Theoretical and experimental investigations of orbital excitations in correlated oxides

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Abstract. Orbital excitations in orbital-ordered transition metal oxides are investigated theoretically and experimentally. Characteristic differences in the collective orbital excitations, termed orbital waves, between the \(e_g\) and \(t_{2g}\) systems are clarified. As a probe to detect the orbital excitations, the scattering processes for the Raman scattering and the resonant and non-resonant inelastic x-ray scatterings are proposed and their scattering cross-sections are calculated. The orbital excitations in hole-doped and undoped manganites are examined experimentally by using resonant inelastic x-ray scattering. The obtained experimental results are compared with the theoretical calculations.
1. Introduction

Since the discovery of the high \( T_c \) superconducting cuprates, electronic structure of the transition-metal oxides has been reexamined from the modern theoretical and experimental points of view. A variety of exotic phenomena such as the high \( T_c \) superconductivity and the colossal magnetoresistance (CMR) are recognized to be consequences of the interplay and competition between the internal degrees of freedom of electrons under the strong electron correlation. The orbital degree of freedom, i.e. the anisotropic electronic cloud, exists in a transition-metal ion where the degeneracy of the angular-momentum quantum number partially remains in a crystal lattice with high symmetry. It is now recognized that this degree of freedom is active in a wide range of the transition-metal oxides and plays a number of crucial roles in the unusual electronic properties [1]–[3].

It was known more than 40 years ago that the orbital degree of freedom shows the long-range order termed the orbital order, and the magnetic interaction under the orbital order is anisotropic and tends to be ferromagnetic in some direction. One of the well-known materials is \( \text{LaMnO}_3 \), a mother compound of the CMR phenomena. The five 3d orbitals are split into the doubly degenerate \( e_g \) orbitals and the triply degenerate \( t_{2g} \) one. In an \( \text{Mn}^{3+} \) ion, one of the four 3d electrons occupies one of the two \( e_g \) orbitals, that is, the orbital degree of freedom. The alternate alignment of the \( 3d_{3z^2-r^2} \) and \( 3d_{yz} \) orbitals is observed in the \( ab \) plane below 780 K [4, 5]. The observed A-type antiferromagnetic structure, where spins order ferromagnetically in the plane and antiferromagnetically along the \( c \)-axis, and the anisotropic spin-wave dispersion relation are understood well in this order of orbitals. Another class of the transition-metal oxides with the orbital degree of freedom is that of vanadium oxides with perovskite structure, \( \text{LaVO}_3 \) [6]. The triply degenerate \( t_{2g} \) orbitals in a \( \text{V}^{3+} \) ion are occupied by two electrons. Below 145 K, the \( d_{xy} \) orbital is occupied by an electron at each V site, and the staggered pattern of the \( d_{yz} \) and \( d_{xz} \) orbitals appears. The C-type antiferromagnetic structure where spins align antiferromagnetically in the plane and ferromagnetically along the \( c \)-axis appears below 143 K.
Apart from the classical orbital order, the orbital degree of freedom is the quantum variable of an electron, as well as spin and charge degrees of freedom, and has its own dynamics. Known as the collective spin excitation, magnon, in the magnetically ordered state, the collective orbital excitation is expected to exist in the long-range orbital order which is termed ‘orbital wave’ and its quantized objects as ‘orbiton’. Another class of the orbital excitation is the individual excitation; e.g. the inter- and intra-site electronic excitations between the different orbital symmetries.

Until recently, this excitation of the orbital was a matter of theoretical prediction. However, the recent experimental progress changes the situation; we have the possibility of detecting the orbital excitation directly by utilizing a plural number of the experimental technique [7]. In particular, the synchrotron radiation source and related techniques are developed rapidly. The x-ray scattering experiments utilizing them are recognized to be a powerful tool to detect the bulk excitation including the orbital excitations [8].

In this paper, we review our recent theoretical and experimental efforts for the orbital excitations in correlated electron systems. The characteristic difference of the orbital waves in the eg and t2g systems, i.e. the perovskite manganites and vanadates, is studied. As a probe to detect the orbital excitations, the scattering processes and the cross-section of Raman scattering, the resonant and non-resonant inelastic x-ray scatterings (IXSs) are examined theoretically. The orbital excitations in hole-doped and undoped manganites are examined experimentally by using the resonant inelastic x-ray scattering (RIXS). The obtained experimental results are compared with the theoretical calculations.

2. Theory of orbital excitation and their observation

2.1. Orbital excitation

In the doubly degenerate orbital system with the Eg symmetry, the orbital degree of freedom is represented mathematically by the pseudo-spin operator with magnitude 1/2 defined as

\[ \hat{T}(i) = \frac{1}{2} \sum_{\gamma \gamma'} \hat{c}_{\gamma}(i) \hat{\sigma}_{\gamma \gamma'} \hat{c}_{\gamma'}(i), \]  

where \( \hat{c}_{\gamma}(i) \) is the electron annihilation operator with spin \( s(= \uparrow, \downarrow) \), orbital \( \gamma (= 3z^2-r^2, x^2-y^2) \) at site \( i \), and \( \hat{\sigma} \) are the Pauli matrices, i.e. the generators of the SU(2) Lie algebra. The orbital-order parameters are represented by the expectation value of the pseudo-spin operator at some momentum. Deviation from the averaged values of the pseudo-spins corresponds to the orbital excitation:

\[ \hat{T}(\vec{k}) = \langle \hat{T}(\vec{k}) \rangle + \delta \hat{T}(\vec{k}), \]  

where \( \hat{T}(\vec{k}) \) is the Fourier transform of the pseudo-spin operator \( \hat{T}(i) \), and \( \langle \cdot \cdot \cdot \rangle \) implies the thermal average. In the case where the transition-metal ion has the triply degenerate orbitals with the T2g symmetry, such as the titanates and vanadates with perovskite crystal structure, the orbital degree of freedom is denoted by the eight orbital operators given by [9]

\[ O_{\Gamma \gamma}(i) = \sum_{ab} c_{a\ell}^\dagger(i) \bar{c}_{a\ell}^{(l)}(i), \]  

where \( O_{\Gamma \gamma}(i) \) is the orbital operator in the \( \Gamma \) representation and \( c_{a\ell} \) and \( \bar{c}_{a\ell} \) are the electron annihilation and creation operators, respectively.
for \( l (= 1 \sim 8) \) where we define (\( \Gamma \gamma, l \)) = (Eu; 8), (Ev; 3), (\( T_2x; 6 \)), (\( T_2y; 4 \)), (\( T_2z; 1 \)), (\( T_1x; 7 \)), (\( T_1y; 5 \)) and (\( T_1z; 2 \)). Suffices \( a \) and \( b \) indicate the three \( t_{2g} \) orbitals with the \( xy \), \( yz \), and \( zx \) symmetries and \( \lambda(l) \)'s are the \( 3 \times 3 \) Hermitian matrices termed the Gell-Mann matrices, i.e. the generators of the SU(3) Lie algebra. Here, we follow the notation of the Gell-Mann matrices defined in the textbook of quantum mechanics by Schiff [10].

OE\( _u(i) \) and OE\( _v(i) \) have the \( E_g \) symmetry describing the polarization of the \( xy \), \( yz \) and \( zx \) orbitals, \( O_{T_2x}(i), O_{T_2y}(i) \) and \( O_{T_2z}(i) \) have the \( T_{2g} \) symmetry for the real mixing of the three orbitals, and \( O_{T_1x}(i), O_{T_1y}(i) \) and \( O_{T_1z}(i) \) have the \( T_{1g} \) symmetry for the complex mixing of the orbitals, i.e. the orbital angular momenta.

