Resonant Inelastic X-ray Scattering from Charge and Orbital Excitations in Manganites

H. Kondo, S. Ishihara, and S. Maekawa

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

(Received November 11, 2018)

We present a theory of the resonant inelastic x-ray scattering (RIXS) to study electronic excitations in orbital ordered manganites. The charge and orbital excitations of the Mn 3d electron are caused by the Coulomb interactions in the intermediate scattering state. The scattering cross section is formulated by the Liouville operator method where the local and itinerant natures of the excitations are taken into account on an equal footing. As a result, the cross section is expressed by the charge and orbital correlation functions associated with local corrections. The RIXS spectra are calculated numerically as functions of momentum and polarization of x ray. Through the calculations, we propose that RIXS provides a great opportunity to study the unique electronic excitations in correlated electron systems with orbital degeneracy.

PACS numbers: 75.30.Vn, 71.10.-w, 78.70.Ck, 78.70.En

I. INTRODUCTION

Since the discovery of High-Tc superconducting cuprates, electronic structure of transition-metal oxides has been reinvestigated from a view point of electron correlation. An important consequence of the strong electron correlation is a variety of electronic phases and unique elementary excitations attributed to the internal degrees of freedom of an electron. The most exotic example is the spin-charge separation in one-dimensional metals where the collective spin and charge excitations behave independently. Even in the two- and three-dimensional systems, it is recognized that characteristic momentum and energy dependence of electronic excitations plays crucial roles in anomalous metallic states near the metal-insulator transition.

In addition to the spin and charge degrees of freedom, manganites with perovskite structure $A_1-xB_xMnO_3$ (A=La, Pr, Nd, Sm; B=Sr, Ca, Ba) have orbital degree of freedom, one of the doubly degenerate $e_g$ orbitals, i.e. 3$d_{3z^2-r^2}$ and 3$d_{x^2-y^2}$ orbitals, is occupied by an electron in a Mn$^{3+}$ ion. LaMnO$_3$ is an antiferromagnetic insulator as is La$_2$CuO$_4$. Moreover, the orbital degree of freedom shows the long range ordering accompanied with the lattice distortion where 3$d_{3z^2-r^2}$ and 3$d_{x^2-y^2}$ orbitals alternately align in the ab plane. With doping of holes, a variety of spin, charge and orbital ordered phases appears. As for the spin degrees of freedom among them, its ordering and excitations have been examined experimentally in detail by the neutron scattering experiments. On the contrary, the charge and orbital orderings and excitations still remain to be studied, since the experimental probes which directly couple with them were limited.

Recently, the charge and orbital orderings in manganites have successfully been observed by the resonant x-ray scattering. Here a Mn 1s electron is excited to the Mn 4$p$ orbital in the intermediate scattering state by tuning the incident x-ray energy to the Mn K edge. On resonance, the x-ray scattering factors become sensitive dramatically to the charge and orbital states of a Mn 3d electron. The polarization dependent scattering intensity is utilized to identify the scattering from the orbital ordering. Nowadays, this technique is applied to several transition metal oxides with charge and orbital orderings.

The availability of the third generation synchrotron radiation sources promises to detect the charge and orbital excitations by the resonant inelastic x-ray scattering (RIXS). The resonant process provides not only huge enhancement of the scattering cross section but also excitations of 3d electrons around a Mn ion where x ray is absorbed. Thus, this probe is sensitive to the local electronic structures around this ion. At the same time, the delocalized character of electrons in a solid is detectable by this method, because x ray covers a wide range of the momentum space. Actually, momentum dependent RIXS spectra have been recently observed in the insulating manganites. These were interpreted as charge excitations from the effective lower Hubbard band to the upper Hubbard one across the Mott gap. Now this technique is on the point to be applied to the manganites with orbital degree of freedom. The Mott gap in the orbital ordered insulating manganites is composed of the upper and lower Hubbard bands with different orbital characters unlike the cuprates. Thus, x ray is scattered from the orbital excitation as well as the charge one in these compounds. The x-ray scattering spectrometer of RIXS for manganites has recently been constructed on a beamline at the SPing-8. Some peak structures are observed in the RXS spectra for LaMnO$_3$ around several eV of the energy transfer. The polarization and momentum resolved measurements will provide a great opportunity to observe excitations in correlated electron systems with orbital degeneracy.

In this paper, we present a theoretical framework of RIXS to study charge and orbital excitations in orbital ordered insulating manganites. We focus on RIXS from the individual charge and orbital excitations caused by the transitions from occupied to unoccupied electronic states across the Mott gap. The present theory
is applicable to analyze the observed RIXS spectra in LaMnO$_3$ mentioned above.

Moreover, an identification of RIXS from the individual excitations promises to detect the collective orbital excitation proposed theoretically in Ref. [23]. The scattering cross section is formulated by the Liouville operator method where the local electron correlation and itinerant nature of the excitations is treated on an equal footing. The cross section is expressed by the charge and orbital correlation functions associated with local corrections. The RIXS spectra are calculated numerically as functions of momentum, polarization and type of the orbital ordered states. Through the calculations, we propose that RIXS provides a great opportunity to study the electronic excitations in correlated electron systems with orbital degeneracy.

In Sec. II, a formulation of the scattering cross section based on the Liouville operator method is presented. The numerical results of the RIXS spectra are shown in Sec. III. Sec. IV is devoted to the summary and discussion.

