Optical Investigations of Charge Gap in Orbital Ordered
La$_{1/2}$Sr$_{3/2}$MnO$_4$

J. H. Jung,$^1$ J. S. Ahn,$^1$ T. W. Noh,$^1$ Jinhyoung Lee,$^2$ Jaejun Yu,$^1$ Y. Moritomo,$^3$ I. Solovyev,$^4$ and K. Terakura$^4$

$^1$Department of Physics, Seoul National University, Seoul 151-742, Korea
$^2$Department of Physics, Sogang University, Seoul 121-742, Korea
$^3$CIRSE, Nagoya University, Nagoya 464-8603 and PRESTO, JST, Japan
$^4$JRCAT, National Institute for Advanced Interdisciplinary Research, Tsukuba, Ibaraki 305, Japan

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Abstract

Temperature and polarization dependent electronic structure of La$_{1/2}$Sr$_{3/2}$MnO$_4$ were investigated by optical conductivity analyses. With decreasing temperature, for $E \parallel ab$, a broad mid-infrared (MIR) peak of La$_{1/2}$Sr$_{3/2}$MnO$_4$ becomes narrower and moves to the higher frequency, while that of Nd$_{1/2}$Sr$_{3/2}$MnO$_4$ nearly temperature independent. We showed that the MIR peak in La$_{1/2}$Sr$_{3/2}$MnO$_4$ originates from orbital ordering associated with CE-type magnetic ordering and that the Jahn-Teller distortion has a significant influence on the width and the position of the MIR peak.

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Due to extensive studies of 3d transition metal oxides, it has been recognized that correlations among spin, charge, and orbital degrees of freedom play important roles in their physical properties [1]. Especially in doped manganites, such a coupling exhibits very interesting phenomena: colossal magnetoresistance [2], magnetic field induced structural phase transition [3], and charge/orbital ordering [4]. Recently, much interest has been focused on the charge/orbital ordering which can be characterized by a real space ordering of Mn$^{3+}$/Mn$^{4+}$ ions at a commensurate value of charge carrier, such as 1/8, 1/2, and 2/3. The charge/orbital ordering usually incorporates with a sharp increase of resistivity, a suppression of magnetic susceptibility, and changes of lattice constants [5].

To get understanding on the charge/orbital ordering, many efforts have been put into La$_{1/2}$Sr$_{3/2}$MnO$_4$ [6–8], which is known to have a CE-type antiferromagnetic (AFM) ordering below $T_N \sim 110$ K. Murakami et al. [8] reported diffraction studies of La$_{1/2}$Sr$_{3/2}$MnO$_4$ using x-ray near the Mn K-absorption edge. From anomalous dispersion of scattering factor for Mn$^{3+}$ and Mn$^{4+}$, they claimed that the charge/orbital ordering was observed directly. To explain why the Mn 3d orbital ordering can influence such Mn 1s → 4p dipole transition, Ishihara et al. [9] suggested Coulomb repulsion between the Mn 3d and 4p electrons. However, Elfimov et al. [10] pointed out that band structure effects rather than the local Coulomb repulsion should dominate the polarization dependence of the K edge scattering.

In this Letter, we report optical conductivity spectra, $\sigma(\omega)$ of La$_{1/2}$Sr$_{3/2}$MnO$_4$ (LSMO) and Nd$_{1/2}$Sr$_{3/2}$MnO$_4$ (NSMO). Note that the former show an charge/orbital ordering around $T_{co} \sim 220$ K, but that the latter does not show any ordering at all [11]. As temperature ($T$) decreases, a mid-infrared (MIR) peak in the LSMO ab-plane becomes narrower and a corresponding optical gap significantly increases. On the contrary, the MIR peak of the NSMO shows little $T$-dependence. To understand these interesting phenomena, we calculated the polarization dependent $\sigma(\omega)$ using the linearized muffin-tin orbital (LMTO) methods and by analysis of the tight binding (TB) model. The LMTO results were in a remarkable agreement with experimental ones, indicating that the strong orbital ordering with the CE-type AFM ordering bring forth the MIR peak. Furthermore, the TB analysis clearly suggests that the
strong $T$-dependences of the optical gap $\Delta$ and the MIR peak of LSMO should be caused cooperatively by the orbital ordering, the CE-type AFM ordering, and the Jahn-Teller (JT) distortion.