When the orbital excitation occurs in an isolated ion between the large energy splitting, this excitation is known to be the d–d excitation between the crystalline field splitting, e.g. the famous \( 4A_2 \rightarrow 4T_2 \) (\( 4T_1 \)) transition in a Cr\(^{3+} \) ion of ruby observed around \( 18 000 \text{ cm}^{-1} \) (\( 25 000 \text{ cm}^{-1} \)). What we are concerned here is the wave-like excitations in the almost-degenerate orbitals propagating coherently in a system. The inter-site interaction between the orbitals and the Hamiltonian describing them are essential for the orbital wave excitation of our interest. We present the following three kinds of orbital Hamiltonians and the orbital excitations expected from these models. Here we restrict ourselves to the case of the doubly degenerate \( e_g \) orbital systems.

1. The virtual electronic exchanges between the nearest-neighbour transition metal sites under the strong Coulomb interactions, the so-called superexchange interactions, cause the interactions between the orbitals. In the case of the cubic perovskite crystal, the Hamiltonian is given as

\[
\mathcal{H} = -2J_1 \sum_{\langle ij \rangle} \left\{ \frac{3}{4} - \vec{S}(i) \cdot \vec{S}(j) \right\} \left\{ \frac{3}{4} - \tau \lambda(i) \tau \lambda(j) \right\} = -2J_2 \sum_{\langle ij \rangle} \left\{ \frac{3}{4} - \vec{S}(i) \cdot \vec{S}(j) \right\} \left\{ \frac{3}{4} + \tau \lambda(i) \tau \lambda(j) + \tau \lambda(i) + \tau \lambda(j) \right\},
\]

where \( \vec{S}(i) \) is the spin operator with a magnitude \( 1/2 \) and \( \tau \lambda(i) \) is a linear combination of the pseudo-spin operators defined by

\[
\tau \lambda(i) = \cos \left( \frac{2\pi n_l}{3} \right) T_{z}(i) + \sin \left( \frac{2\pi n_l}{3} \right) T_{x}(i),
\]

with \((n_x, n_y, n_z) = (1, 2, 3) \) and a direction \( l \) of a bond connecting \( i \) and \( j \) sites. \( J_1 \) and \( J_2 \) are the exchange parameters of the order of (transfer integral)\(^2 \)/on-site Coulomb interaction. This model is derived from the generalized Hubbard model, where the doubly degenerate \( e_g \) orbital and the on-site Coulomb interactions are taken into account [11]–[13]. It is worth noting that the \( x \) and \( z \) components of the pseudo-spin operators only appear in this Hamiltonian and there is no continuous symmetry in the orbital pseudo-spin space, unlike the SU(2) symmetry in the spin space. The orbital waves calculated for LaMnO\(_3\) based on the Hamiltonian in equation (4) are introduced later in detail. The spin–orbital excitations are also investigated in the simplified anisotropic orbital model [14, 15]

\[
\mathcal{H} = J \sum_{\langle ij \rangle} \left[ 4 \vec{S}(i) \cdot \vec{S}(j) \left( \tau \lambda(i) - \frac{1}{2} \right) \left( \tau \lambda(j) - \frac{1}{2} \right) + \left( \tau \lambda(i) + \frac{1}{2} \right) \left( \tau \lambda(j) + \frac{1}{2} \right) \right],
\]

which is obtained from equation (4) by assuming \( J_1 = J_2 \) corresponding to neglecting the ferromagnetic Hund coupling in a transition metal ion. The orbital interaction by considering
both the electron–electron and electron–lattice interactions are also investigated by several authors [16]–[19].

2. The orbital wave in a model in which the orbital space has a continuous symmetry [20]–[22]. The excitation in the orbital-ordered state is essentially the same as the spin wave in the Heisenberg model, i.e. the gapless Goldstone mode. A particularly interesting example is the so-called one-dimensional SU(4) spin–orbital model [23]–[25];

\[ \mathcal{H} = J \sum_{\langle ij \rangle} \left\{ \vec{S}(i) \cdot \vec{S}(j) + \frac{1}{4} \right\} \left\{ \vec{T}(i) \cdot \vec{T}(j) + \frac{1}{4} \right\}. \] (7)

This model has a SU(4) symmetry where the generators are \( \vec{S}(i), \vec{T}(i) \) and \( \vec{S}(i) \vec{T}(i) \). One of the important issues expected from this model is the frustration; when both \( \vec{S}(i) \) and \( \vec{T}(i) \) are aligned antiferromagnetically, the term of \( \{ \vec{S}(i) \cdot \vec{S}(j) \} \{ \vec{T}(i) \cdot \vec{T}(j) \} \) increases the energy. Then, the non-trivial ground state in this model is found by the numerical analyses to be a singlet with a periodicity \( 4a \), and the elementary excitations, i.e. the spin–orbital coupled excitations, are gapless and soften at \( \vec{k} = \pi/2 \) and \( \pi \).

3. The orbital–lattice coupled excitation [26, 27]. The dispersion relation of the collective excitation is dominated by the orbital–phonon interaction and the electronic exchange interaction. The vibronic collective excitation associated with the Jahn–Teller effect is called a ‘vibron’ [28].

We introduce the theoretical results of the orbital wave for the actual orbital-ordered materials, the perovskite manganites and vanadates, based on the superexchange interaction between the inter-site orbitals. The orbital order in LaMnO\(_3\) appears below \( T_{OO} = 780 \) K where the Jahn–Teller type lattice distortion of the MnO\(_6\) octahedron starts increasing alternately in the \( ab \) plane. The scattering intensity of the resonant x-ray scattering (RXS), which is a probe to detect the orbital order, is also observed below this temperature. The ordered pattern of the orbital is the so-called C-type, that is, the periodicity of the orbital order is given by the momentum \( \vec{k}_O = (\frac{\pi}{a}, \frac{\pi}{a}, 0) \) with the cubic perovskite lattice parameter \( a \). The two kinds of orbital in the ordered phase are described by the orbital angles \( (\theta_A/\theta_B) = (\frac{2\pi}{3} - \frac{2\pi}{3}, \frac{2\pi}{3}) \) which are defined by \( \theta \equiv \tan^{-1}(\langle T_x \rangle/\langle T_z \rangle) \). These correspond to the \( d_{3z^2-r^2} \) and \( d_{3y^2-r^2} \) orbitals. In other words, the orbital order parameters are represented by the orbital pseudo-spin operators as

\[ (\langle T_x(\vec{k}) \rangle, \langle T_y(\vec{k}) \rangle, \langle T_z(\vec{k}) \rangle) = \left( \frac{\sqrt{3}}{4} \delta_{\vec{k}=(\frac{\pi}{3},\frac{\pi}{3},0)}, 0, -\frac{1}{4} \delta_{\vec{k}=(0,0,0)} \right), \] (8)

It is supposed that the main interaction between the inter-site orbitals is caused by the virtual exchange of electrons, and the Hamiltonian given by equation (4) is suitable for the orbital order and excitation in LaMnO\(_3\). It is convenient to introduce the rotating frame in the \( T_z–T_x \) plane at each Mn site as

\[ \begin{pmatrix} \vec{T}_z(i) \\ \vec{T}_x(i) \end{pmatrix} = \begin{pmatrix} \cos \theta(i) & \sin \theta(i) \\ -\sin \theta(i) & \cos \theta(i) \end{pmatrix} \begin{pmatrix} T_z(i) \\ T_x(i) \end{pmatrix}, \] (9)

where the rotating angle \( \theta(i) \) is chosen to be \( \frac{2\pi}{3} \) at the sublattice \( A \) and \( -\frac{2\pi}{3} \) at \( B \). The Holstein–Primakoff transformation based on the \( 1/S \) expansion is applied to \( \vec{T}_{z(\alpha)}(i) \) [13, 29, 30].
For the site belonging to the sublattice \( A \), we have

\[
\tilde{T}_z(i) \sim \frac{1}{2} - a^\dagger(i)a(i), \\
\tilde{T}_x(i) \sim \frac{1}{2}\{a^\dagger(i) + a(i)\},
\]

where \( a(i) \) is the annihilation operator of orbiton at site \( i \). The numerical results of the orbital wave dispersion relation [13] in the A-type antiferromagnetic structure are presented in figure 1. Here, we assume the static d-type Jahn–Teller lattice distortion and neglect the interaction between orbiton and phonon. This may be reasonable because (1) the orbiton energy being of the order of \( J \) is larger than the Jahn–Teller phonon energy around 80 meV, and (2) the cooperative Jahn–Teller distortion gives a similar type of the orbital interaction with the electronic interaction [17]. The orbital–phonon coupled excitation is discussed in [26, 27] in detail.

