Theory of Raman scattering from orbital excitations in manganese oxides

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We present a theory of the Raman scattering from the orbital wave excitations in manganese oxides. Two excitation processes of the Raman scattering are proposed. The Raman scattering cross sections are formulated by using the pseudospin operator for orbital degree of freedom in a Mn ion. The Raman spectra from the orbital wave excitations are calculated and their implications in the recent experimental results reported in LaMnO$_3$ are discussed.

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I. INTRODUCTION

Since the discovery of the colossal magnetoresistance, much attention has been attracted to manganese oxides with perovskite structure. A variety of anomalous phenomena including gigantic decrease of the resistivity are observed in the vicinity of the phase transition from the charge and orbital ordered state to the ferromagnetic metallic one in the oxides. One of the key factors to bring about the phenomena is the orbital degree of freedom in a Mn ion. Due to the strong Hund coupling and crystalline field, two $e_g$ orbitals are degenerate and one of the $3d_{x^2−y^2}$ and $3d_{z^2}$ orbitals is occupied by an electron in a Mn$^{3+}$. Extensive studies of the orbital ordering have been done. It is well known that orbital ordering associated with the Jahn-Teller (JT) type lattice distortion plays an important role to stabilize the layered antiferromagnetic (A-AF) ordering in LaMnO$_3$, where spins align parallel (antiparallel) in the $xy$ plane (along the $z$ axis). It has been reported that the observed orbital ordering is cooperatively stabilized by the superexchange (SE)-type electronic interaction, JT, higher-order JT and electron-strain couplings. A variety of magnetic structures with the orbital orderings are also observed in the doped manganites. On the other hand, the dynamics of orbital still remains to be clarified. In the orbital ordered state, the collective electron excitations from occupied orbital to unoccupied one have been theoretically predicted. This excitation is termed orbital wave (OW) and its quantized particle is called orbiton. The OW is expected to affect various low-energy properties, such as magnon and phonon dispersions, and transport. However, the OW excitations have not been observed because the experimental technique was limited. To clarify the dynamics of the orbital degree of freedom and its effects on the physical properties in manganese oxides, it is indispensable to establish a method to observe the OW.

As a probe to observe the OW, Ishihara et al. proposed the resonant inelastic x-ray scattering by which dispersion relation of the OW can be detected. One of the possible methods to detect the orbital excitations is the Raman scattering. Although only the excitations with the total momentum $\mathbf{k}_{\text{tot}} = 0$ are detected, the Raman scattering has the following advantages: its energy resolution is of the order of 1 cm$^{-1}$ which is higher than that of the resonant x-ray scattering (order of 1000 cm$^{-1}$) and the different modes of the excitations are distinguished by the polarization analyses of the incident and scattered photons. Recently, the Raman scattering experiment in the single crystal of LaMnO$_3$ was carried out and peak structures were found around 150 meV. These spectra can be attributed to neither the multphonon nor the magnon excitations by the detailed analyses of the polarization dependence and temperature dependence of the Raman-shift energy. Thus, a theory of the Raman scattering from the remaining degree of freedom, i.e., the orbital excitation, is required to be developed.

In this paper, we present a detailed theoretical framework of the Raman scattering from the OW excitations in orbital ordered manganites. We propose two excitation processes. One of them is analogous to that in the two-magnon Raman scattering in antiferromagnets. In contrast to the magnon Raman scattering, the intensities of the Raman spectra from one- and two-orbiton excitations are of the same order of magnitudes in this process. In another scattering process, photon induces transfer of electrons between Mn $e_g$ and O $2p$ orbitals, and one-orbiton excitation is brought about. We formulate the scattering cross sections by using the pseudospin operator for the orbital degree of freedom in a Mn ion and calculate the Raman spectra from the OW excitations. It is shown that the recent Raman scattering experiments in LaMnO$_3$ are well explained by the OW excitations.

In Sec. II, the model Hamiltonian is introduced and dispersion relation of the OW is investigated. In Sec. III and Sec. IV, the excitation processes for the Raman scattering are proposed and the cross sections are formulated, respectively. Numerical results are presented in Sec. V, where comparison between theory and experiment is shown. The last section is devoted to the summary and discussion.

