ELSEVIER

Physica B 237–238 (1997) 51–53

PHYSICA B

# Raman scattering by orbital waves in perovskite $LaMnO_3$

J. Inoue[a,*], S. Okamoto[a], S. Ishihara[b], W. Koshibae[c], Y. Kawamura[a], S. Maekawa[a,d]

[a] *Department of Applied Physics, Nagoya University, Nagoya 464-01, Japan*
[b] *Department of Applied Physics, University of Tokyo, Tokyo 113, Japan*
[c] *CIRSE, Nagoya University, Nagoya 464-01, Japan*
[d] *Institute for Materials Research, Tohoku University, Sendai 980-77, Japan*

**Abstract**

Magnon Raman scattering is proposed as a possible method to observe the orbital ordering in the perovskite $LaMnO_3$. Calculated results of the peak positions of the spectra in a semi-classical method show an anisotropic feature of the spectra.

*Keywords:* Perovskites; Orbital ordering; Raman scattering

Recently perovskite manganites attracted renewed interest because of the colossal magnetoresistance [1]. The insulating phase of the manganities, $LaMnO_3$, shows a layered-type antiferromagnetic (AF) ordering, the so-called A-type AF. The Jahn–Teller distortion due to the orbital degeneracy of the $e_g$ states has been suggested to be an origin of the A-type AF in $LaMnO_3$ [2,3]. On the other hand, we have recently proposed that the on-site Coulomb interaction between $e_g$ electrons is crucial to magnetic structures in manganites [4–6]. The strong on-site Coulomb interaction within the degenerate orbitals gives rise to a coupling between spins and orbitals, and this coupling brings about various spin and orbital orderings. Previously, we have shown in a mean field approximation [5] that the A-type AF in $LaMnO_3$ is realized when the strong on-site Coulomb interaction is included and the $[d_{3x^2-r^2}, d_{3y^2-r^2}]$ type orbital ordering [7] is assumed. The result has been confirmed in the exact diagonalization method for small clusters [6], that is, the spin and orbital correlation functions indicate the appearance of the A-type AF and the orbital ordering mentioned above. We have concluded that the A-type AF is realized by self-adjusting the orbitals to lower the ground state (GS) energy. Thus, the orbital ordering is crucial to the magnetic structures. However, there is no direct observation of the orbital ordering in the manganites so far. In this paper, we propose that the inelastic light scattering, i.e., the magnon Raman scattering, is a possible candidate to observe the orbital ordering directly and present results of the Raman spectra calculated in a simple semi-classical theory bearing $LaMnO_3$ in mind.

The Raman spectra $I(\omega)$ is given by $I(\omega) = \sum_f |\langle f|H_R|0\rangle|^2 \delta(\omega - E_f + E_0)$, where $|0\rangle$ and $|f\rangle$ are the GS and a final state in the Raman process, respectively. $H_R$ is an interaction Hamiltonian between electrons and the light. In usual two magnon process, $H_R$ is given by a Heisenberg-type Hamiltonian with the polarization vectors of the electric field of the light. In the present case where the orbital degree of freedom exists, the expression of $H_R$ should be determined from the beginning. Once $H_R$ is given, $I(\omega)$ can be expanded by moments, $m_i$, where $m_1$ represents the peak position of the spectra. By using $H_R$ and the Hamiltonian $H$ of the system, $m_1 = \langle 0|H_R[H, H_R]|0\rangle / \langle 0|H_R^2|0\rangle$.

* Corresponding author.


*PII* S0921-4526(97)00045-8

In the Ising limit, the Hamiltonian $H$ of $LaMnO_3$ is given by Ref. [5],

$$H = -\tilde{J}\sum_{\langle ij\rangle}\left(\tfrac{3}{4}+S_i^zS_j^z\right)\times[\tfrac{1}{2}(t_{ij}^{aa2}+t_{ij}^{bb2}+t_{ij}^{ab2}+t_{ij}^{ba2})-2(t_{ij}^{aa2}+t_{ij}^{bb2}+t_{ij}^{ab2}+t_{ij}^{ba2})T_i^zT_j^z]+K\sum_i S_i^z(t_{2g})S_i^z+J_{t_{2g}}\sum_{\langle ij\rangle}S_i^z(t_{2g})S_j^z(t_{2g}), \quad (1)$$

where the first term is an effective interaction between $e_g$ spins derived by eliminating the on-site Coulomb interaction, the second and third terms are the Hund coupling ($K<0$) and AF interaction between $t_{2g}$ spins, respectively. Here, $S^z$ and $T^z$ are the $z$-components of the spin and pseudospin operators representing the spin and orbital degrees of freedom of $e_g$ electrons, respectively, $\tilde{J}=t_0^2/(U'-J')$ with the inter-orbital Coulomb ($U'$) and inter-orbital exchange ($J'$) interactions within the same ion, and hopping integral $t_0$ between two neighboring $d_{x^2-y^2}$ orbitals in the $x$ direction. $t_{ij}^{ab}$ is a hopping integral, normalized by $t_0$, between $a$ orbital on $i$ site to $b$ orbital on $j$ site. When $|K|$ is fairly large and $J_{t_{2g}}$ is small, the GS of $H$ is ferromagnetic (F) in the spin space and AF in the orbital space.