The four branches of the dispersions are attributed to the four inequivalent Mn ions in a unit cell of LaMnO\(_3\). The eigenstates of these excitations are represented by the linear combinations of the \( e_g \) orbital excited states at each Mn site [31];

\[
\psi_{A_{1g}} = \{\psi(1) + \psi(2) + \psi(3) + \psi(4)\}, \\
\psi_{B_{2g}} = \{\psi(1) - \psi(2) - \psi(3) + \psi(4)\}, \\
\psi_{B_{1g}} = \{\psi(1) - \psi(2) + \psi(3) - \psi(4)\}, \\
\psi_{B_{3g}} = \{\psi(1) + \psi(2) - \psi(3) - \psi(4)\}.
\]

The wave function \( \psi(i) \) indicates the orbital excited state at site \( i \), i.e. the occupied orbital is changed from \( \theta(i) \) into \( \theta(i) + \pi \). Sites \( l \) of \( \psi(l) \) indicate the position of Mn ions; \( \tilde{r}(i) \) for \( l = 1 \), \( \tilde{r}(i) + a\hat{x} \) for \( l = 2 \), \( \tilde{r}(i) + c\hat{z} \) for \( l = 3 \) and \( \tilde{r}(i) + a\hat{x} + c\hat{z} \) for \( l = 4 \). The energy gap shown in the orbital-wave dispersion is caused by the following reasons: (1) the anisotropy of the pseudo-spin space in the Hamiltonian equation (4), i.e. the anisotropy gap, (2) the breaking of the cubic symmetry due to the anisotropic A-type antiferromagnetic order, and (3) the static Jahn–Teller type distortion acting as an external field on the pseudo-spin.

The perovskite vanadates RVO\(_3\) with the \( t_{2g} \) orbital degree of freedom is recognized to be another class of orbital system where the collective orbital excitation is expected to be realized.

**Figure 1.** Dispersion relation of the orbital wave in LaMnO\(_3\).
The two kinds of spin and orbital-ordered phases are observed in the ground state. The three-dimensional staggered spin order, termed the G-type antiferromagnetic order, is associated with the rod-type orbital order, termed the C-type orbital order, i.e. abbreviated as (SG/OC) phase. In this orbital order, observed at low temperatures in YVO₃, the dₓᵧ orbital is occupied by an electron at each site and the dₓz and dᵧz orbitals are aligned alternately. Another spin/orbital order is termed the (SC/OG) phase, where the C-type antiferromagnetic order is associated with the G-type orbital case. This is observed in LaVO₃. The orbital Hamiltonian corresponding to equation (4) is obtained in the triply degenerate t₂g orbital systems as [9]

\[ \mathcal{H}_J = \mathcal{H}_{4A^2} + \mathcal{H}_{2E} + \mathcal{H}_{2T_1} + \mathcal{H}_{2T_2}, \]

where \(4A^2, 2E, 2T_1\) and \(2T_2\) indicate the intermediate \((t_{2g})^3\) configurations of the exchange processes. The leading term involves the high-spin \(4A^2\) state explicitly given as

\[ \mathcal{H}_{4A^2} = -\frac{J_{4A^2}}{6} \sum_{(ij)} \left( 2 + \vec{S}(i) \cdot \vec{S}(j) \right) \left( -A^l_+ + A^l_- + B^l - 2C^l \right), \]

where \(\vec{S}(i)\) is the spin operator with magnitude \(S = 1\). \(J_{4A^2}\) is the exchange interaction. Other terms of the Hamiltonian are also expressed as the products of the spin and orbital parts. The orbital sector in \(\mathcal{H}_{4A^2}\) involving \(A^l, B^l\) and \(C^l\), where \(l = (x, y, z)\) indicates a direction of a bond, is expressed by the local orbital operators at sites \(i\) and \(j\) as

\[ A^l_\pm = \left\{ \frac{2}{3} - \frac{2}{3} \mathcal{O}_{Eu}(i) \right\} \left\{ \frac{2}{3} - \frac{2}{3} \mathcal{O}_{Eu}(j) \right\} \pm \mathcal{O}_{Eu}(i) \mathcal{O}_{Eu}(j), \]

\[ B^l = \left\{ \frac{2}{3} + \frac{2}{3} \mathcal{O}_{Eu}(i) \right\} \left\{ \frac{2}{3} - \frac{2}{3} \mathcal{O}_{Eu}(j) \right\} + \left\{ \frac{2}{3} - \frac{2}{3} \mathcal{O}_{Eu}(i) \right\} \left\{ \frac{2}{3} + \frac{2}{3} \mathcal{O}_{Eu}(j) \right\}, \]

\[ C^l = 2(\mathcal{O}_{T_2l}(i) \mathcal{O}_{T_2l}(j) + \mathcal{O}_{T_3l}(i) \mathcal{O}_{T_3l}(j)). \]

\(\mathcal{O}_{Eu}(i)\) and \(\mathcal{O}_{Eu}(i)\) are defined by

\[ \begin{pmatrix} \mathcal{O}_{Eu}(i) \\ \mathcal{O}_{Ev}(i) \end{pmatrix} = \begin{pmatrix} \cos \frac{2\pi}{3} m_l & \sin \frac{2\pi}{3} m_l \\ -\sin \frac{2\pi}{3} m_l & \cos \frac{2\pi}{3} m_l \end{pmatrix} \begin{pmatrix} \mathcal{O}_{Eu}(i) \\ \mathcal{O}_{Ev}(i) \end{pmatrix}, \]

with \(m_l = (1, 2, 3)\) for a direction of the bond \(l = (x, y, z)\).

As well as the eₓ orbital systems, the orbital order parameter in RVO₃ is given by the expectation value of the orbital operator \(O_{1/2}(i)\), and the dispersion relations are obtained by the Holstein–Primakoff transformation for the generators in the SU(3) algebra. For example, at a site where the dₓᵧ orbital is occupied by a hole, there are two excitation modes; an excitation between the dₓᵧ and dₓz orbitals denoted by a boson operator \(y(y^\dagger)\), and that between dₓy
and $d_{zx}$ denoted by $x (x^\dagger)$. The orbital operators $O_{\Gamma_\gamma}(i)$ are transformed into these boson operators as [32]

\begin{align}
O_{E_a}(i) &= \sqrt{\frac{2}{3}} - \sqrt{\frac{3}{2}} \{ n_x(i) + n_y(i) \}, \\
O_{E_b}(i) &= \frac{1}{\sqrt{2}} \{ n_x(i) - n_x(i) \}, \\
O_{T_{\alpha z}}(i) &= \begin{pmatrix} -i \\ 1 \end{pmatrix} \alpha \{ y(i)^\dagger x(i) \pm x(i)^\dagger y(i) \}, \\
O_{T_{\alpha y}}(i) &= \begin{pmatrix} i \\ 1 \end{pmatrix} \alpha \{ \sqrt{1 - N(i)} y(i) \pm y(i)^\dagger \sqrt{1 - N(i)} \}, \\
O_{T_{\alpha x}}(i) &= \begin{pmatrix} -i \\ 1 \end{pmatrix} \alpha \{ x(i)^\dagger \sqrt{1 - N(i)} \pm \sqrt{1 - N(i)} x(i) \}.
\end{align}

(21)

with $\alpha = (1, 2)$. The plus and minus signs in $O_{T_{\alpha z}}(i)$, $O_{T_{\alpha y}}(i)$ and $O_{T_{\alpha x}}(i)$ are for the $\alpha = 1$ and $\alpha = 2$ cases, respectively. We define $N(i) = n_x(i) + n_y(i)$ with $n_x(i) = x(i)^\dagger x(i)$ and $n_y(i) = y(i)^\dagger y(i)$. In the linear spin-wave approximation, the factor $\sqrt{1 - N(i)}$ is replaced by 1.