II. ORBITAL WAVE

Let us set up the model Hamiltonian describing the electronic state of manganese oxides. We consider the tight-binding Hamiltonian in the cubic lattice consisting of Mn ions. At each site, two $e_g$ orbitals are introduced and $t_{2g}$ electrons are treated as a localized spin ($S_{t_{2g}}$) with $S_{t_{2g}}$...
orbital Coulomb interactions and the exchange interaction operator of the electrons given by

\[ \mathcal{H}_t = \mathcal{H}_J + \mathcal{H}_H + \mathcal{H}_{AF} + \mathcal{H}_{JT}. \]

The first term represents the SE interactions between NN \( e_g \) electrons given by

\[
\mathcal{H}_J = -2J_1 \sum_{ij} \left( \frac{3}{4} + \vec{S}_i \cdot \vec{S}_j \right) \left[ 1 - r'_i r'_j \right] - 2J_2 \sum_{ij} \left[ \frac{1}{4} - \vec{S}_i \cdot \vec{S}_j \right] \left[ \frac{3}{4} + r'_i r'_j + r'_i r'_j \right],
\]

where \( J_1 \) and \( J_2 \) indicate the SE interactions. \( \vec{S}_i \) is the spin operator of the \( e_g \) electron with \( S = 1/2 \). \( r'_i = \cos[(2\pi/3)m_1]T_{ix} - \sin[(2\pi/3)m_1]T_{i y} \) with \((m_x, m_y, m_z) = (1, -1, 0)\). \( l \) denotes a direction of a bond connecting \( i \) and \( j \) sites. \( \vec{T}_j \) is the pseudospin operator for the orbital degree of freedom. \( \bar{T}_{ij} = +(-)1/2 \) corresponds to the state where the \( d_{3z^2-r^2} \) orbital is occupied by an electron. The second and third terms in Eq. (1) are given by

\[ \mathcal{H}_H + \mathcal{H}_{AF} = -J_H \sum_i \vec{S}_i \cdot \vec{S}_{2g} + J_{AF} \sum_{ij} \vec{S}_{2g} \cdot \vec{S}_{2g}. \]

Here, the anisotropy of the SE interactions originating from the tetragonal (\( D_{4h} \)) lattice distortion is taken into account as

\[ = 3/2 \]. We introduce three kinds of intrasite Coulomb interactions for \( e_g \) electrons, i.e., the intra-(\( U \)) and inter-(\( U' \)) orbital Coulomb interactions and the exchange interaction (\( I \)), and the energy splitting between two \( e_g \) orbitals due to the distortion of a MnO\(_6\) octahedron. We also introduce the Hund coupling (\( J_H \)) between \( e_g \) and \( t_{2g} \) spins and the antiferromagnetic SE interaction (\( J_{AF} \)) between nearest-neighbor (NN) \( t_{2g} \) spins. Among these energy parameters, the intrasite Coulomb interactions are the largest.\(^{29} \) Thus, by excluding the doubly occupied states in the \( e_g \) orbitals, the following effective Hamiltonian for the low-energy electronic state is derived:\(^{12} \)

\[ \sqrt{J_{1(2)}^2/J_{AF}^2} = \sqrt{J_{AF}^2/J_{AF}^2} = \frac{I_0}{I_0} = R. \]

\( I_0 \) is the transfer intensity between NN \( d_{3p^2-r^2} \) orbitals along the \( \rho \) axis. The last term in Eq. (1) is given by

\[ \mathcal{H}_{JT} = -g_{JT} \sum_{ii} Q_{ii} T_{ii}, \]

with \( g_{JT} \) being the electron-lattice coupling constant. The normal modes of the lattice distortion in a \( O_6 \) octahedron are expressed as \((Q_x, Q_y, Q_z) = (\cos \theta'_{i}, \sin \theta'_i, \sin \theta'_i)\). The lattice degree of freedom is assumed to be frozen in this paper, since the electronic process that we are interested in here has much higher energy than the phonon energy which is, at most, 75 meV in LaMnO\(_3\).\(^{32,33} \)

We introduce the orbital states at the paramagnetic and A-AF phases by applying the mean-field approximation.\(^{34} \) A unit cell with four Mn sites termed \( A_1, A_2, B_1, \) and \( B_2 \) are adopted (see Fig. 1). \( A(B) \) and \( 1(2) \) classify the orbital and spin sublattices, respectively. The following spin order pa-

FIG. 1. (a) A unit cell of the orthorhombic structure (straight lines). Open and filled circles represent Mn and O ions, respectively. Broken lines show a unit cell of the cubic perovskite structure. Arrows indicate the displacements of O ions in the orthorhombic structures where \( \delta_1 \) is an amplitude of the displacement. (b) Alternate rotations of MnO\(_6\) octahedra around \( x' \) axis. \( \beta \) is an angle of the rotation.

