition and enhances the local character of the } 4p \text{ electrons. The scattering intensity at the orbital superlattice reflection defined by } I_{O}(\phi = \pi/2) = |\Delta f_{\parallel} - \Delta f_{\perp}|^2/(2|A|^2/m_t\omega d)^2 [24] \text{ is shown in the inset.} \]
of Fig. 1(a). Here, the azimuthal angle ($\phi$) is the rotating one of the sample around the scattering vector. For $\phi = 0$ ($\pi/2$), the electric vector of x-ray is perpendicular (parallel) to the $xy$ plane. A sharp peak near the edge together with a small intensity above the edge appear in $I_0(\phi)$. Both structures are observed in LaSr$_2$Mn$_2$O$_7$ [14]. In Fig. 1(b), we show ASF at the site where the $d_{x^2-y^2}$ orbital is occupied in the $[d_{x^2-y^2}/d_{y^2-z^2}]$-type orbital ordered state. The anisotropy between $\text{Im}A_f(\pi/2,y)$ and $\text{Im}A_f(z)$ becomes more remarkable near the edge due to the Coulomb interaction.

The anisotropies of ASF directly reflect on the polarization dependence of the scattering intensity. Let us consider the charge and orbital ordered states realized in the layered manganite at $x = 0.5$ [14]. The scattering intensities at the orbital and charge reflection points in the [$\theta - \phi$]-type orbital ordered state are given by $I_O(\phi) = |(\Delta f_x - \Delta f_y) \sin \phi|^2 / (2|A|^2/m_{pt}d^2)$ and $I_C(\phi) = |(\Delta f_x + \Delta f_y) \sin \phi + 2\Delta f_z \cos \phi|^2 / (2|A|^2/m_{pt}d^2)$, respectively [13]. The polarization dependencies of $I_O(\phi)$ and $I_C(\phi)$ are attributed to the anisotropies between $\Delta f_x$ and $\Delta f_y$ due to the local Coulomb interactions and between $\Delta f_x + \Delta f_y$ and $\Delta f_z$ due to the effects of the 4$p$ band, respectively; the itinerant and local characters of the excited 4$p$ electrons reflect on $I_C(\phi)$ and $I_O(\phi)$, respectively. The theoretical results of $I_O(\phi)$ and $I_C(\phi)$ near the edge are plotted together with the experimental data in LaSr$_2$Mn$_2$O$_7$ [14] in Fig. 2. We find good agreement with theory and experiment. Thus, we conclude that ASF in LaSr$_2$Mn$_2$O$_7$ near the edge is dominated by $\Delta f_x(y)$ and the degeneracy between $\Delta f_x$ and $\Delta f_y$ is lifted by the Coulomb interactions in the [$\theta - \phi$]-type orbital ordered state. On the other hand, the $\theta$-dependence of ASF is not so remarkable as to determine the value of $\theta$. However, from the following facts, we deduce that the $[d_{3z^2-r^2}/d_{3y^2-r^2}]$-type ordered state is more favorable in LaSr$_2$Mn$_2$O$_7$ rather than the $[d_{x^2-z^2}/d_{y^2-z^2}]$-type one; in the layered structure, the $[d_{3z^2-r^2}/d_{3y^2-r^2}]$-type ordered state gains more kinetic energy than the $[d_{x^2-z^2}/d_{y^2-z^2}]$-type one, because the 3$d$ band in the former state is wider than that in the latter, as discussed in the case of the 4$p$ band. This is consistent with the zigzag-type ferromagnetic spin alignment observed in the $xy$ plane [13]. In the $[d_{3z^2-r^2}/d_{3y^2-r^2}]$-type ordered state, the hopping integral in the $z$ direction is small, where the same kinds of charge and orbital are stacked [14]. As a result, the double exchange interaction in this direction is suppressed and the superexchange interaction between $t_{2g}$ spins causes the antiferromagnetic spin alignment as observed experimentally [13].

The anisotropy of ASF in the layered structure is quite different from that in the cubic structure where the 4$p$ band does not contribute to the anisotropy. ASF calculated on the condition $t_0^\perp/t_\sigma^\perp = t_0^\parallel/t_\sigma^\parallel = 1$ is shown in
The imaginary part of ASF. The isotropic 4p band is assumed. The $d_{xy}$ orbital is occupied in the $[d_{x^2-y^2}/d_{y^2-x^2}]$-type orbital ordered states. The straight, dashed and dotted lines show ASF for $\alpha = x, y$ and $z$, respectively. $\text{Im} \Delta f_y$ and $\text{Im} \Delta f_z$ are almost degenerate. The inset shows the polarization dependence of the scattering intensity at the charge superlattice reflection $I_C(\phi)$. The straight and broken lines show $I_C(\phi)$ for the $[d_{x^2-y^2}/d_{y^2-x^2}]$- and $[z^2-d_{x^2-y^2}]/d_{y^2-x^2}]$-type orbital ordered states, respectively.

Fig. 3 where the $d$ and broken lines show $I_S$ and $I_F$ respectively. The dotted and dashed lines show ASF for $\alpha = x, y$ and $z$, respectively. $\text{Im} \Delta f_y$ and $\text{Im} \Delta f_z$ are almost degenerate. The inset shows the polarization dependence of the scattering intensity at the charge superlattice reflection $I_C(\phi)$. The straight and broken lines show $I_C(\phi)$ for the $[d_{x^2-y^2}/d_{y^2-x^2}]$- and $[z^2-d_{x^2-y^2}]/d_{y^2-x^2}]$-type orbital ordered states, respectively.

The anisotropy of ASF in the layered manganites is highly in contrast to that in the layered nickelates and cuprates. In the latter compounds, the $K$-edge is dominated by the $z$ component and the $x(y)$ component is located above $2 \sim 10$ eV from the edge. Since the octahedron is elongated along the $z$ axis (more than 20% in cuprates and 15% in nickelates), the large hybridization between $4P_{x(y)}$ and $O2p$ orbitals pushes the $4P_{x(y)}$ band to the higher energy region. On the contrary, in the layered manganites around $x = 0.5$, the elongation is less than 1% and the orbital degree of freedom for the $4p$ electrons survives in the local sense as well as that for the $3d$ ones. Thus, contribution from the quasi-two dimensional band is relevant near the edge.

To conclude, we have studied RXS in layered manganites by taking into account the effects of the $4p$ bands and the local Coulomb interactions. The anisotropies between $\Delta f_z$ and $\Delta f_y$ and between $\Delta f_x$ and $\Delta f_y$ are reflected from the local and itinerant character of the $4p$ electrons, respectively. The calculated results well reproduce the experimental ones in La$_2$Sr$_2$Mn$_2$O$_7$.

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