The numerical results of the dispersion relations in the (SC/OG) and (SG/OC) phases are presented in figure 2 [32]. In both the (SC/OG) and (SG/OC) phases, there are four modes of the orbital wave attributed to the two different orbital occupied sites in a unit cell; there are the excitations $y_A (d_{xy} \rightarrow d_{yz})$ and $z_A (d_{zx} \rightarrow d_{yz})$ at site A where the $d_{xy}$ and $d_{zx}$ orbitals...
are occupied, and the excitations \( x_B (d_{x'y} \rightarrow d_{z'}) \) and \( z_B (d_{y'z} \rightarrow d_{x'}) \) at site B where the \( d_{x'y} \) and \( d_{y'z} \) orbitals are occupied. Two of the four, i.e. \( y_A \) and \( x_B \), are the local modes within the linear spin-wave theory and do not show dispersion. The remaining modes, \( z_A \) and \( z_B \), are dispersive along the \( z \) direction. In the \((\text{SC}/\text{OG})\) phase, this energy has its minimum at \( k_z = 0 \) and the energy gap is attributed to the anisotropy in the orbital space, i.e. a lack of the SU(3) symmetry, in the orbital part of the Hamiltonian. In comparison with the orbital wave in the \((\text{SC}/\text{OG})\) phase, the orbital wave in the \((\text{SG}/\text{OC})\) phase is barely stable; on decreasing the spin correlation, a remarkable softening around \( \vec{k} = (0, 0, \frac{\pi}{a}) \) occurs.

2.2. Orbiton and Raman scattering

One of the issues of the collective orbital excitation in the orbital-ordered state, orbiton, is the experimental methods to detect this new elementary excitation in a solid. The optical absorption/reflection does not act as a probe to detect the orbiton because the two \( e_g \) orbitals have the same parity, except for the optical transition associated with excitations of the odd-parity lattice vibration. Raman scattering caused by the second-order electron–photon process can be used as a probe to detect orbital waves [31]–[33]. It is known that the magnons in an antiferromagnetic order are observed by the Raman scattering as a two-magnon scattering. The orbiton is also expected to be excited by photons through the inter-site exchange processes of electrons in the orbital-ordered state.

The main Raman scattering processes are different between the \( e_g \) and \( t_{2g} \) systems as shown in figure 3. In the \((d_{3z^2-r^2}/d_{3y'z'-r'})\) orbital-ordered state in LaMnO\(_3\), one-orbiton scattering is possible; consider an Mn–O bond where the orbital \( \gamma \) is occupied by an electron at the Mn site. One of the O 2p electrons is excited by a photon to the unoccupied \( \bar{\gamma} \) orbital at the Mn site, and then the electron of the \( \gamma \) orbital is transferred into the O 2p orbital by a second photon. Finally, the occupied orbital at the Mn site is changed and the orbiton is created by photons. This process is schematically represented by

\[
|\gamma\rangle \rightarrow |(e_g)^2 L\rangle \rightarrow |ar{\gamma}\rangle,
\]

where \( L \) indicates the O 2p state occupied by a hole. Consider the Raman scattering by orbiton where the energy, momentum and polarization of the initial (scattered) photon are \( \omega_i (\omega_f) \), \( \vec{k}_i (\vec{k}_f) \), with \( \gamma \) being the momentum of the orbiton.
and \(\lambda_i(\lambda_f)\), respectively. The differential scattering cross-section from an orbiton is given as

\[
\frac{d^2\sigma}{d\Omega dE_f} = \sigma_T \frac{\omega_f}{\omega_i} \left( \frac{ma^2}{\hbar^2} \right)^2 \frac{1}{2\pi\hbar} \int dte^{i\hbar(\omega_f-\omega_i)t} \sum_{ll'} P_{ll'} S_{ll'}^{\text{II}}(t),
\]

with \(\sigma_T = (e^2/mc^2)^2\) and \(a\) is the bond length. \(P_{ll'}\) is the polarization factor given by

\[
P_{ll'} = \langle \mathbf{e}_{ki\lambda_i} l | \mathbf{e}_{kf\lambda_f} l \rangle \langle \mathbf{e}_{ki\lambda_i} l | \mathbf{e}_{kf\lambda_f} l \rangle
\]

with the polarization vector \(\mathbf{e}_{ki\lambda}\), and \(S_{ll'}^{\text{II}}(t)\) is the dynamical correlation function defined by

\[
S_{ll'}^{\text{II}}(t) = \langle \mathcal{K}_l^1(t) \mathcal{K}_l^{\dagger}(0) \rangle.
\]

Let us introduce the annihilation operator \(\tilde{\psi}_\alpha(\mathbf{k})\) for orbiton with the energy \(E_\alpha(\mathbf{k})\) and mode \(\alpha\) which are obtained by diagonalizing the Hamiltonian represented by the Holstein–Primakoff boson operators \(\psi(\mathbf{k})\). This transformation is described by the matrix \(V(\mathbf{k})\) as

\[
\tilde{\psi}_\alpha(\mathbf{k}) = \sum_{\beta} \psi_\beta(\mathbf{k}) V_{\beta\alpha}(\mathbf{k}).
\]

By using this orbiton operator, \(\mathcal{K}_l^1(t)\) in the one-orbiton process is given by

\[
\mathcal{K}_l^1 = \frac{1}{2} \sum_{\alpha} \left\{ g_{l\alpha}^1 \tilde{\psi}_\alpha(0) + g_{l\alpha}^{1\dagger} \tilde{\psi}_\alpha^\dagger(0) \right\}
\]

with the coefficients \(g_{l\alpha}^1\). Finally, we show that the dynamical correlation function reflects the orbiton at the momentum \(\mathbf{k} = 0\) as

\[
S_{ll'}^{\text{II}}(\omega) = 4N \sum_{\alpha=1}^N g_{l\alpha} g_{l\alpha}^* \delta(\omega - E_\alpha(0)).
\]

In contrast with the eg orbital system, the Raman scattering from the orbiton in the t2g systems is mainly caused by two-orbiton processes. Consider a pair of the nearest-neighbouring transition-metal sites where the occupied orbitals are different. Through the second-order processes of the interaction between photons and electrons, electrons at the two sites are exchanged and, at the final state, the occupied orbitals are changed at both sites, as shown in figure 3(b). Schematically, this process is represented as [32]

\[
|a^1(i)b^1(j)\rangle \rightarrow |a^1(i)b^1(i)\rangle \rightarrow |b^1(i)a^1(j)\rangle.
\]

This is analogous to two-magnon Raman scattering in an antiferromagnet. The scattering cross-section in this process is given by equations (23) and (25) with

\[
\mathcal{K}_l^1 = \sum_{\mathbf{k},\alpha,\beta} \tilde{\psi}_{\alpha}(\mathbf{k})^\dagger h_{\alpha\beta}(\mathbf{k}) \tilde{\psi}_{\beta}(\mathbf{k})
\]
and the coefficients $h^i_{\alpha\beta}(\vec{k})$. The Fourier transform of the dynamical correlation function in the two-orbiton Raman scattering is given by

$$S_{ll}^{\|}(\omega) = N \sum_{\vec{k}} \sum_{\alpha\beta} \delta \left\{ \omega - E^i_{\alpha}(\vec{k}) - E^i_{\beta}(\vec{k}) \right\} h^i_{\alpha\beta}(\vec{k}) h^{i*}_{\beta\alpha}(\vec{k}).$$  \hspace{1cm} (31)

We neglect orbiton–orbiton interaction, for simplicity, and $S_{ll}^{\|}(\omega)$ is represented by the convolution of the two-orbiton modes.