FIG. 2. Dispersion relations of OW in (a) paramagnetic and (b) A-AF phases. The Brillouin zone for the tetragonal lattice is adopted. Parameter values are chosen to be \( J_2/J_1 = 0.35 \), \( R = 1.07 \), \( g_{JT} = 1.0 \), and \( \theta_{ij} = 2 \pi /3 \). Orbital state for the paramagnetic (A-AF) phase is denoted by \((\theta_{B1(2)}, \theta_{B1(2)}) = (\theta_A, -\theta_A)\) with \( \theta_A = 0.52 \pi (0.47 \pi) \). An asterisk in (b) shows the mode which becomes Raman active when the monoclinic lattice distortion is introduced (see Fig. 7).
Parameters are introduced: \( \langle S_{iz} \rangle \) and \( \langle S_{iz}' \rangle \) (= \( 3 \langle S_{iz} \rangle \)) with \( \langle \cdots \rangle \) representing the thermal average. For the JT distortion of MnO\(_6\) octahedra, C-type ordering with \( \theta_{A1(12)}^{JT} = (2 \pi/3, -2 \pi/3) \) is adopted by considering the observed lattice distortion in LaMnO\(_3\). Even in the paramagnetic phase, due to the introduced JT coupling, the C-type orbital order realizes.\(^{17}\) For the orbital degree of freedom, we introduce the bosonic operator. Here, spins are assumed to be frozen. In Figs. 2(a) and 2(b), the dispersion relations of the OW in the paramagnetic and A-AF states, respectively, are shown. Parameters are chosen to be \( J_2/J_1 = 0.35 \), \( R = 1.07 \), and \( g_{JT}Q/J_1 = 0.7 \). \( J_1 \) is estimated to be about 50 meV from the dispersion relation of the spin wave, the Néel temperature for A-AF and the orbital ordering temperature.\(^{13}\) It is shown that the orbital excitation has a gap in both cases. However, we note the origins of these gaps are different as follows: The gaps in paramagnetic and A-AF phases are given by \( \epsilon \) \( \approx \cos \theta (\langle T_{iz} \rangle + \sin \theta (\langle T_{ix} \rangle) \) and \( \{ \sqrt{3}/2 \} g_{JT}Q \langle 0 \rangle \rangle J_2 \} \langle 2 \rangle \) \( \langle J_1 \rangle + \langle J_2 \rangle \} \langle 2 \rangle \) respectively, where \( \theta_4 \) is chosen to be \( \pi/2 \). While the gap in the paramagnetic phase decreases with decreasing \( g_{JT}Q \), the gap in the A-AF phase remains finite. This is because the former originates from the anisotropic magnetic structure.\(^{12}\) \( \mu = (a,b) \) with \( a = \pm \) and \( b = \pm \) in Fig. 2 denotes the mode of the OW, where \( a \) \( b \) represents the relative phase of the Holstein-Primakoff bosons in the \( xy \) plane (along the \( z \) axis). Among four modes, the energy of the mode \( \langle \cdots \rangle \) is the highest and its eigenoperator includes the following linear combination of the pseudospin operators:

\[
\alpha_{k=0}^{(+)} = \sqrt{\frac{N_m}{N}} \sum_i \cos \theta_4 \{ \cos \theta^{(+)} + \sinh \theta^{(+)} \} x (T_{A1(1x)} + T_{B1(1x)} + T_{A2(1x)} + T_{B2(1x)}) + i \{ \cosh \theta^{(+)} - \sin \theta^{(+)} \} \{ T_{A1(1y)} - T_{B1(1y)} + T_{A2(1y)} - T_{B2(1y)} \},
\]

where the prime indicates summation over unit cells. \( \cosh \theta^{(+)} \) and \( \sinh \theta^{(+)} \) are the coefficients of the Bogoliubov transformation. \( N_m \) is the number of sites in the unit cell. The symmetry properties of each mode of the OW and their selection rule in the Raman scattering are presented in the Appendix.

The collective orbital excitations in the orbital ordered state are studied by applying the Holstein-Primakoff transformation to the pseudospin operators: \( \tilde{T}_{iz} = 1/2 - a_i^\dagger a_i \) and \( \tilde{T}_{ix} = 1/2 - a_i^\dagger a_i + a_i \) with \( a_i \) being the bosonic operator. Here, spins are assumed to be frozen. In Figs. 2(a) and 2(b), the dispersion relations of the OW in the paramagnetic and A-AF states, respectively, are shown. Parameters are chosen to be \( J_2/J_1 = 0.35 \), \( R = 1.07 \), and \( g_{JT}Q/J_1 = 0.7 \). \( J_1 \) is estimated to be about 50 meV from the dispersion relation of the spin wave, the Néel temperature for A-AF and the orbital ordering temperature.\(^{13}\) It is shown that the orbital excitation has a gap in both cases. However, we note the origins of these gaps are different as follows: The gaps in paramagnetic and A-AF phases are given by \( \epsilon \) \( \approx \cos \theta (\langle T_{iz} \rangle + \sin \theta (\langle T_{ix} \rangle) \) and \( \{ \sqrt{3}/2 \} g_{JT}Q \langle 0 \rangle \rangle J_2 \} \langle 2 \rangle \) \( \langle J_1 \rangle + \langle J_2 \rangle \} \langle 2 \rangle \) respectively, where \( \theta_4 \) is chosen to be \( \pi/2 \). While the gap in the paramagnetic phase decreases with decreasing \( g_{JT}Q \), the gap in the A-AF phase remains finite. This is because the former originates from the anisotropic magnetic structure.\(^{12}\) \( \mu = (a,b) \) with \( a = \pm \) and \( b = \pm \) in Fig. 2 denotes the mode of the OW, where \( a \) \( b \) represents the relative phase of the Holstein-Primakoff bosons in the \( xy \) plane (along the \( z \) axis). Among four modes, the energy of the mode \( \langle \cdots \rangle \) is the highest and its eigenoperator includes the following linear combination of the pseudospin operators:

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where the prime indicates summation over unit cells. \( \cosh \theta^{(+)} \) and \( \sinh \theta^{(+)} \) are the coefficients of the Bogoliubov transformation. \( N_m \) is the number of sites in the unit cell. The symmetry properties of each mode of the OW and their selection rule in the Raman scattering are presented in the Appendix.
is excited to the neighboring Mn $e_g$ orbital. $\rho_{\sigma}$ represents the O $2p$ orbital mixing with the Mn $e_g$ one through the $\sigma$ bond. One of the two electrons in this Mn site returns to the empty O site by emitting a photon. When the occupied orbital in the Mn site in the final state is different from that in the initial state, one-orbiton excitation is brought about. This process is termed the $d$-$p$ process. In contrast to the $d$-$d$ process and the magnon Raman scattering in antiferromagnets, one orbiton is excited in the $d$-$p$ process.

IV. RAMAN SCATTERING CROSS SECTION

In this section, we present the formulation for the cross sections in the $d$-$d$ and $d$-$p$ processes.

A. $d$-$d$ process

The cross section (CS) from the OW excitations is calculated in the system where the $e_g$ electrons and photons are coupled. We adopt the following model Hamiltonian:

\[ \mathcal{H}_{d-d} = \mathcal{H}_{ee}^{d-d} + \mathcal{H}_{ph}^{d-d} + \mathcal{H}_{ee-ph}^{d-d}. \]  

The first and the second terms represent the intrasite electron-electron interactions and the intersite electron transfer, respectively. These are given by

\[ \mathcal{H}_{ee}^{d-d} = \mathcal{H}_H + U \sum_{i\gamma} n_{i\gamma} n_{i\gamma'} + U' \sum_{\gamma\gamma'} n_{i\gamma} n_{i-\gamma}, \]

\[ + J \sum_{\gamma\gamma'} \langle t_{ij}^{\gamma\gamma'} \rangle \delta_{\gamma\gamma'}^d \delta_{ij}^d + H.c. \]

\[ \mathcal{H}_{ph}^{d-d} = \sum_{(ij)} \sum_{\gamma\gamma'} \langle t_{ij}^{\gamma\gamma'} \rangle \delta_{\gamma\gamma'}^d \delta_{ij}^d + H.c. \]

with $\hat{e}_\lambda$ being the unit vector along the polarization $\lambda$, $\vec{J}_{ij}$ represents the electronic current between $\gamma$ orbital at $i$ site and $\gamma'$ orbital at $j$ site given by

\[ \vec{J}_{ij} = i \frac{1}{\hbar} \vec{r}_{ij} \sum_{\sigma} d_{\gamma\sigma}^i d_{\gamma'\sigma}^j + H.c., \]

with $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$.

Being based on the Hamiltonian $\mathcal{H}_{d-d}$, the scattering matrix is calculated. The initial and final states of the scattering are described by the eigen states of $\mathcal{H}$ and the intermediate state is described by those of $\mathcal{H}_{ee}^{d-d}$. The scattering matrix in the $d$-$d$ process is obtained as

\[ S_{ff}^{d-d} = \frac{4\pi Ci}{V} \delta(E_f - E_i) \sum_{(ij)} \left( \hat{e}_{\lambda f}^j \hat{e}_{\lambda i}^i \right) \sum_{\gamma\gamma'} \langle t_{ij}^{\gamma\gamma'} \rangle \delta_{\gamma\gamma'}^d \delta_{ij}^d \]

\[ \times \{ 2 \vec{J}_1(\hat{\tau} \cdot \hat{S}_i \cdot \hat{S}_j)(\vec{r}_i - \vec{r}_j) \]

\[ + 2 \vec{J}_2(\hat{\tau} \cdot \hat{S}_i \cdot \hat{S}_j)(\vec{r}_i + \vec{r}_j) \} \]

with $C = \pi e^2/(\hbar^2 \sqrt{\omega_k \omega_l})$. $E_{i(f)}$ represents the energy of the initial (final) state, $\vec{J}_1$ and $\vec{J}_2$ are defined as $\vec{J}_1 = I_{dd} l_{dd}^p(U' - \hbar \omega_{k})$ and $\vec{J}_2 = I_{dd} l_{dd}^p(U + \hbar \omega_{k})$.