II. MODEL AND FORMULATION

Let us formulate the scattering cross section of RIXS in insulating manganites with orbital ordering. Consider the scattering of x ray with momentum $\vec{k}_i$, energy $\omega_i$ and polarization $\lambda_i$ to $\vec{k}_f$, $\omega_f$ and $\lambda_f$. The electronic states at the initial, intermediate and final states in the scattering process are denoted as $|i\rangle$, $|m\rangle$ and $|f\rangle$ with energy $\varepsilon_i$, $\varepsilon_m$ and $\varepsilon_f$, respectively. The differential cross section of RIXS is given by

$$
\frac{d^2\sigma}{d\Omega d\omega_f} = A \frac{\omega_f}{\omega_i} \sum_f |S|^2 \delta(\varepsilon_f + \omega_f - \varepsilon_i - \omega_i),
$$

where

$$
S = \sum_m \left\{ \frac{\langle f \mid \vec{j}_{-k_i} \cdot \vec{\epsilon}_{k_i \lambda_i} \mid m \rangle \langle m \mid \vec{j}_{k_f} \cdot \vec{\epsilon}_{k_f \lambda_f} \mid i \rangle}{\varepsilon_i - \varepsilon_m - \omega_f} + \frac{\langle f \mid \vec{j}_{k_f} \cdot \vec{\epsilon}_{k_f \lambda_f} \mid m \rangle \langle m \mid \vec{j}_{-k_i} \cdot \vec{\epsilon}_{k_i \lambda_i} \mid i \rangle}{\varepsilon_i - \varepsilon_m + \omega_i + i\Gamma} \right\},
$$

and $A = (e^2/mc^2)^2$. $\vec{\epsilon}_{k\lambda}$ is the polarization vector of x ray, $\Gamma$ is the damping of a core hole and $\vec{j}_k$ is the current operator defined by $\vec{j}_k = \sum \epsilon e^{-i\vec{k} \cdot \vec{r}}$. Since the dipole transition is dominant in RIXS at the Mn$^{3+}$ K-edge, this operator is given by

$$
j_{l\sigma} = \frac{B}{\sqrt{m}} \sum_{\alpha} \hat{p}_{l\alpha}^\dagger s_{l\sigma} + H.c.,
$$

$p_{l\alpha}^\dagger$ and $s_{l\sigma}$ are the creation operator of a Mn 4$p_{\alpha}$ electron and the annihilation one of a Mn 1$s$ electron, respectively, at site $l$ with Cartesian coordinate $\alpha$ and spin $\sigma$. The coupling constant $B$ in Eq. (4) between the current and x ray is defined by

$$
B = \frac{1}{2} \int d\vec{r} \phi_4 p_{\alpha}(\vec{r})^* (-i\nabla_\alpha) \phi_{l\sigma}(\vec{r}),
$$

with the atomic wave function $\phi_m(\vec{r})$ ($m = 4p, 1s$). As shown in Ref. [23], the differential scattering cross section is represented by the correlation function of the electronic polarizability operator $\alpha_{l\beta\alpha}$ as

$$
\frac{d^2\sigma}{d\Omega d\omega_f} = A \frac{\omega_f}{\omega_i} \sum_{\alpha\beta\alpha'} P_{\beta\alpha'} P_{\beta\alpha} \Pi_{\beta\alpha'\beta\alpha}(\omega, \vec{K}),
$$

where $\Pi_{\beta\alpha'\beta\alpha}(\omega, \vec{K})$ is the Fourier transform of the correlation function of this operator given by

$$
\Pi_{\beta\alpha'\beta\alpha}(\omega, \vec{K}) = \frac{1}{2\pi} \int dt e^{i\omega t} \sum_{i'l'} e^{-i\vec{K} \cdot (\vec{r}_{i'} - \vec{r}_i)} \langle i\mid \alpha_{l\beta\alpha'}(t') \rangle^\dagger \alpha_{l\beta\alpha}(0) \langle i\rangle,
$$

with $\vec{K} = \vec{k}_i - \vec{k}_f$, $\omega = \omega_i - \omega_f$ and $P_{\beta\alpha} = (\vec{\epsilon}_{k_f \lambda_f})_{\beta} (\vec{\epsilon}_{k_i \lambda_i})_{\alpha}$. $\alpha_{l\beta\alpha}(t)$ is the Heisenberg representation of the electronic polarizability $\alpha_{l\beta\alpha}$ at site $l$. Now this operator is represented by the Liouville operator $L$ as follows;

$$
l_{l\beta\alpha} = j_{l\beta} \frac{1}{L - \omega_i + i\Gamma} j_{l\alpha} + j_{l\beta} \frac{1}{L + \omega_i} j_{l\alpha}.
$$

$L$ is defined by the equation of motion for a Heisenberg operator $O(t)$;

$$
i\partial_t O(t) = [O(t), H] = -LO(t).
$$

On resonance, the first term in Eq. (6) provides dominant processes in the scattering.