We prepared LSMO and NSMO single crystals using the floating zone methods. Details of sample growth and characterizations were reported earlier [11]. Near normal incident reflectivity spectra $R(\omega)$ were measured from 0.01 to 6.0 eV with various temperatures and polarizations. Just before reflectivity measurements, we polished the crystals up to 0.3 $\mu$m using diamond pastes. To subtract surface scattering effects, a gold normalization technique was used. Using the Kramers-Kronig (KK) transformation, $\sigma(\omega)$ were obtained [12]. To reduce errors of the KK analysis, we also independently measured $\sigma(\omega)$ in the frequency region of 1.5 $\sim$ 5.0 eV using the spectroscopic ellipsometry (SE). For such optically uniaxial samples, we should measure ratios of reflectances for $p$- and $s$- polarized lights at several incident angles and then calculated optical constants [13]. The SE results agreed quite well with the KK results, demonstrating the validity of our KK analysis.

Figures 1(a) and (b) show the polarization dependent $\sigma(\omega)$ of LSMO and NSMO at 290 K, respectively. Note that the behaviors of $\sigma(\omega)$ at 290 K are quite similar for both crystals, suggesting the optical transitions related with the La and the Nd ions should be located at the energy region higher than 4.0 eV. The $\sigma(\omega)$ in the ab-plane ($E \parallel ab$) are quite different from those along the c-axis ($E \parallel c$). [Similar anisotropy could be seen in a bilayer manganite, La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ [14].] Gap values were estimated from crossing points of abscissa with linear extrapolations of $\sigma(\omega)$. For both crystals, $\sigma(\omega)$ for $E \parallel ab$ show broad peaks around 1.0 and 3.5 eV with $\Delta \sim 0.2$ eV, and $\sigma(\omega)$ for $E \parallel c$ show peaks around 1.2 and 4.0 eV with $\Delta \sim 0.7$ eV. Since the broad peaks located above 2.0 eV are similar to those in cubic perovskite manganites [15], these features can be assigned to O 2$p \rightarrow$ Mn $e_g$ transitions.

Although $\sigma(\omega)$ for both crystals are very similar at 290 K, their $T$-dependences are quite different. Figures 2(a) and (b) show $T$-dependent $\sigma(\omega)$ of LSMO and NSMO for $E \parallel ab$. [$T$-dependences of $\sigma(\omega)$ for $E \parallel c$ are quite small.] For LSMO, there are large spectral weight
changes up to 2.0 eV. With decreasing $T$, the spectral weight below 0.8 eV is transferred to a higher energy: $\Delta$ increases significantly and the broad peak around 1.0 eV becomes narrower. For NSMO, there is little $T$-dependence in $\sigma(\omega)$ and $\Delta$ is also nearly independent of $T$. From this comparison, we can argue that the large spectral changes in LSMO should come from the charge/orbital ordering associated with the CE-type AFM ordering.

To get further insights, we compared our experimental results with theoretical predictions. Figure 3 shows $\sigma(\omega)$ calculated for $Y_{1/2}Sr_{3/2}MnO_4$ using the LMTO method \[16\]. [Even though we calculated for $Y_{1/2}Sr_{3/2}MnO_4$, the main features of $\sigma(\omega)$ are thought to be nearly the same as LSMO.] Since we used the phenomenological Lorentzian broadening with $\Delta \varepsilon \simeq 0.13$ eV, the value of $\sigma(0)$ is finite even in the insulating state. The overall features, especially polarization dependence, of the theoretical $\sigma(\omega)$ are nearly the same as those in Fig. 1(a). Due to the limitation of the LMTO method for the higher-energy excitations, the theoretical value for $\sigma(\omega)$ around 4.0 eV is by a factor of two smaller than the experimental value. As shown in Fig. 3, the oxygen displacement $\delta$ between Mn(1) and Mn(2) along the zigzag chain can induce large spectral weight changes below 2.0 eV.