Rewriting the pseudospin operators in Eq. (13) by using the Holstein-Primakoff bosons, and obtain the CS. The CS from the one-orbiton excitation is given by

\[ P_{1}^{d-d} = \frac{2N_i}{(2\pi^2)^2} \sum_{\mu \nu \gamma} \left( \hat{e}_{\lambda f}^j \hat{e}_{\lambda i}^i \right) \delta_{\nu\gamma} \mathcal{K}_{nn} \{ V_{ep} \}

\[ + W_{ep}(0) \}

\[ + (1 + n_{\mu \nu}) \delta(\Delta E - \epsilon_{\gamma \gamma'}) \}

where $\rho = \hat{\tau}, \hat{\tau}, \hat{\tau}$. $K_{\gamma \gamma'}^{pp}$, is given by

\[ K_{\gamma \gamma'}^{pp} = \vec{J}_1(\hat{\tau} + S_{\rho})S_{\rho}^{C_{\gamma \gamma'}} - \vec{J}_2(\hat{\tau} - S_{\rho})S_{\rho}^{C_{\gamma \gamma'}} + S_{\rho}^{C_{\gamma \gamma'}} \]

with $S_{\rho} = (\hat{S}_i \cdot \hat{S}_i + \rho)$. $S_{\rho}^{C_{\gamma \gamma'}} = \sin(\theta_{\gamma \gamma'} + (2\pi/3)\mu_p)$, and $C_{\gamma \gamma'} = \cos(\theta_{\gamma \gamma'} + (2\pi/3)\mu_p)$. $V_{ep}(\hat{k})$ and $W_{ep}(\hat{k})$ are the coefficients of the Bogoliubov transformation connecting the boson operator for the $\rho$th ion to that for the $\mu$th eigenmode with the energy $\epsilon_{\nu \gamma'}$

\[ a_{\mu \nu} = V_{ep}(\hat{k})a_{\mu \nu} + W_{ep}(\hat{k})a_{\mu \nu} \]

$n_{\rho \mu \nu}$ is the Bose distribution function and $\Delta E = \hbar \omega_{k}$, $-\hbar \omega_{k}$ represents the Raman-shift energy. The CS from the two-orbiton excitation is given by
\[ I_{2}^{d-d} = \frac{\alpha_2^2 C^2 N}{\hbar(2\pi c^2)^2} \sum_{\nu=\nu'} \sum_{\rho=\rho'} \left( \hat{\epsilon}_{\lambda', \rho'} \left( \hat{\epsilon}_{\lambda, \rho} \right)^* \right) \times \left[ L_{\nu' \rho}^\dagger V_{\nu \rho}(\vec{k}) W_{\nu' \rho}(\vec{k}) + \mathcal{M}_{\nu' \rho}^\dagger(\vec{k}) \delta_{\nu', \rho} \left\{ V_{\nu \rho}(\vec{k}) \right\} \right]^2 + \mathcal{W}_{\nu \rho}(\vec{k}) \left\{ V_{\nu' \rho'}(\vec{k}) - \mathcal{W}_{\nu' \rho'}(\vec{k}) \right\} \right] \times (1 + n_{\mu} - n_{\mu'} + 1) \delta(\Delta E - \epsilon_{\mu} - \epsilon_{\mu'}), \tag{17} \]

with

\[ L_{\nu' \rho}^\dagger = I_{1}^{2}(\vec{x} + S_{\rho}) C_{\nu}^\dagger C_{\rho}^\dagger - I_{2}(\vec{x} - S_{\rho}) (C_{\nu}^\dagger C_{\rho}^\dagger + 2 C_{\nu}^\dagger), \tag{18} \]

\[ \mathcal{M}_{\nu' \rho}^\dagger(\vec{k}) = 2\left[ I_{1}(\vec{x} + S_{\rho}) - I_{2}(\vec{x} - S_{\rho}) \right] S_{\rho}^\dagger S_{\nu}^\dagger \cos k_{\rho}. \tag{19} \]

In Eq. (17), the anti-Stokes parts are neglected for simplicity. The interaction between both orbitons in the final state is neglected. This interaction is expected to shift the two-orbition Raman spectrum to the lower-energy region as the magnon-magnon interaction does in the two-magnon Raman scattering.\(^{36}\)

**B. d-p process**

To calculate the CS, let us start with the following model Hamiltonian where Mn \( e_{g} \) and O \( p_{\sigma} \) orbitals and the electron-photon coupling are taken into account,

\[ \mathcal{H}_{d-p} = \mathcal{H}_e^{d-p} + \mathcal{H}_r^{d-p} + \mathcal{H}_{ph} + \mathcal{H}_{e-ph}. \tag{20} \]