In the intermediate scattering state of RIXS, a Mn 1$s$ electron is excited to the Mn 4$p$ orbital at a Mn site where x ray is absorbed. As discussed in Ref. [23], one of the dominant interactions which cause charge and orbital excitations of the Mn 3$d$ electrons is the local Coulomb interactions between 3$d$ electrons and the 1$s$ hole and/or the 4$p$ electron at this site. Thus, the RIXS spectra largely depend on the local electronic structure. Once the excitations occur at a Mn site, these propagate in a crystal lattice. Such itinerant nature of the electronic excitations can be observed by the momentum resolved measurements, since the wave length of x ray is comparable to the lattice constant. In order to take into account these two characteristics of RIXS on an equal footing, we adopt the following two steps in the formulation of the scattering cross section of RIXS: [1] The polarizability operator $\alpha_{l\beta\alpha}$ in Eq. (4) is expanded by the local operator products at a Mn site $l$. Here the Hamiltonian $H_l$ defined at this site is utilized. [2] The correlation function $\langle i\mid \alpha_{l\beta\alpha'}(t) \rangle^\dagger \alpha_{l\beta\alpha}(0) \langle i\rangle$ in Eq. (6) is calculated by the tight-binding Hamiltonian for the Mn 3$d$ electrons $H_{3d}$.
defined in a crystal lattice. Contributions from the O
2p orbitals which are not included in the present model
explicitly will be discussed in Sec. IV.
Let us introduce the Hamiltonian $H_l$ defined at site $l$
where x ray is absorbed:
\[ H_l = H_l^{(3d)} + H_l^{(1s,4p)} + H_l^{(3d-1s,4p)}. \]
The first term $H_l^{(3d)}$ represents the Mn 3d system where
two $e_g$ orbitals and a localized spin for $t_{2g}$ electrons are
considered. This is represented by a sum of the two terms;
\[ H_l^{(3d)} = H_l^I + H_l^U, \]
where
\[ H_l^I = \sum_{\gamma} \varepsilon_d d_{\gamma\sigma} d_{\gamma\sigma}, \]
and
\[ H_l^U = U \sum_{\gamma} n_{\gamma\uparrow} n_{\gamma\downarrow} + U \frac{1}{2} \sum_{\gamma} n_{\gamma\uparrow} n_{\gamma\downarrow} - J_H s_{\downarrow} \cdot \vec{s}_{\downarrow}. \]
\[ d_{\gamma\sigma} is the annihilation operator of the 3d $e_g$ electron at site $l$ with orbital $\gamma(=3z^2-r^2, r^2, x^2-y^2)$ and spin
\[ \sigma (\uparrow,\downarrow). n_{\gamma\sigma} = \sum_\sigma n_{\gamma\sigma} = \sum_\sigma d_{\gamma\sigma} d_{\gamma\sigma}^{\dagger} is the number \]
operator, $s_{\downarrow} = \frac{1}{2} \sum_\sigma \sum_{\sigma'} d_{\gamma\sigma}^{\dagger} \bar{s}_{\sigma\sigma'} d_{\gamma\sigma'}$ is the spin operator for the $e_g$ electrons and $\vec{s}_{\downarrow} is the spin operator for the
\[ t_{2g} electrons with S = 3/2. -\sigma (\downarrow) indicates a spin \]
(orbital) which has an opposite direction to $\sigma (\uparrow). U, U' \]
and $J$ in Eq. (2) are the intra- and inter-orbital Coulomb
interactions and the exchange interactions, respectively, and $J_H is the Hund coupling between $e_g$ and $t_{2g}$ spins.
The second term in Eq. (3) describes the Mn 1s and 4p
electron energy levels:
\[ H_l^{(1s,4p)} = \varepsilon_s \sum_{\sigma} s_{\sigma}\sigma s_{\sigma} + \varepsilon_p \sum_{\alpha\sigma} p_{\alpha\sigma} p_{\alpha\sigma}, \]
and the third term gives the Coulomb interactions be-
 tween the Mn 1s, 3d and 4p electrons:
\[ H_l^{(3d-1s,4p)} = n_{\gamma\alpha} \left( V_{sd} n_{\gamma\uparrow} + V_{dp} n_{\gamma\downarrow} \right) \]
\[ + \sum_{\gamma,\alpha} n_{\gamma\alpha}^{\dagger} \left( V_{dp}^{\gamma\alpha} n_{\gamma\uparrow} + W_{dp}^{\gamma\alpha} m_{\gamma\sigma} \right). \]
where $n_{\gamma} = \sum_\sigma n_{\gamma\sigma}$ and $n_{\gamma}^{\dagger} = \sum_\sigma n_{\gamma\sigma}^{\dagger}$.
The first two terms in Eq. (14) correspond to the core
hole potentials and the second two describe the Coulomb
interactions between the Mn 3d and 4p electrons. The
latter involve the operator $m_{\gamma\sigma} = \sum_\sigma d_{\gamma\sigma}^{\dagger} d_{\gamma\sigma}$ which
describes the orbital fluctuation for 3d electrons. Explicit
forms of the diagonal and off-diagonal components of the
Coulomb interactions $V_{dp}^{\gamma\alpha}$ and $W_{dp}^{\gamma\alpha}$ are given as
\[ V_{dp}^{\gamma\alpha} = F_0 + 4F_2 \cos\left( \theta_\gamma - \frac{2\pi}{3} m_\alpha \right), \]
and
\[ W_{dp}^{\gamma\alpha} = 4F_2 \sin\left( \theta_\gamma - \frac{2\pi}{3} m_\alpha \right), \]
respectively, with $(m_x, m_y, m_z) = (1,2,3)$. $F_0(2)$ is the
Slater integral between 3d and 4p electrons and an angle
$\theta_\gamma$ specifies the occupied 3d orbital as
\[ \cos\left( \frac{\theta_\gamma}{2} \right) = \cos\left( \frac{\theta_\gamma}{2} \right) d_{3x^2-r^2} - \sin\left( \frac{\theta_\gamma}{2} \right) d_{3y^2-z^2}. \]
Being based on $H_l$ given in Eq. (3), $\alpha_{l\beta\alpha}$ is expanded
by the local operator products at site $l$. The Liouville
operator $L$ is divided into the unperturbed and perturbed
parts, i.e. $L = L_0 + L'$. $L_0$ and $L'$ correspond to the
Hamiltonian $H_l^0 = H_l^I + H_l^{(1s,4p)} + \langle H_l^{(3d)} \rangle_H + \langle H_l^{(3d-1s,4p)} \rangle_H$ and $H_l' = \Delta(H_l^I) + \Delta(H_l^{(3d-1s,4p)})$, re-
spectively, where $\Delta = \langle \bar{O} \rangle_H + \Delta(\bar{O})$ for an operator $\bar{O}$
and $(\bar{O})_H$ is its Hartree part. Up to the first order of $L'$,
$\alpha_{l\beta\alpha}$ is expressed as follows,
\[ \alpha_{l\beta\alpha} = \frac{|B|^2}{m} \sum_{\sigma_1\sigma_2} J_{l\alpha\sigma_2}^D \left( \frac{1}{L_0 - \omega_i + i\Gamma} \right) J_{l\alpha\sigma_1}, \]
with $J_{l\alpha\sigma} = p_{l\alpha\sigma} s_{l\sigma}$. The first and second terms cor-
respond to the elastic and inelastic scatterings, respecti-
vely. The second term is calculated by utilizing the
equations of motion of the operators and is given by
\[ \alpha_{l\beta\alpha} = \frac{|B|^2}{m} \delta_{\alpha\beta} \sum_{\sigma_1\sigma_2} J_{l\alpha\sigma_2}^D J_{l\alpha\sigma_1} \sum_{m=1,2} \sum_{\gamma\sigma} O_{l\gamma\sigma}^{(m)} D_{l\gamma\sigma}^{(m)}, \]
with
\[ D_{l\gamma\sigma}^{(m)} = \frac{1}{E_{l\gamma\sigma} - \omega_i + i\Gamma} C_{l\gamma\sigma}^{(m)} \frac{1}{E_{l\gamma\sigma} - \omega_i + i\Gamma}, \]
\[ m = (1,2) describes the intra- \( (m = 1) \) and inter-orbital \( (m = 2) \) excitations for the 3d electrons. The operator
$O_{l\gamma\sigma}^{(m)}$ represents these excitations and $C_{l\gamma\sigma}^{(m)}$ and $E_{l\gamma\sigma}$
are their amplitudes and excitation energies, respectively.
The explicit forms of them are given as follows,
\[ O_{l\gamma\sigma}^{(1)} = \delta_{m\gamma\sigma}, \quad O_{l\gamma\sigma}^{(2)} = \delta_{m\gamma\sigma}, \]
\[ C_{l\gamma\sigma}^{(1)} = V_{sd} - V_{dp}^{\gamma\sigma}, \quad C_{l\gamma\sigma}^{(2)} = -W_{dp}^{\gamma\sigma}. \]
\[ E_{\gamma\sigma}^{(1)} = -E_{\alpha}, \quad E_{\gamma\sigma}^{(2)} = -(\varepsilon_{-\gamma\sigma} - \varepsilon_{\gamma\sigma} + E_{\alpha}), \]  
(23)