One of the important issues is what drives the charge/orbital ordering. As possible candidates, the intersite Coulomb repulsion \[17\] and the JT distortion \[18\] have been considered. Compared to LSMO, NSMO is known to have a shorter distance of the Mn-O-Mn straight bond \[11\], which results in a larger intersite Coulomb interaction and a larger hopping energy of $e_g$ conduction electrons. However, as shown in insets of Fig. 2, the measured values of $\Delta$ for LSMO are larger than those of NSMO. It implies that the conduction electron screening in NSMO should be dominant, which leads to no magnetic spin ordering. These results are consistent with recent neutron scattering data which showed no magnetic ordering in NSMO \[13\] and an AFM ordered phase in the MnO$_2$ layer of LSMO \[7\]. Our first principles calculations \[21\] revealed that the CE-type AFM ordering produce a strong orbital ordering even without the JT distortion. Once the orbital ordering occurs, the JT distortion will be induced. Then it will enhance the orbital ordering and stabilize the CE-type AFM ordering cooperatively. [Being consistent with this argument, the magnitude of the JT distortion in
the ab-plane of LSMO is larger than that of NSMO \[11\].

To clarify effects of the orbital ordering and the JT distortion on the electronic structure of LSMO, we set up a TB model for the MnO$_2$ plane in LSMO by taking account of only $e_g$ orbitals at the Mn sites \[20\]. [Here, the TB orbital $|e_g\rangle$ should be considered as a Wannier state, i.e. a superposition of the Mn 3$d$ and the O 2$p$ states.] The model Hamiltonian \[21\] can be written as

$$H = \sum_{\langle ij \rangle \alpha \beta \sigma} t_{ij}^{\alpha \beta} d_{i \alpha \sigma}^\dagger d_{j \beta \sigma} - J_H \sum_{i \alpha \sigma i' \sigma'} S_i^\dagger \cdot \sigma_{\sigma \sigma'} d_{i \alpha \sigma}^\dagger d_{i' \sigma'} + g \sum_{i \alpha \beta \sigma} \vec{Q}_i \cdot \vec{\tau}_{\alpha \beta} d_{i \alpha \sigma}^\dagger d_{i \beta \sigma} + \sum_i \frac{c}{2} \vec{Q}_i^2,$$

where $d_{i \alpha \sigma}$ represents an annihilation operator for the state at the site $i$ with the orbital index $\alpha$ and spin index $\sigma$. It is noted that the $e_g$ states consist of two orbitals, $|x^2-y^2\rangle$ and $|3z^2-r^2\rangle$. The second term corresponds to the Hund coupling of the $e_g$ conduction electrons with the $t_{2g}$ localized spin $\vec{S}_i$ at the site $i$, the third term to the JT type electron-lattice interaction with the coupling constant $g$, and the last term to the elastic energy of the JT phonon mode $\vec{Q} = (Q_2, Q_3)$. $\vec{\sigma}$ and $\vec{\tau}$ are Pauli matrices. The parameters in the electronic part of the TB Hamiltonian were determined as $t_{dd\sigma} = 0.7$ eV, $J_H = 0.75$ eV, $g = 3.85$ eV/Å, and $c = 13.58$ eV/Å$^2$ \[21\].