The difference between the Raman scatterings in the $e_g$ and $t_{2g}$ orbital systems is attributed to whether the orbital occupancy is conserved or not. In the case of the $e_g$ orbital system, the conservation of the total orbital quantum number, e.g. $\sum_i T_{iz}$ is broken due to the transfer integral between the different kinds of orbitals. That is, one-orbiton scattering is possible in this case, and the Raman scattering cross-section is proportional to the dynamical correlation function for the orbiton operator at momentum $\vec{k} = 0$. On the other hand, in the $t_{2g}$ orbital case, the electron numbers of each orbital are conserved in the electron-exchange processes caused by photons. Thus, one-orbiton scattering is prohibited and the lowest-order process is the two-orbiton one, which is similar to two-magnon Raman scattering in an antiferromagnet.

Recently, peak structures in the Raman scattering spectra were found around 120–170 cm$^{-1}$ in LaMnO$_3$ [7]. Several mechanisms have been proposed for these peak structures and the situation is still under debate [7], [34]–[36]. The theoretical Raman spectra based on the orbital wave associated with the experimental data are shown in figure 4. The relative intensity of the peak structures depends strongly on the polarization configuration. The polarization and energy dependences and relative intensity of the Raman scattering peaks are well explained by the theoretical calculations based on orbital wave scattering. It is reasonable to consider
that the plausible origin of this peak structure is orbital waves. The new peak structure in the Raman spectra is also observed in the orbital-ordered LaVO$_3$ at $\sim$65 meV [37]. Examining the polarization, temperature and initial-photon energy dependences of this structure, this is interpreted as originating from the two-orbital excitation proposed above.

2.3. Orbiton and x-ray scattering

Although Raman scattering is a suitable tool to detect the orbital waves, information on the orbiton dispersion relation obtained by this method is restricted. The RIXS and the non-resonant IXS are possible methods to detect the dispersion relation. These experimental methods have already been used as momentum-resolved probes to detect bulk excitations in solids [54, 55], and have been rapidly developed due to the recent availability of third-generation synchrotron light sources. In this section, we introduce, from the theoretical side, resonant and non-resonant inelastic scatterings as probes of orbital excitations. The present theory is restricted to the case of the eg orbital-ordered systems.

2.3.1. Non-resonant x-ray scattering

It is well known that the anisotropic charge distribution of electrons, i.e. the orbital degree of freedom, reflects on the momentum dependence of the atomic scattering factor (ASF), \( f(\mathbf{K}) \), in the x-ray and neutron scatterings. The pioneering work was done by Akimitsu and co-workers: the magnetic scattering factor reflecting ASF in the orbital-ordered K$_2$CuF$_4$ was observed directly by utilizing polarized neutron scattering experiments [39]. As an extension of the static x-ray scattering, the orbital excitations are expected to be observed by the (non-resonant) IXS. The scattering cross-section of the non-resonant x-ray scattering is

\[
\frac{d\sigma^2}{d\Omega d\omega_f} = \sigma_T \frac{\omega_f}{\omega_i} (\mathbf{e}_i \cdot \mathbf{e}_f)^2 S(\mathbf{k}_i - \mathbf{k}_f, \omega_i - \omega_f),
\]

with the charge correlation function \( S(\mathbf{K}, \omega) \). Within the linear spin wave approximation, \( S(\mathbf{K}, \omega) \) is given by

\[
S(\mathbf{K}, \omega) = N \sum_{mn} e^{-i\mathbf{K} \cdot (\mathbf{r}_n - \mathbf{r}_m)} G_n(\mathbf{K}) G_m^*(\mathbf{K}) \sum_m \delta(\omega - E_m(\mathbf{K})) (U_{\mathbf{K}n'm} U_{\mathbf{K}nm}^* + V_{\mathbf{K}n'm} V_{\mathbf{K}nm}^*). \quad (33)
\]

Here, \( E_m(\mathbf{K}) \) is the energy of the orbital wave with momentum \( \mathbf{K} \) and mode \( m \), and \( U_{nm} \) and \( V_{nm} \) are the coefficients in the Bogoliubov transformation from the operator at site \( n \) to the one for mode \( m \). \( G_n(\mathbf{K}) \) is a combination of ASF defined by

\[
G_n(\mathbf{K}) = \frac{1}{2} \sin \theta_n \left[ f_{z^2-y^2}(\mathbf{K}) - f_{3z^2-r^2}(\mathbf{K}) \right] + \cos \theta_n f_{3z^2-r^2} \langle x^2-y^2 \rangle(\mathbf{K}), \quad (34)
\]

where \( f_{3z^2-r^2}(x^2-y^2) \) is ASF for the \( 3z^2-r^2(x^2-y^2) \) orbital and \( f_{3z^2-r^2} \langle x^2-y^2 \rangle(\mathbf{K}) = \langle 3z^2 - r^2 | e^{i\mathbf{K} \cdot \mathbf{r}} | x^2-y^2 \rangle \). The scattering intensity \( I_m(\mathbf{K}) \) for mode \( m \) defined by

\[
S(\mathbf{K}, \omega) = N \sum_m \delta(\omega - E_m(\mathbf{K})) I_m(\mathbf{K}), \quad (35)
\]

is presented in figure 5. There are the selection rules, e.g. (1) in the \((h \, 0 \, 0)\) scan, the B$_{1g}$ and A$_{1g}$ modes are observed at \( h = \text{odd} \) and even, respectively. (2) In the \((h \, h \, 0)\) scan, the mode A$_{1g}$
is only observed. One of the advantages in the usual IXS experiments, is the energy resolution being of the order of 10 meV which is enough to detect the orbiton. On the other hand, the scattering intensity is proportional to the square of the charge valence $Z^2$. As shown above, the effective ASF in this formulation is less than a charge unit $e$ which is smaller than the ionic charge $Ze$ by the phonon scattering. In the actual situation, the orbital-wave excitations may be associated with a certain amount of ionic clouds, and the effective charge in this orbiton excitation is expected to be larger in this calculation for the ‘bare’ orbiton. The recent experimental results of IXS for orbital-ordered compounds are reported in [38].

2.3.2. RIXS. RXS is an x-ray diffraction experiment to detect the orbital order in correlated electron systems [40, 41]. By tuning the incident x-ray energy around the absorption edge of a certain atom, the scattering factor strongly depends on the polarization of x-ray and the anisotropic distribution of the electronic cloud, i.e. the orbital, can be detected. This was first applied to the orbital order in manganites, La$_{0.5}$Sr$_{0.5}$MnO$_4$ and LaMnO$_3$ [40, 41], and independently in V$_2$O$_3$ [42]. Nowadays, the experimental technique of RXS has rapidly developed [45]–[47], and is applied to a wide variety of correlated electron systems [43, 44].