where \( \hat{O} = (\hat{O}) + \delta \hat{O} \) for an operator \( \hat{O} \) and

\[ E_{\alpha} = \varepsilon_s - \varepsilon_p + V_{sd}\langle n_l \rangle - \sum_\gamma V_{dp}^{\alpha} - V_{sp}, \]
(24)

\[ \varepsilon_{\gamma\sigma} = \varepsilon_d + U\langle n_{l\gamma\sigma} \rangle + U'\langle n_{l\gamma\sigma} \rangle - J\langle n_{l\gamma\sigma} \rangle \]

\[ - J_H \frac{1}{2}\varepsilon_\sigma \langle S_t^\sigma \rangle + V_{sd}\langle n_l^\sigma \rangle + \sum_\alpha V_{dp}^{\alpha}\langle n_l^\alpha \rangle, \]
(25)

with \((\varepsilon_1, \varepsilon_2) = (1, -1)\). Then, Eq. (19) denotes the following inelastic scattering processes: the incident x ray excites an electron from the 1s orbital to the 4p one with the excitation energy \( E_{\alpha} \) at a Mn site \( l \) where x ray is absorbed. In the intermediate scattering state, charge and orbital excitations represented by \( O_{l\gamma\sigma}^{(m)} \) occur with amplitudes \( C_{l\gamma\sigma}^{(m)} \) at this Mn site. Finally, the 4p electron returns back to the 1s orbital with emitting the second x ray. The final form of the correlation function of the polarizability is given by

\[ \Pi_{\beta'\alpha'}^{\gamma}\beta\alpha(\omega, \vec{K}) = \frac{1}{2\pi i} \int dt e^{i\omega t} \sum_{l'} e^{-i\vec{K} \cdot (\vec{r}_{l'} - \vec{r}_l)} \times \Pi_{\beta'\alpha'}^{\gamma}\beta\alpha(t, \vec{r}_{l'} - \vec{r}_l), \]
(26)

with

\[ \Pi_{\beta'\alpha'}^{\gamma}\beta\alpha(t, \vec{r}_{l'} - \vec{r}_l) = \frac{|B|^4}{m^4} \delta_{\beta'\alpha'} \delta_{\beta\alpha} \sum_{\alpha m} \sum_{\sigma} D_{\gamma\sigma}^{(m')} C_{l'\gamma\sigma}^{(m')}(t) C_{l\gamma\sigma}^{(m')}(0). \]
(27)

Here it is assumed that \( J_{l\alpha\gamma}^I J_{l\alpha\sigma} = \delta_{l\alpha} \delta_{\gamma\sigma} \) and \( \langle i | \cdots | j \rangle \) is replaced by the thermal average \( \langle \cdots \rangle \). We note that the scattering cross section is expressed by the correlation functions of the charge and orbital fluctuations of the Mn 3d electrons associated with the local corrections \( D_{\gamma\sigma}^{(m)} \).