The first and second terms describe the intrasite electron-electron interactions and electron hopping as \( \mathcal{H}_e^{d-p} = \mathcal{H}_e^{d-d} + \frac{1}{2} \sum_{i, \delta, \sigma} \Delta p_{i, \delta} p_{i, \delta} \), and

\[ \mathcal{H}_r^{d-p} = \sum_{i, \gamma, \delta} \mathcal{t}_{i, \gamma, \delta} p_{i, \delta} \mathcal{P}_{i, \delta, \alpha} + \text{H.c.}, \tag{21} \]

respectively, where \( \Delta \) is the energy level of O \( p_{\sigma} \) orbital, and \( p_{i, \delta} \) is the annihilation operator of the electron with \( \sigma \) spin at \( \vec{r}_{i} + l_{pd} \vec{\delta}_{i} \). \( l_{pd} \) is the distance between NN Mn and O sites. \( \vec{\delta}_{i} \) is the unit vector along the local \( \pm x, y, z \) direction reflecting the rotation of MnO\(_6\)\). \( t_{i, \gamma, \delta} \) represents the transfer intensity between NN Mn \( e_{g} \) and O \( p_{\sigma} \) orbitals and is given by

\[ t_{i, \gamma, \delta} = t_{pd} \begin{pmatrix} 1 & 1 & 1 \\ -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ \frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 \end{pmatrix}_{\gamma, \delta}, \tag{22} \]

for \( \delta=x, y, z \) and \( t_{i, \gamma, \delta} = -t_{i, \gamma, \delta} \). \( t_{pd} \) is the transfer intensity between Mn \( d_{z^2-r^2} \) orbital at \( \vec{r}_{i} \) and O \( p_{z} \) orbital at \( \vec{r}_{i} + l_{pd} \vec{z}_{i} \). The electron-photon interaction is represented by the fourth term in Eq. (20),

\[ \mathcal{H}_{e-ph} = \frac{4 \pi C I}{V} \delta(\mathcal{E}_{f} - \mathcal{E}_{i}) \sum_{\rho} \left( \hat{\epsilon}_{\lambda, \rho} \hat{\rho}_{\lambda, \rho} \right)^2 \]

\[ \times \mathcal{S}_{i, \gamma}^{d-p} \left\{ V_{\nu \rho}(0) + W_{\nu \rho}(0) \right\}^2 \]

\[ \times \left\{ (1 + n_{\mu} - n_{\mu'} + 1) \delta(\Delta E - \epsilon_{\mu} - \epsilon_{\mu'}) \right\}, \tag{26} \]

**V. NUMERICAL RESULTS**

In this section, we present the numerical results for the Raman spectra.

**A. d-d process**

Numerical results for the Raman spectra given by the summation of \( I_{1}^{d-d} \) and \( I_{2}^{d-d} \) are presented in Fig. 4. Figures 4(a), 4(b) and 4(c), 4(d) are the results in the paramagnetic and A-AF phases, respectively. \( I_{0}^{d-d} \) is defined as \( I_{0}^{d-d} = \frac{\alpha_2^2 C^2 N}{\hbar(2\pi c^2)^2} \mathcal{J}_{1}^2 \) and is assumed to be independent of \( \omega_{f} \) and \( \omega_{i} \), for simplicity. Parameter value is chosen to be \( \mathcal{J}_{2}/\mathcal{J}_{1} = 0.35 \). Other parameter values are the same as those in Fig. 2. Sharp spectra in the region \( 3.0 < \Delta E/\mathcal{J}_{1} < 3.6 \) (3.5 < \( \Delta E/\mathcal{J}_{1} < 4.5 \) and broad ones in the region \( 2.0 < \Delta E/\mathcal{J}_{1} < 7.0 \) (5.0 < \( \Delta E/\mathcal{J}_{1} < 9.0 \)) in the paramagnetic (A-AF) phase originate from one- and two-orbition excitations, respectively. In the \( (x, y) \) and \( (z, x) \) polarizations, the one- and two-orbition excitations are not brought about. In these configurations, polarization of the scattered photon is perpendicular to that of the incident photon and both the polarizations are parallel to the bonds between NN Mn sites. Therefore, matrix element \( S_{i, \gamma}^{d-p} \) in Eq. (13) vanishes and orbital excitations
are prohibited. We notice the following relations of the relative intensity in the two-orbital Raman spectra: \( I(x, x) \sim I(x', x') > I(z, z) \gg I(x', y') \). These relations reflect the C-type orbital ordering with \( \theta_{A1} = 0.507\pi (0.481\pi) \) in the paramagnetic (A-AF) phase. In these orbital orderings, SE interaction between NN \( \epsilon_g \) electrons in the \( xy \) plane is much stronger than that along the \( z \) axis. Therefore, the intensity in the \( (z, z) \) polarization is smaller than those in the \( (x, x) \) and \( (x', x') \) polarizations. Small intensity in the \( (x', y') \) configuration is attributed to the interference effect between the orbitals with different symmetry. In the spectra from two-orbital excitations, several peaks and edges are shown. As the two-magnon Raman spectra reflect the density of states (DOS) of the magnon, the two-orbital Raman spectra reflect the DOS of the orbital. Position of the each peak corresponds to the van Hove singularity of the DOS of the orbital.