RIXS is an inelastic version of RXS. RIXS has now rapidly progressed as a probe to detect electronic excitations in both the theoretical and experimental sides [48]–[53]. Unique characteristics of RIXS are summarized: (1) the momentum dependent excitations can be detected because of the short wave-length of the hard x-ray, (2) the element-specific excitations are induced by tuning the incident x-ray energy to the absorption edge in a certain element, and (3) through the polarization analyses, the symmetry of the excitations is investigated. Very recently, the RIXS experiments have been applied to the colossal magnetoresistive manganites [8, 56, 57]. The systematic RIXS measurements for hole-doped and undoped manganites La$_{1-x}$Sr$_x$MnO$_3$ with $x = 0, 0.12, 0.3$ and $0.4$ have been done in SPring-8 where the energy, momentum and polarization dependences for charge and orbital excitations around a few eV have been investigated [8, 56].

Figure 5. Scattering amplitude of the non-resonant IXS from an orbiton.
Details of the experimental results are presented in the next section. Unfortunately, up to now, the energy resolution has been limited to be of the order of 0.1 eV which is comparable or larger than the orbiton energy. Thus, the investigation of the orbital excitation by this method is so far restricted to the electronic excitation around a few eV. Even in this energy range, when the initial and final orbital states have different orbital symmetry, this is recognized to be an individual orbital excitation.

In the RIXS processes, the initial x-ray energy is tuned around the Mn K edge. The 1s electron is excited to the unoccupied 4p levels in the intermediate states where the electronic excitations are induced through the interaction with the 4p electron and/or the 1s core hole. Finally, the 4p electron is relaxed into the 1s hole and the electronic excitations remain. We formulate the scattering cross-section in this excitation process where we consider the scattering of the incident x-rays with momentum \( \vec{k}_i \), energy \( \omega_i \) and polarization \( \lambda_i \) to \( \vec{k}_f \), \( \omega_f \) and \( \lambda_f \). We start with the conventional expression of the differential scattering cross-section given by

\[
\frac{d^2 \sigma}{d\Omega d\omega_f} = \sigma T \frac{\omega_f}{\omega_i} \sum_f |S|^2 \delta(\epsilon_f + \omega_f - \epsilon_i - \omega_i),
\]

where

\[
S = \sum_m \left\{ \frac{\langle f | \vec{j}_{-k_i} \cdot \vec{e}_{k_i\lambda_i} | m \rangle \langle m | \vec{j}_{k_f} \cdot \vec{e}_{k_f\lambda_f} | i \rangle}{\epsilon_i - \epsilon_m - \omega_f} + \frac{\langle f | \vec{j}_{k_f} \cdot \vec{e}_{k_f\lambda_f} | m \rangle \langle m | \vec{j}_{-k_i} \cdot \vec{e}_{k_i\lambda_i} | i \rangle}{\epsilon_i - \epsilon_m + \omega_i + i\Gamma} \right\},
\]

\( \vec{e}_{\lambda} \) is the polarization vector of x-ray, \( \Gamma \) is the damping of a core hole and \( \vec{j}_k \) is the current operator corresponding to the transition between Mn 1s and 4p orbitals. Here, the scattering cross-section is formulated by the Liouville-operator method, and is finally obtained as \([58, 59]\):

\[
\frac{d^2 \sigma}{d\Omega d\omega_f} = \sigma_e \frac{\omega_f}{\omega_i} \sum_{\gamma'\gamma\sigma'\sigma} P^{\gamma'\lambda_f\gamma}_{\gamma\sigma} P^{\lambda_f\lambda_i}_{\gamma'\sigma'} \Pi(\omega, \vec{K}),
\]

with \( \omega = \omega_i - \omega_f \) and \( \vec{K} = \vec{k}_i - \vec{k}_f \). \( P^{\gamma'\lambda_f\gamma}_{\gamma\sigma} \) describes the polarization part given by

\[
P^{\gamma'\lambda_f\gamma}_{\gamma\sigma} = \sum_{\alpha=x,y,z} (\vec{e}_{k_f\lambda_f})_\alpha D_{\gamma\sigma\alpha}(\vec{e}_{k_i\lambda_i})_\alpha,
\]

and \( \Pi(\omega_i - \omega_f, \vec{k}_i - \vec{k}_f) \) is the Fourier transform of the correlation function of the orbital pseudo-spin operators defined by

\[
\Pi(t, \vec{r}_i - \vec{r}_f) = \frac{|B|^4}{m^2} \langle \bar{T}_{\sigma\lambda}(i, t) \bar{T}_{\sigma\lambda}(j, 0) \rangle,
\]

where \( B \) is the matrix element of the dipole transition and \( D_{\gamma\sigma} \) gives the amplitude of the orbital excitations from the 3d orbital by x-ray with polarization \( \alpha \).

The RIXS spectra for hole-doped and undoped manganites are obtained based on the generalized Hubbard Hamiltonian where the doubly degenerate 3d \( e_g \) orbitals and the on-site Coulomb interactions are introduced. The correlation function of the pseudo-spin operators \( \Pi(\omega_i - \omega_f, \vec{k}_i - \vec{k}_f) \) is calculated by using the Hartree–Fock approximation. The calculated
spectra are shown in figure 6. The spectra have a finite gap for the A-type antiferromagnetic state with the \((d_{3z^2-r^2}/d_{3z^2-r^2})\) type orbital-ordered state at the hole concentration \(x = 0\) (LaMnO\(_3\)). This excitation is recognized to be an orbital-flip transition across the gap between the upper and lower Hubbard bands (LHBs). Because the symmetries of the orbital for the lower and upper Hubbard bands (UHBs) are different, the electronic excitation changes the symmetry of the orbital. The connection between the theoretical results and the experimental RIXS spectra in LaMnO\(_3\) is discussed in the next section in more detail.

With doping of holes, the stable orbital state is changed as the \((d_{3z^2-r^2} + d_{x^2-y^2}/d_{3z^2-r^2} - d_{x^2-y^2})\)-type in the ferromagnetic state at \(x = 0.1\), and the \(d_{x^2-y^2}\)-type in the A-type antiferromagnetic one at \(x = 0.5\). The spectra show the finite intensity in the lower energy region, that is the intra-band transition, since the system becomes a metal. A significant change of the spectral shape for the intra-band transition in the higher-energy range is attributed to the change of the orbital state. Through systematic comparisons with the experimental results, the present calculations help us to understand how the electronic structures change by doping of holes into the orbital-ordered Mott insulator.

3. Experiments

In this section, we review the recent experimental results of RIXS in the orbitally ordered Mott insulator LaMnO\(_3\) and its hole-doped compounds La\(_1-x\)Sr\(_x\)MnO\(_3\) \((x = 0.2, 0.4)\). The individual orbital excitation across the Mott gap is observed in LaMnO\(_3\). The excitation has a weak dispersion and characteristic azimuthal-angle dependence, which are well explained by the theory. The spectra of the doped compounds also show the trace of the Mott gap and weak azimuthal-angle dependence though the energy gap is partially filled by the doping. We also found an anisotropic temperature dependence of the scattering intensities in the sample of \(x = 0.2\).