The correlation function \( \langle O_{l'\gamma\sigma}^{(m')}^{(t)} | O_{l\gamma\sigma}^{(m)}(0) \rangle \) in Eq. (27) is calculated by the tight-binding Hamiltonian \( H_{3d} \) for the Mn 3d electrons defined in a crystal lattice:

\[ H_{3d} = \sum_l H_l^{(3d)} + H_t, \]
(28)

where \( H_l^{(3d)} \) is given in Eq. (10). The second term represents the electron hopping between nearest neighboring Mn sites \( l \) and \( l' \) with orbitals \( \gamma \) and \( \gamma' \), respectively.

\[ H_t = \sum_{l'l'\gamma'\gamma'\sigma} t_{l'\alpha}^{\gamma'\beta\gamma\sigma} \delta_{l\alpha}\delta_{l'\gamma}\delta_{\gamma'\sigma} + H.c., \]
(29)

where \( t_{l'\alpha}^{\gamma'\beta\gamma\sigma} \) is the hopping integral and its orbital dependence is determined by the Slater-Koster parameters \( \Gamma \).

We apply the present formulae of the scattering cross section to LaMnO\(_3\). A simple cubic lattice consisting of Mn\(^{3+}\) is considered. The A-type antiferromagnetic structure and the C-type orbital ordered one, where \( d_{3z^2-r^2} \) and \( d_{3y^2-r^2} \) orbitals alternately align in the \( ab \) plane, is introduced by considering the Jahn-Teller type lattice distortion observed in LaMnO\(_3\). The mean field approximation is adopted in \( H_{3d} \); \( \langle S_k^z \rangle = \frac{1}{4} (S_k^z) = \frac{1}{2} \delta_{k=} (000), \langle n_{k3z^2-r^2} \rangle = \frac{1}{2} \delta_{k=} (000), \rangle \langle n_{k4z^2-y^2} \rangle = \frac{1}{2} \delta_{k=} (000) \) and \( (m_{k3z^2-r^2} = \langle m_{kk2-y^2} \rangle = \frac{1}{2} \delta_{k=} (\pi 0) \) where \( \hat{O}_k \) is the Fourier transform of an operator \( \hat{O}_l \). As for the lattice degree of freedom, the adiabatic approximation is introduced in the intermediate and final scattering states where the lattice distortions are assumed to be unchanged from those in the initial scattering state. Contributions from the Jahn-Teller coupling to the excitation energies are interpreted to be included implicitly in the inter-orbital Coulomb interaction \( \hat{U}' \).

### III. NUMERICAL RESULTS

The calculated results of the RIXS spectra are presented in Fig. 1. \( \Pi_{\beta'\alpha'}^{\gamma}\beta\alpha(\omega, \vec{K}) \) defined in Eqs. (26) and (27) is plotted as a function of the energy transfer \( \omega \) of x ray. The elastic component located at \( \omega = 0 \) is not
The momentum transfer $\vec{K}$ is chosen to be $(q00)$ for Fig. 1(a) and $(q00)$ for Fig. 1(b) where the notation in a simple cubic lattice is used. The polarization of x ray is assumed to be parallel to the $x$ direction, i.e. $\alpha = \alpha' = \beta = \beta' = x$. The energy parameters are chosen to be $U = 9$, $U' = 7$, $J = J_H = 1$, $V_{sd} = 9.5$, $F_0 = 7$, $F_2 = 0.35$ and $t = 1.5$ in units of $t_0$ which is the hopping integral between $d_{3z^2-r^2}$ orbitals in the $z$ direction. $t_0$ is estimated to be about $0.5\sim 0.7$eV. The energy of the incident x ray is redefined as $\omega_i = \omega_i - (\varepsilon_p - \varepsilon_s - V_{sp} - V_{sd})$ in Eq. (24). We assume that the smallest energy among $E^{(m)}_{\gamma\sigma\alpha}$ and $E_\sigma$ in Eq. (24) corresponds to the excitation energy at the $K$ edge and $\omega_i$ is fixed at this energy. The RIXS spectra shown in Fig. 1 do not have an intensity up to about $2t_0$ which corresponds to the Mott gap. That is, the spectra are attributed to the individual electronic excitations from occupied to unoccupied electronic states across the Mott gap. The remarkable momentum dependence is seen in the RIXS spectra; near the $(000)$ point, two peaks and one shoulder are observed at about $5t_0$ and $6t_0$ and $7.5t_0$, respectively. These are denoted as $A$, $B$ and $C$ in the figure. The lowest peak structure becomes remarkable with increasing $\vec{K}$ along the $<h00>$ direction. On the other hand, this structure is smeared out near the $(\frac{7}{2}\frac{7}{2}0)$ point.