**B. \( d-p \) process**

In Figures 5, numerical results of the Raman spectra in the \( d-p \) process are shown. Figures 5(a) and 5(b)–5(d) are the results in the paramagnetic and A-AF phases, respectively. \( \tilde{t}_p^{d-p} \) is defined as \( \tilde{t}_p^{d-p} = \alpha_{c}^2 e^{2}/N/\xi(2\pi)^2 J \xi \) and is assumed to be independent of \( \omega_{c} \), for simplicity. Parameter values are chosen to be \( \delta_{1}/l_{pd}=0.04 \) and \( \beta=\pi/18 \). Changes in the distance and transfer intensity between Mn and O ions are taken into account as a prefactor of \( \rho_{p} \) in Eq. (26) up to the order of \( O(\delta_{1}/l_{pd}) \). Other parameter values are the same as those in Fig. 2. We find that the relative intensity of the two spectra from the \( A_g \) and \( B_{1g} \) modes in the \( (x, x) \) configuration in the \( d-p \) process is different from that in the \( d-d \) process, i.e., in the \( d-p \) process, the spectrum of the \( A_g \) mode becomes larger than that of the \( B_{1g} \) mode. As shown in Eq. (5), in the \( A_g \) mode, the orbital excitation at each site occurs in-phase. Therefore, the interference effect in the in-phase \( A_g \) mode increases its intensity in the \( d-p \) process. On the other hand, in the \( d-d \) process, orbital excitation is dominated by the process where the two electrons in the NN Mn sites are exchanged with each other. This reflects the AF-type orbital ordering in the ground state. A minus sign in the scattering matrix arises from the exchange of electrons and the interference effects are reduced.

**C. Effect of the lattice distortion**

It has been reported that the lattice structure of LaMnO₃ is of the monoclinic when the oxygen partial pressure during the synthesis is low. A sample used in the recent Raman scattering experiments shows the monoclinic structure. We examine the effect of the monoclinic distortion on the Raman spectra for the detailed comparison between the theory and the experiments.

We adopt a model of the monoclinic structure shown in Fig. 6. Displacements of the O ions indicated by arrows are considered up to the order of \( O(\delta_{1}/l_{pd}) \). The transfer intensity between NN Mn \( \epsilon_g \) orbitals in the \( xy \) plane is given by \( \tilde{t}_p^{d-p}(\delta) = \tilde{t}_p(0)(1 + \delta l_{pd})^{-3.5} (1 - \delta l_{pd})^{-3.5} \) and does not change in the order of \( O(\delta_{1}/l_{pd}) \). \( J_{13}^{xy}[z(z/\xi)^2] \) does not change, either. On the contrary, \( t_{pd} \) changes as \( t_{pd}(\delta) = t_{pd}(0)(1 \pm 3.5\delta l_{pd}) \). This indicates the Raman spectra in the \( d-p \) process are sensitive to the the oxygen displacement. We concentrate on the \( d-p \) process, below.

In Fig. 7, the numerical results with the monoclinic distortion are shown. Here, the dispersion relation of the OW is calculated in the unit cell which includes eight Mn sites with the A-AF ordering. Parameter values are chosen to be \( (\delta_{1}, \delta_{2}, \delta_{3}, \delta_{4})/l_{pd} = (0.03, 0.11, 0.07, 0.15) \), \( \beta=\pi/18 \) and \( R = 1.15 \). Other parameters are the same as those in Fig. 2. We
dones with the monoclinic distortion in the experimental results are compared with our theoretical case. I OW excitations.

There also appear new peaks at 3.1 J\textsuperscript{1}. The peak position corresponds to the energy of the OW at the X point marked by an asterisk in Fig. 2(b). This mode becomes zone center mode and Raman active in the monoclinic structure.