3.1. Experimental technique of RIXS

As mentioned in the previous section, the RIXS technique is very powerful for studying electronic excitations because photons are directly coupled with electrons and the cross-section
can be significantly enhanced by exploiting the resonant condition. The scattering process is charge neutral so that final-state effects are eliminated, which is different from photoemission and x-ray absorption spectroscopy experiments. The RIXS is also a bulk sensitive probe and can elucidate the electronic states in high pressures and magnetic fields. After the pioneering work by Kao et al [51], RIXS has been applied to many transition metal oxides, especially cuprates related to high-$T_C$ superconductors [52, 53], [61]–[67]. The information on the dispersion relation of the UHB has been examined in detail. Meanwhile, the RIXS study on manganites has started at SPring-8 [8]. Manganites have become extremely important because the orbital degree of freedom causes a variety of exotic phenomena such as the CMR. The RIXS signal of manganites, however, is very weak compared with that of cuprates, because the K-absorption-edge energy of the manganese ion is much lower than that of the copper ion. In spite of the experimental difficulties, the experiments are going well, because the recent high brilliance of x-rays from undulator beam lines at third generation synchrotron facilities has made it possible to obtain such a weak signal of RIXS.

A series of experiments has been carried out at a JAERI (Japan Atomic Energy Research Institute) beam line 11XU of SPring-8 [68]. Incident x-rays from the standard undulator were monochromatized by a double-crystal diamond (1 1 1). We use Si (3 3 3) as a second monochromator when we need to get a higher-energy resolution. In these experiments, the spectrometer was tuned for x-rays of 6.55 keV, the K-absorption edge of the manganese ion. The beam was focused onto a sample by a horizontally bent mirror, which was the Pt-coated fused-quartz mirror of 50 cm long. The beam size at the sample was typically 0.12 mm (horizontal) × 1.4 mm (vertical). The photon flux at the sample was about $2 \times 10^{12}$ photons s$^{-1}$. The inelastic x-ray spectrometer consists of $2\theta$, $\omega$, $\chi$, and $\phi$ sample tables attached with $x$ and $y$ tables. The sample, the analyser and the detector are placed approximately on a Rowland circle of about 2 m in diameter. The energy was analysed by a Johann-type spherically bent diced Ge (5 3 1) crystal. The total energy resolution, which was determined from the quasi-elastic scattering from a sample, was about 500 meV full-width at half-maximum. This is mainly due to the misorientation of the analyser crystals from the spherical surface. The energy resolution could be improved by applying the detector slit to about 130 meV.

Single crystal samples of La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0, 0.2, 0.4$) were grown by the floating-zone method. Several samples were cut and polished to have [1 0 0] and [1 1 0] directions normal to the surface. In this paper, we take the Pbnm notation for all samples to easily compare with each other though the crystal structure of the compound with $x = 0.4$ is rhombohedral. All the data of LaMnO$_3$ and the $x = 0.4$ samples were measured at room temperature, while the $x = 0.2$ sample was mounted on the spectrometer in a closed cycle refrigerator for the measurement of temperature dependence.

3.2. RIXS spectra of the undoped compound LaMnO$_3$

It is essential for our understanding of manganite physics to observe orbital excitations. However, dynamics of the orbital degree of freedom have not been intensively investigated so far unlike spin and lattice dynamics, because the experimental technique to detect the excitations has been very limited. In orbitally ordered insulators, the dynamics of the orbital is classified into two different excitations. One is a collective orbital excitation termed an orbital wave, which corresponds to the spin wave in magnetically ordered materials. The other is individual orbital excitation, i.e. the particle–hole excitation, which is related to the Stoner excitations in ordered magnetic
systems. In orbitally ordered insulators, highest occupied and lowest unoccupied electronic states have different orbital characters. The particle–hole excitation across the Mott gap changes the symmetry of the electronic cloud; this is the latter orbital excitation. In this study, we direct our attention to this individual orbital excitation owing to the limited energy resolution of the spectrometer.

Figure 7 shows the inelastic scattering as a function of energy loss for several incident energies \( E_i \) across the Mn K absorption edge at the momentum transfer \( \vec{q} = (1.6, 1.6, 0) \) [8]. The resonant nature of the scattering is obviously observed. The three resonant peaks are observed at 2.5, 8 and 11 eV at \( E_i = 6.556 \) keV. The additional broad peak in the higher energy-loss region is the Mn K\( \beta_5 \) emission which is due to the transition from 3d to 1s state. In the spectrum of \( E_i = 6.554 \) keV, only the excitation at 2.5 eV is observed, while the 2.5 eV peak vanishes and the 8 and 11 eV peaks remain at \( E_i = 6.560 \) keV. This implies different origins for these three peaks. The resonant nature of all the peaks indicates that manganese bands take part in these transitions. According to optical conductivity and photon-emission measurements, we can ascribe the 8 eV peak to the transition from O 2p to empty Mn 3d bands and the 11 eV peak from O 2p to Mn 4s/4p bands. On the other hand, the 2.5 eV peak is considered to be a transition from the effective LHB to the UHB across the Mott gap. This is the lowest excitation in LaMnO\(_3\). In the orbitally ordered state, the occupied orbitals are \( 3x^2 - r^2 \) and \( 3y^2 - r^2 \). These orbitals strongly hybridized with the oxygen 2p orbitals with the same symmetries; these states constitute the highest occupied \( e_g \) band, which is dispersive. In contrast, the lowest unoccupied \( e_g \) band consists of the 3d\( _{x^2 - y^2} \) and 3d\( _{z^2 - r^2} \) orbitals which has different orbital symmetry from that of the LHB. Therefore, the excitations from the LHB to the UHB change the symmetry of the orbitals. This is a unique characteristic of this excitation.

The momentum dependence of the inelastic scattering along \((h h 0)\) and \((h 0 0)\) is examined in the \( q \) regions \((1.6 \leq h \leq 2.7)\) and \((2.4 \leq h \leq 3.9)\), respectively. These three peaks show a
Figure 8. The electronic band structure for the orbital-ordered LaMnO$_3$ [59]. The alternate ordering of the $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbital in the $ab$ plane is assumed. The broken line indicates the chemical potential located at the centre of the highest occupied and lowest unoccupied bands.

rather flat dispersion. The 2.5 eV peaks are extracted by subtracting the data of $E_i = 6.560$ keV from the data of $E_i = 6.556$ keV, and fitted by a Lorentzian curve. It is found from the peak position of the 2.5 eV peak that the energy dispersion is less than a few hundred meV. This is also supported by the detailed theoretical calculation introduced in the previous section. The dispersion of the centre of the curve exhibits a weak momentum dependence within $0.1 t_0$ where $t_0$ is the transfer integral between $3d_{3z^2-r^2}$ orbitals along the $c$-axis. This almost flat dispersion is attributed to the effects of orbital order. In figure 8, we present the electronic band structure for the orbital-ordered LaMnO$_3$. The Hartree–Fock approximation is applied to the generalized Hubbard model with the $e_g$ orbital degree of freedom [59]. The valence band, termed the LHB, located around $-3 < E/t_0 < 0$ and the conduction band, termed the UHB, around $E/t_0 \sim 5$ are mainly formed from the $(3d_{3z^2-r^2}/3d_{3y^2-r^2})$ and $(3d_{x^2-z^2}/3d_{x^2-y^2})$ orbitals respectively. The RIXS spectra are approximately given by the convolution of these upper and LHBs. Since the electron hopping between the unoccupied orbitals is forbidden in the $ab$ plane, the dispersion of the UHB is almost flat as seen in figure 8. As a result, the RXS spectra are dominated by the density of state of the LHB and show almost flat dispersion.