The energy and momentum dependence of the RIXS spectra is well explained by the Hartree-Fock band structure presented in Fig. 2. The eight bands each of which are doubly degenerate are attributed to the four Mn ions with spin and orbital degrees of freedom in a unit cell. The occupied bands have the $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbital characters, which are termed the majority orbitals hereafter, and the lowest unoccupied bands have the $d_{x^2-z^2}$ and $d_{z^2-x^2}$ orbital ones (the minority orbitals). The Mott gap opens between the two and is of the order of $U' - J$ in the limit of $U' >> t_0$. The unoccupied bands with higher energies correspond to the minority spin bands. The dispersion relations of all bands are weak in the $z$ direction, because the electron hopping is suppressed in this direction due to the $A$ type antiferromagnetic structure. It is interpreted that the main RIXS spectra in Fig. 1 are attributed to the transition from the occupied band (the lower Hubbard band) to the lowest unoccupied band (the upper Hubbard band). Weak spectral weights in the regions of $8.5 < \omega/t_0$ originate in the excitations to the higher bands. These transitions are almost prohibited, since the operators $O_{\gamma\sigma}^{(m)}$ in Eqs. (21) do not change the spin states of the $3d$ electrons. It is noted that the lowest unoccupied bands show the almost flat dispersion relation, because the electron hopping between the $d_{2-x^2}$ and $d_{2-z^2}$ orbitals is forbidden in the $xy$ plane. Thus, the global shape of the main spectra reflects from the density of states of the occupied band. The dominant contributions to the peak $A$ around $\vec{K} = (000)$, $(\pi00)$, and $(\frac{\pi}{2}\frac{\pi}{2}0)$ in Fig. 1 are attributed to the transitions denoted as $A_1$, $A_X$ and $A_M$ in Fig. 2, respectively. It is noted that the difference between the transitions $A_M$ and $A_X$ is caused by the curvature of the unoccupied band; $\nabla_{x,y} E^{(u)}(\vec{k}) < 0$ around $\vec{k} = (\pi00)$ and $\nabla_{x,y} E^{(u)}(\vec{k}) > 0$ around $\vec{k} = (\frac{\pi}{2}\frac{\pi}{2}0)$ where $E^{(u)}(k)$ is the energy of the lowest unoccupied band and

![FIG. 2.](image-url)

![FIG. 3.](image-url)

**FIG. 2.** The electron energy bands for the $(d_{3z^2-r^2}, d_{3y^2-r^2})$-type orbital ordered state. The broken line represents the chemical potential located at the center of the occupied and lowest unoccupied bands. The parameter values are the same with those in Fig. 1. The origin of the vertical axis is arbitrary. The dotted arrows indicated by $A_\gamma$, $A_X$ and $A_M$ represent the main contributions to the peak $A$ in the RIXS spectra (see Fig. 1) around $\vec{K} = (000)$, $(\pi00)$ and $(\frac{\pi}{2}\frac{\pi}{2}0)$, respectively.

**FIG. 3.** The polarization dependence of the RIXS spectra $\Pi_{\alpha'\sigma'\alpha}(\omega, \vec{K})$ for the $(d_{3z^2-r^2}, d_{3y^2-r^2})$-type orbital ordered state. The momentum transfer is $\vec{K} = (000)$. The solid and broken lines represent the spectra for $\alpha = \alpha' = \beta = \beta' = x$ (the $x$ polarization) and $\alpha = \alpha' = \beta = \beta' = z$ (the $z$ polarization), respectively. Other parameter values are the same with those in Fig. 1.
\( \nabla_{x,y} \) is a differential operator in the \((k_x, k_y)\) plane. As for the occupied band, we find that \( \nabla_{x,y} E^{(o)}(\vec{k}) < 0 \) around \( \vec{k} = (000) \) where \( E^{(o)}(\vec{k}) \) is the energy of the occupied band. Thus, the van Hove singularity, where the condition \( \nabla_{x,y} E^{(o)}(\vec{k}) - \nabla_{x,y} E^{(o)}(\vec{k}') = 0 \) is satisfied, exists in a wide region of the momentum space for the \( A_X \) transition. The difference between \( \nabla_{x,y} E^{(o)}(\vec{k}) \)'s around \( \vec{k} = (\pi 00) \) and \( (\pi 00) \) is attributed to the fact that hopping integrals between the occupied orbitals \( (d_{3z^2-r^2}, d_{3y^2-r^2}) \) and the unoccupied ones \( (d_{3x^2-y^2}, d_{2x^2-z^2}) \) disappear at the \((\pi 00)\) point. Consequently, the peak \( A \) becomes remarkable around \( \vec{k} = (\pi 00) \) as seen in Fig. 1.

The polarization dependence of the RIXS spectra is shown in Fig. 3. The polarization of x-ray is chosen to be parallel to the x direction \( (\alpha = \alpha' = \beta = \beta' = x) \) for Fig. 3(a) and the z direction \( (\alpha = \alpha' = \beta = \beta' = z) \) for Fig. 3(b). The momentum transfer is fixed at \( \vec{K} = (\pi 00) \) in both cases. The spectrum is much enhanced for the \( \pi \) polarization, although the global shape of the spectrum is insensitive to the polarization. This result arises from the factor \( C_{\gamma\alpha}^{(m)} \) given in Eq. (22), \( C_{\gamma\alpha}^{(m2)} = -W_{dp}^{-\alpha} \) is an amplitude of the excitations from the occupied 3d orbital \( \gamma \) to the unoccupied orbital \( -\gamma \), when the 4\( p_\alpha \) orbital is occupied by an electron. Consider the two kinds of Mn sites where \( d_{3z^2-r^2} \) and \( d_{3y^2-r^2} \) orbitals are occupied. In the case where a 1s electron is excited to the 4\( p_\alpha \) orbital by x-ray, the amplitudes \( W_{dp}^{3z^2-r^2,\alpha}, W_{dp}^{3y^2-r^2,\alpha} \) are given by \( (0, 2\sqrt{3}F_2) \) for \( \alpha = x \) and \( (2\sqrt{3}F_2, -2\sqrt{3}F_2) \) for \( \alpha = z \). We note that \( W_{dp}^{3\pi^2-r^2,\alpha} \) is zero because of the symmetry of the wave functions. This is clearly shown by the explicit form of this interaction:

\[
W_{dp}^{3\pi^2-r^2,\alpha} = \int d\vec{r}d\vec{r}' \phi^*_{4p_\alpha}(\vec{r})\phi_{4p_\alpha}(\vec{r})\phi_{3d_{3\gamma^2-r^2}}(\vec{r})\phi_{3d_{3\gamma^2-r^2}}(\vec{r}') \]

where \( \phi_{\gamma}(\vec{r}) \) is the atomic wave function of the orbital \( \gamma \) and \( v(\vec{r}) \) is the Coulomb interaction. The integrand changes its sign under replacement of \( y \) by \( z \). Thus, the orbital excitation does not occur at the \( d_{3\gamma^2-r^2} \) site by x-ray with the \( x \) polarization.