Now, let us compare our theoretical results with the recent experimental ones reported in a single crystal of LaMnO\textsubscript{3}.\textsuperscript{28} In addition to the phonon Raman spectra below 100 meV\textsuperscript{32,33} the sharp spectra are observed at 120–170 meV (see the insets of Fig. 7). The OW is considered as an origin of the new spectra. In the Raman scattering experiment, the 514.5 nm (2.4 eV) line of an Ar\textsuperscript{+} laser was used. The energy of the incident photon is expected to be almost the same as the electron excitation energy from O 2p to Mn e\textsubscript{g}.\textsuperscript{41} In this case, J\textsuperscript{d-p} is strongly enhanced compared with J\textsuperscript{d-d}.\textsuperscript{42} Thus, the experimental results are compared with our theoretical ones with the monoclinic distortion in the d-p process. As shown in Fig. 7, the characteristic features of polarization dependence and relative intensity of the experimental Raman spectra in the region of 120–170 meV are well reproduced by our theoretical ones. Thus, the Raman spectra observed in the region of 120–170 meV in LaMnO\textsubscript{3} are attributed to the OW excitations.

VI. SUMMARY AND DISCUSSION

In this study, we have theoretically investigated the Raman scattering as a probe to detect the OW excitation in manganites. We proposed two excitation processes for the Raman scattering, i.e., the d-d and d-p processes. The d-d process is analogous to the two-magnon Raman scattering process in antiferromagnets. However, scattering intensity from one- and two-orbital excitations are of the same order of magnitude. In the d-p process, photon induces transfer of electrons between Mn e\textsubscript{g} and O 2p orbitals, and one-orbital excitations are brought about. Because LaMnO\textsubscript{3} is a charge-transfer type insulator where the optical gap is about 1 eV, the d-p process is expected to dominate the Raman scattering using the visible light. It was shown that the theoretical results of the Raman spectra from the one-orbital excitations well explain the experimental Raman spectra observed in LaMnO\textsubscript{3}.

As mentioned in Sec. II, the OW in the A-AF phase has a gap originating from the anisotropic spin structure. We expect that the gap is suppressed by applying a magnetic field. This change will be detected as a shift of the peak positions of the spectra. The gap-less OW may also be observed in the ferromagnetic-insulating manganites such as La\textsubscript{0.88}Sr\textsubscript{0.12}MnO\textsubscript{3}, where the orbital ordering is experimentally confirmed.\textsuperscript{33} In Sec. V, we compared the theoretical...
results in the $d$-$p$ process with the experiments\textsuperscript{28} by considering the incident photon energy. It is expected that the spectral intensities in the $d$-$d$ process are enhanced with increasing the incident photon energy and resonating with the electron excitation between the lower and the upper Hubbard bands. When the Raman scattering experiment using such a high-energy photon is carried out in LaMnO$_3$, the Raman spectra from the two-orbital excitations will be observed around 200–350 meV and much information of the OW will be obtained.

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**APPENDIX: SYMMETRY PROPERTY OF ORBITAL WAVE**

We present in this appendix the symmetry properties of OW introduced in Sec. II and their selection rules in the Raman scattering. It is shown that the irreducible representations of the modes $(-\pm)$, $(-\pm)$, $(\pm)$, and $(\pm)$ at $\vec{k}=0$ are identified as $A_g$, $B_{2g}$, $B_{1g}$, and $B_{3g}$ in the $D_{2h}$ group, respectively. From the irreducible representations, the allowed-mode symmetries of the orbital waves in several polarization configurations are assigned. In this paper, polarization configuration of incident and scattered photons is denoted by $(\zeta, \eta)$ with $\zeta, \eta=x, y, z, x', y'$. Here, $x$, $y$, and $z$ axes are taken to be the directions of the bonds connecting NN Mn sites and $x'=x+y (y'=-x+y)$. $x'$, $z$ and $-y'$ axes correspond to $a$, $b$, and $c$ axes in $Pnma$ structure, respectively (see Fig. 1). Polarization configurations and the allowed-mode symmetries of the orbital waves are summarized as follows:

\[ (x,x) \rightarrow A_g + B_{1g}, \]
\[ (y,y) \rightarrow A_g + B_{1g}, \]
\[ (z,z) \rightarrow A_g, \]
\[ (x,y) \rightarrow A_g, \]
\[ (z,x) \rightarrow B_{2g} + B_{3g}, \]
\[ (x',x') \rightarrow A_g, \]
\[ (x',y') \rightarrow B_{1g}. \]
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42 The relative strength of the scattering intensity between the d-d and the d-p processes is estimated as follows. Using $l_{dd} \approx 2l_{dp}$ and $t_0 \approx t_{pd}/\Delta$ with $t_{pd} \approx 1.8$ and $\Delta \approx 4.5$ eV (Ref. 29), and keeping the leading terms in $I_{0}^{d-d}$ and $I_{0}^{d-p}$, we obtain $I_{0}^{d-d}/I_{0}^{d-p} \approx 0.42 [U^{'2} - \frac{3}{2} J_H \Delta - h \omega_{\xi}^2 I (U^{'2} - I - h \omega_{\xi}^2)]^2$. The fraction of $I_{0}^{d-d}$ is less than 20% when $h \omega_{\xi}^2 < U^{'2} - I - (3/4) J_H \Delta$.