The other pronounced feature of the RIXS spectra is the polarization dependence. We measured the dependence by changing the azimuthal angle $\Psi$, which is the rotation of the
sample about the scattering vector. Figure 9 shows the scattering intensity of the 2.5 eV peak at \( \vec{q} = (3.4, 0, 0) \) as a function of \( \Psi \). The open and closed circles represent the integrated and the peak intensity at the energy transfer 2.5 eV, respectively. Both intensities exhibit a characteristic oscillation with a two-fold symmetry. We simultaneously measured the Mn K\( \beta_5 \) fluorescence line, the intensity is independent of the azimuthal angle. This indicates that the observed azimuthal angle dependence comes from intrinsic origins. The solid line shows the integrated intensity of the theoretically calculated RIXS spectra for the orbital-ordered LaMnO\(_3\) as a function of the azimuthal angle. The calculated intensity shows an oscillation with a periodicity \( \pi \) and becomes a minimum at \( \pm \pi/2 \). This dependence is expressed by a linear combination of \( A \sin^2 \Psi + B \sin^2 \Psi \cos^2 \Psi + C \cos^2 \Psi \), where the first term is common with the \( \Psi \) dependence of RXS and the second and third terms are unique in the inelastic scattering. Due to these terms, the minimum value of the intensity becomes finite and the \( \Psi \) dependence of the intensity includes the higher harmonics. The theoretical results explain qualitatively the experimental data for the 2.5 eV peak. The quantitative difference between theory and experiments is seen in the oscillation amplitude, i.e. the minimum value of the scattering intensity at \( \Psi = \pm \pi/2 \). This may be attributed to the mean-field calculation, where the orbital fluctuation is neglected and the oscillation amplitude is supposed to be overestimated.

3.3. RIXS spectra of the doped compounds La\(_{1-x}\)Sr\(_x\)MnO\(_3\)

The carrier-doping into Mott insulators causes various remarkable phenomena such as high \( T_C \) superconductivity and CMR. The electronic state of these compounds is quite changed in the wide-energy range from that of the undoped compounds. The reconstructed electronic structure near the Fermi level is essential for the electronic and magnetic properties. The optical measurement is useful to get the relevant information near zero momentum transfer but we need to know the momentum dependence of the electronic structure to understand the properties. As we mentioned, the RIXS is an ideal tool to study the momentum dependence of the electron excitations around a few eV.

**Figure 9.** Azimuthal angle dependence of the 2.5 eV peak in LaMnO\(_3\) at \( \vec{q} = (3.4, 0, 0) \) [8]. ○, integrated intensity; ●, peak intensity; and ×, intensity of the Mn K\( \beta_5 \) fluorescence.
We can dope the hole into LaMnO$_3$ by substituting Sr for La. In the hole-doped compound La$_{1-x}$Sr$_x$MnO$_3$, the CMR is observed around the ferromagnetic transition. The inset of figure 10 shows the phase diagram [69]. In the low-doping region, a canted antiferromagnetic insulating and a ferromagnetic insulating phase appears at low temperatures, while a ferromagnetic metallic state becomes stable in the high-doping region. We have carried out the RIXS experiments in the metallic region and compared them with those of the undoped one.

Figure 10 shows RIXS spectra of $\vec{q} = (2.7, 0, 0)$ in the compounds with $x = 0, 0.2$ and $0.4$ at the resonant energy $E_i = 6.556$ keV [56]. We focus the lowest energy excitation across the Mott gap in the undoped compound. The peak structure in the energy region around 2 eV has been observed in the ferromagnetic metallic states of both samples of $x = 0.2$ ($T = 7$ K) and 0.4 ($T = 300$ K). A large spectral weight is observed at the excitation from the LHB to the UHB. This result implies that the strong electron correlation remains even in the metallic state. The spectral weight of these peaks, however, shows a little lower energy shift by hole-doping. In the rigid band picture, the gap should become larger because the hole-doping lowers the Fermi level. This means that the rigid band picture is not applicable and the hole-doping decreases the effective electron correlations.
The momentum transfer dependence of the low-energy excitation in the sample of \( x = 0.4 \) has been examined to compare with that of LaMnO\(_3\). The spectra along \( \vec{q} = (h, 0, 0) \) were measured in the \( q \) range (2.7 \( \leq h \leq 4.1 \)). It is found that the magnitude of the dispersion is small and at most 0.4 eV which is comparable to that of LaMnO\(_3\). This result also suggests that the short-range correlation of the orbitals remains even in the metallic state because the dispersionless character is attributed to the orbital state of the UHB. The other evidence of the short-range orbital correlation can be obtained by the polarization dependence of the scattering intensities. Figure 11 shows the scattering intensity for an energy transfer of 2 eV at \( \vec{q} = (2.7, 0, 0) \) as a function of the azimuthal angle [56]. The data are normalized by the fluorescence yield simultaneously obtained. We can clearly see a two-fold symmetry like LaMnO\(_3\). This two-fold symmetry is weak compared with the undoped case: when we fit the oscillation part using a function of \( A(1 + B \cos 2\Psi) \), we obtain \( B = 0.38 \) and 0.19 for LaMnO\(_3\) and La\(_{0.6}\)Sr\(_{0.4}\)MnO\(_3\), respectively. This means that the excitation between two \( e_g \) orbitals is more isotropic in the doped sample than that in the undoped sample. The gap structure of the RIXS spectra, the momentum dependence, and the polarization dependence indicate that the orbital correlation still remains even in the highly doped metallic phase owing to the Coulomb interaction between the two \( e_g \) orbitals.

Finally, we focus on the temperature dependence of the RIXS spectra in La\(_{0.6}\)Sr\(_{0.4}\)MnO\(_3\), where the paramagnetic insulator is transformed into the ferromagnetic metal at 309 K. The compound also shows a structural phase transition at 100 K from rhombohedral to orthorhombic. We have found that the intensity around 2–4 eV fairly increases with decreasing temperature along \( \vec{q} = (h, 0, 0) \) at \( E_i = 6.556 \) keV. On the other hand, the intensity at \( \vec{q} = (h, h, 0) \) is almost independent of temperature. Figure 12 shows the temperature dependence of RIXS intensities at a fixed energy transfer of 2.25 eV at \( \vec{q} = (3.3, 0, 0) \) and \( (2.2, 2.2, 0) \) [56]. We can see the increase in the intensities at \( \vec{q} = (3.3, 0, 0) \) with decreasing temperature, while the intensities at \( \vec{q} = (2.2, 2.2, 0) \) is almost constant. Namely, the temperature dependence in the inter-band excitations from the LHB to the UHB depends on the direction of the scattering vector. Because the double exchange interaction dominates in the ferromagnetic metal, the ferromagnetic spin order of \( e_g \) electrons increases the transition probability from the LHB to the UHB. The change in the RIXS intensity along \( (h, 0, 0) \) direction may be attributed to the evolution of the double exchange interaction.
Figure 12. Temperature dependence of the RIXS intensity at a fixed energy transfer of 2.25 eV in La$_{0.8}$Sr$_{0.2}$MnO$_3$ [56]. •, intensity at $\vec{q} = (3.3, 0, 0)$; ○, intensity at $\vec{q} = (2.2, 2.2, 0)$; and the arrow indicates the ferromagnetic transition temperature.

exchange ferromagnetic interaction. The temperature dependence is qualitatively consistent with that of the magnetization [69]. On the other hand, the temperature dependence along the $\langle h, h, 0 \rangle$ direction cannot be simply understood at this stage. Although the ferromagnetic superexchange interaction along this direction might play an important role on the RIXS intensities, this is still under debate.

4. Summary

We have reviewed, in this paper, our recent theoretical and experimental results of the orbital excitations in the transition-metal oxides with strong electron correlation. We show the several characteristics of the orbital excitations in the $e_g$ and $t_{2g}$ orbital systems, as well as the experimental results in order to detect them. The orbital excitations are one of the fundamental elementary excitations in solids, and are expected to largely affect their magnetic, optical and transport properties, as are the magnetic excitations. The rapid development of the synchrotron radiation experiments in combination with the theoretical studies will uncover the whole picture of the orbital excitations for the foreseeable future.

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