RIXS spectra calculated in several-types of the orbital ordered states are compared in Fig. 4. We consider the C-type orbital ordered state where the two orbital sublattices exist. The occupied orbitals are denoted by the angles \( (\theta_A, \theta_B) \) defined in Eq. (17). These values are chosen to be \( (\pi/3, -\pi/3) \) for Fig. 4(a) and \( (\pi/2, -\pi/2) \) for Fig. 4(b) which correspond to the
The off-diagonal Coulomb interaction $W$ and $(\frac{1}{\sqrt{2}}[d_{x^2−z^2} + d_{y^2−z^2}], \frac{1}{\sqrt{2}}[d_{3x^2−r^2} + d_{3y^2−r^2}])$ orbital ordered states, respectively. The momentum transfer is fixed at $K = (\pi, 0)$. The Hartree-Fock energy bands in these orbital states are also presented in Fig. 5. We note that the energy and polarization dependence of the spectra in Fig. 4(a) is similar to that for the $(2\pi/3, −2\pi/3)$ state presented in Fig. 1. This is because the occupied and lowest unoccupied bands in the state have the $d_{x^2−z^2}, d_{y^2−z^2}$, $d_{3x^2−r^2}, d_{3y^2−r^2}$ orbital characters, respectively, which are opposite to those in the $(2\pi/3, −2\pi/3)$ orbital ordered state, as seen in Figs. 1 and 5(a). On the contrary, RIXS spectra for the $(\pi/2, −\pi/2)$ state show mainly two peak structures located around $\omega = 6t_0$ and $7.5t_0$. These peaks are indicated as $A$ and $B$ in Fig. 4(b). It is worth noting that the dispersion relations of the occupied and lowest unoccupied bands in Fig. 5(b) are almost symmetrical with respect to the center of the Mott gap because of the symmetry of this orbital ordered state. Thus, the excitation energies for some transitions, for example, the transitions $A_x\chi_1$ and $A_x\chi_2$, are nearly degenerate unlike the $(\pi/3, −\pi/3)$ and $(2\pi/3, −2\pi/3)$ orbital ordered states. The spectra in this orbital ordered state are more sensitive to the polarization of x ray than those in the $(\pi/3, −\pi/3)$ and $(2\pi/3, −2\pi/3)$ states. This fact arises from the larger anisotropy of the off-diagonal Coulomb interaction, i.e., $(W_{dp}^{\pi/2, \alpha}, W_{dp}^{−\pi/2, \alpha}) = (2F_2, −2F_2)$ for the $x$ polarization and $(4F_2, 4F_2)$ for the $z$ polarization where $W_{dp}^{\pi/2, \alpha}$ is the off-diagonal Coulomb interaction $W_{dp}^{\gamma, \alpha}$ for the $3d$ orbital of $\theta = ±\pi/2$.

IV. SUMMARY AND DISCUSSION

We present, in this paper, a theoretical framework of RIXS from charge and orbital excitations in insulating manganites with orbital ordering. We formulate the scattering cross section by the Liouville operator method from the stand point that both the local and itinerant nature of the excitations reflects on the RIXS spectra. Then, the cross section is expressed by the correlation functions of the charge and orbital excitations associated with the local corrections. The general formalism for the scattering cross section is applied to LaMnO$_3$ where the $A$-type antiferromagnetic order and the $C$-type orbital order of the $(3d_{x^2−r^2}, 3d_{3y^2−r^2})$-type are realized. The calculated spectra from the individual excitations are interpreted by the electronic transition from the occupied to lowest unoccupied states across the Mott gap. However, the spectra are not the simple joint density of states itself; the local correlation effects dominate the unique polarization and orbital dependence of the spectra.

Let us discuss the relevance of the present results to the experimental ones in manganites. LaMnO$_3$ is a charge transfer type insulator where the insulating gap is formed between the unoccupied Mn $e_g$ band (the upper Hubbard band) and the O 2p band with the $e_g$ symmetry being strongly hybridized with the Mn 3d ones. The value of this gap $\Delta$ is estimated to be about 2−3eV [25]. Below this highest occupied band, the so-called non-bonding O 2p bands exist. In the present model, where the oxygen ions are not explicitly taken into account, the lower Hubbard band is interpreted to be this highest occupied band with the strong hybridization between O 2p and Mn 3d orbitals. The calculated RIXS spectra are attributed to the transition from this band to the upper Hubbard one and its energy transfer is about $\Delta$. In the region of higher energy transfer, RIXS spectra arising from the transition from the non-bonding O 2p bands to the upper Hubbard ones are expected to appear, as is observed at about 6eV in insulating cuprates [11]. Below $\Delta$, on the other hand, RIXS from the collective orbital excitation termed orbital wave $\pi/2$ is expected to occur. The energy of this excitation is characterized by the inter-site interaction between orbitals. This interaction is of the order of 0.1eV. An absolute value of the scattering intensity for the calculated RIXS spectra is roughly estimated to be of the order of $10^{-24}$cm$^2$ where we assume $B = 2A$ in Eq. (8) and $t_0 = 0.7eV$. This is about 50−100 times larger than the scattering cross section for the Thomson scattering $(e^2/mc^2)^2$ which implies an intensity of 1count/sec/1eV for the conventional experimental arrangement [13]. It is enough to detect in the present state of the experiments, although the estimation is semi-quantitative. With doping of holes into LaMnO$_3$, a finite intensity of the spectra may appear inside the gap of the spectra. At the same time, a change of the types of the orbital ordered state is expected to occur [11] and is to be detected by RIXS as shown in the present theory.