$H_R$ for $e_g$ electrons can be derived by applying the method proposed by Shastry and Shraiman [8] where the second-order perturbation is applied to the interaction between electrons and the light for a given GS. When the GS is F in the spin space and AF in the orbital space, only orbital excitations contribute to the magnon Raman scattering. Therefore, $H_R$ includes terms such as $T_i^+T_j^-, T_i^zT_j^+$ and their conjugates, where $i$ and $j$ are the nearest neighbor sites within the $x$–$y$ plane. Here, $T^{\pm}$ denotes the transverse component of the psuedospin operator **T**. Note that the orbital ordering along $z$-axis does not contribute to the spectra in this orbital ordering. By calculating the moment $m_1$ using Holstein–Primakoff bosons for a given final configuration of spins, the peak position $\omega$ of the spectra can be obtained such that $\omega=(16/3)\tilde{J}$ and $(32/3)\tilde{J}$ for $T_i^zT_j^{\pm}$ and $T_i^+T_j^-$ terms, respectively. The spectra are anisotropic, i.e., they depend on whether the polarization vectors of the incident and scattered lights are along the $z$-axis or $x(y)$-axis. The values of $\omega$ evaluated from $E_f$ for a given final configuration of spins are nearly the same with those given above. Note, however, the peak positions calculated in the semi-classical model are somewhat higher than those in the full quantum theory.

When the GS is the A-type AF, the $x$–$y$ component of $H_R$ includes only $T_i^zT_j^{\pm}$, while $z$ component includes $T_i^zT_j^+, S_i^+S_j^-, S_i^+S_j^-T_i^zT_j^{\pm}, S_i^+S_j^-T_i^+T_j^-$, and their conjugates because of the AF spin ordering along $z$-axis. It is interesting to note that the spins and orbitals couple to contribute to the Raman spectra. In this case, $\omega=(28/9)\tilde{J}$ for $x$–$y$ component and $\omega=4\tilde{J}-3K, (28/9)\tilde{J}, (40/9)\tilde{J}-3K$ and $(16/3)\tilde{J}-3K$ for $T_i^zT_j^{\pm}, S_i^+S_j^-, S_i^+S_j^-T_i^zT_j^{\pm}$ and $S_i^+S_j^-T_i^+T_j^-$ of the $z$ component, respectively. As the reversal of two spins in the final state violates the Hund coupling, $-3K$ appears in the frequency of the spectra. The spectra are also anisotropic in this case. However, as $|K|$ can be large, 2–3 eV, some of the peaks may not be observed and the spectra may be isotropic apparently. The value of $\tilde{J}$ is larger than $J_{t_{2g}}$ by about one order of magnitude [5, 6], and the latter is estimated from the Néel temperature $T_N=120$ K of $CaMnO_3$ to be 1–2 meV. So, the Raman spectra will be observed in a frequency region of order of a few hundreds $cm^{-1}$.

So far, we have neglected the effect of lattices, i.e., level splitting of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals. If there is a distortion of the octahedrons, the Raman spectra may appear at higher-frequency region. We also neglected the contribution from $t_{2g}$ spins. They may contribute as higher-order processes and the intensity due to these processes may be weak. Because we dealt with Ising-like Hamiltonian in the present analysis, the GS is F in spin ordering and AF in orbital ordering. Even if the A-type AF is properly treated by using the full Hamiltionian, the qualitative features argued in this paper will be unchanged.

In conclusion, the Raman scattering has been proposed to observe the orbital ordering in $LaMnO_3$. The spectra will be anisotropic depending on the type of orbital ordering. The frequency of the spectra will be order of a few hundreds $cm^{-1}$ when the distortion of the octahedron is negligible.

The work was supported by a Grant-in-Aid for Scientific Research on Priority-Areas from Ministry of Education, Science and Culture of Japan, and New

Energy and Industrial Technology Development Organization (NEDO).

## References

[1] Y. Tokura et al., J. Phys. Soc. Japan 63 (1994) 3931.
[2] T. Mizokawa and A. Fujimori, Phys. Rev. B 51 (1995) 12 880.
[3] I. Solovyev, N. Hamada and K. Terakura, Phys. Rev. Lett. 76 (1996) 4825.
[4] J. Inoue and S. Maekawa, Phys. Rev. Lett. 74 (1995) 3407.
[5] S. Ishihara, J. Inoue and S. Maekawa, Physica C 263 (1996) 130.
[6] W. Koshibae et al., to be published.
[7] G. Matsumoto, J. Phys. Soc. Japan 29 (1970) 606.
[8] B.S. Shastry and B.I. Shraiman, Phys. Rev. Lett. 65 (1990) 1068.