ACKNOWLEDGMENTS

Authors would like to thank Y. Endoh, J. Mizuki, T. Inami, and Y. Murakami for their valuable discussions. This work was supported by the Grant in Aid from Ministry of Education, Science and Culture of Japan, CREST and NEDO. Part of the numerical calculation was performed in the HITACS-3800/380 supercomputing facilities in IMR, Tohoku University.

1 See, for example, M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70 1039 (2000).
2 Y. Tokura, and N. Nagaosa, Science 288, 462 (2000).
3 E. O. Wollan, and W. C. Koehler, Phys. Rev. 100, 545 (1955).
4 J. B. Goodenough, Phys. Rev. 100, 564 (1955).
5 J. Kanamori, J. Phys. Chem. Sol. 10, 87 (1959).
6 G. Matsumoto, J. Phys. Soc. Jpn. 29, 606 (1970).
7 J. Rodriguez-Carvajal, M. Hennion, F. Moussa, and A. H. Moudden, Phys. Rev. B 57, R3189 (1998).
8 Y. Ito, and J. Akimitsu, J. Phys. Soc. Jpn. 40, 1333 (1976).
9 Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, H. Moritomo, and Y. Tokura, Phys. Rev. Lett. 80, 1932 (1998).
10 Y. Murakami, J. P. Hill, D. Gibbs, M. Blume, I. Koyama, M. Tanaka, H. Kawata, T. Arima, T. Tokura, K. Hirota, and Y. Endoh, Phys. Rev. Lett. 81, 582 (1998).
11 Y. Endoh, K. Hirota, S. Ishihara, S. Okamoto, Y. Murakami A. Nishizawa, T. Fukuda, H. Kimura, N. Nojiri, K. Kaneko, and S. Maekawa, Phys. Rev. Lett. 82, 4328 (1999).
12 K. Nakamura, T. Arima, A. Nakazawa, Y. Wakabayashi, and Y. Murakami, Phys. Rev. B 60, 2425 (1999).
13 M. v. Zimmermann, J. P. Hill, D. Gibbs, M. Blume, D. Casa, B. Keimer, Y. Murakami, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. 83, 4872 (1999).
14 L. Paolasini, C. Vettier, F. de Bergevin, F. Yakhou, D. Mannix, A. Stunault, and W. Neubeck, Phys. Rev. Lett. 82 (1999) 4719.
15 For a review see Raman emission by x-ray scattering edited by D. L. Ederer, and J. H. McGuire, (World Scientific, Singapore, 1996).
16 E. D. Isaacs, P. M. Platzman, P. Metcalf, and J. M. Honig, Phys. Rev. Lett. 76, 4211 (1996).
17 J. P. Hill, C.-C. Kao, W. A. L. Calieve, M. Matsubara, A. Kotani, J. L. Peng, and R. L. Greene, Phys. Rev. Lett. 80, 4976 (1998).
18 P. M. Platzman, and E. D. Isaacs, Phy. Rev. B 57, 11107 (1998).
19 P. Abbamonte, C. A. Burns, E. D. Isaacs, P. M. Platzman, L. L. Miler, S. W. Cheong, and M. V. Klein, Phy. Rev. Lett. 83, 860 (1999).
20 K. Tsutsui, T. Tohyama, and S. Maekawa Phy. Rev. Lett. 83, 3705 (2000), and K. Tsutsui, T. Tohyama, and S. Maekawa Phys. Rev. B 61, 7180 (2000).
21 M. Z. Hasan, E. D. Isaacs, Z. -X. Shen, L. L. Miller, K. Tsutsui, T. Tohyama, and S. Maekawa, Science 288, 1811 (1999).
22 T. Inami, T. Fukuda, J. Mizuki, Y. Murakami, K. Hirota, and Y. Endoh, Nucl. Instr. and Meth. (to be published).
23 S. Ishihara, and S. Maekawa, Phy. Rev. B 62, 2338 (2000).
24 M. Blume, J. Appl. Phys. 57, 3615 (1985).
25 S. Ishihara, and S. Maekawa, Phys. Rev. B 62, R9252 (2000).
26 D. Forster, in Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions (Addison-Wesley, Massachusetts, 1990), and P. Fulde, in Electron Correlations in Molecules and Solids (Springer-Verlag, Berlin, 1993).
27 J. C. Slater, and G. F. Koster, Phys. Rev. 94, 1498 (1954).
28 T. Saitoh, A. E. Bocquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B 51, 13942 (1995).
29 T. Arima and Y. Tokura, J. Phys. Soc. Jpn. 64, 2488 (1995).
30 S. Ishihara, J. Inoue, and S. Maekawa, Physica C 263, 130 (1996), and Phys. Rev. B 55, 8280 (1997).
31 K. Hirota, N. Kaneko, A. Nishizawa, Y. Endoh, M. C. Martin, and G. Shirane, Physica B 237-238, 36 (1997).