Assuming the CE-type AFM ordering of the $t_{2g}$ spins, we obtained the density of state (DOS) without any JT distortion. As shown in Fig. 4(a), DOS has three separate main peaks, each of which corresponds to bonding (B), non-bonding (N), and anti-bonding (A) states of the Mn(1) and the Mn(2) $e_g$ orbitals. The B states are fully occupied and separated by the unoccupied N states with a band gap of $\sim 0.2$ eV. Due to the peculiar nature of the 1D zigzag chain geometry in the CE-type AFM configuration, the $|3x^2-r^2\rangle_1$ orbitals at the Mn(1) sites are strongly hybridized with the $|x^2-y^2\rangle_2$ components of the $e_g$ orbitals at the neighboring Mn(2) sites along the chain, while the inter-chain hybridization is suppressed by the exchange splitting due to AFM coupling. The strong hybridization along the zigzag chains separate the B and A states by $\sim 2.0$ eV. As a result, the $|3x^2-r^2\rangle_1$ orbital state dominates the occupancy at the Mn(1) site and leads to the orbital ordered structure in the
MnO$_2$ layer.

The orbital ordered electronic structure together with the JT distortion in the CE-type AFM state leads to interesting consequences on the interband transition. While the Mn(1) site maintains its inversion symmetry, the Mn(2) site at the edge of the zigzag chain has no inversion symmetry due to the CE-type AFM ordering. Thus, the $e_g$-type Wannier state at the Mn(2) site becomes a mixture of the $d$- and the $p$-orbital states. Since both types of Mn atoms are on the mirror plane with respect to the $z$-reflection, no dipole transition is allowed for $E \parallel c$. On the other hand, in the case of $E \parallel ab$, the dipole transition at the Mn(2) site becomes allowed because $\langle B_{Mn(2)}|p_{x,y}|N_{Mn(2)} \rangle \neq 0$. Therefore, we expect that $\sigma(\omega)$ for $E \parallel c$ should be strongly suppressed below 2.0 eV, while the $\sigma(\omega)$ for $E \parallel ab$ have its first peak near 1.0 eV which corresponds to the B $\rightarrow$ N interband transition. These TB analyses are consistent with the experimental result of Fig. 1(a) as well as the LMTO result of Fig. 3.

In Fig. 4(b), we show the joint DOS (JDOS) projected on the Mn(2) site. When the frequency and polarization dependences of dipole matrix element are neglected, $\sigma(\omega)$ is considered to be proportional to the JDOS, since the dipole transition at the Mn(2) site without inversion symmetry is a major contributor. The solid line represents the JDOS without any JT distortion, and the dashed line with the oxygen distortion of $\delta = 0.10$ a.u. We can obtain the JT distortion, $Q_2 \approx 3\delta \sqrt{2}$ and $Q_3 \approx -3\delta \sqrt{6}$ for Mn(1), and $Q_2 \approx 0$ and $Q_3 \approx 3\delta \sqrt{6}$ for Mn(2) by restricting the volumes of the octahedra unchanged. The peak near 1.0 eV corresponds to the B $\rightarrow$ N transition, and the peak near 2.0 eV corresponds to the B $\rightarrow$ A transition. The overall shape is in close agreement with the LMTO result of Fig. 3, but the B $\rightarrow$ A feature turns out to be very weak in the experimental spectrum, shown in Fig. 2(a) [22]. In Fig. 4(b), it is emphasized that the increasing JT distortion results in the narrowing of the B band and consequently the width of the B $\rightarrow$ N transition as well, which is quite consistent with experimental observation on the $T$-dependence of $\sigma(\omega)$. As $T$ decreases, a fluctuation in the CE-type AFM ordering is suppressed, the JT distortion increases and the orbital ordering is enhanced. The observed strong $T$-dependence of $\sigma(\omega)$
of LSMO is the result of cooperative enhancement of the orbital ordering.

Even though the $T$-dependence of the MIR peak below $T_{CO}$ in LSMO can be well understood by the orbital ordered electronic structure with the JT distortion, the $\sigma(\omega)$ of either LSMO above $T_{CO}$ or NSMO at all $T$ still exhibit the similar MIR features. Like in the case of Fe$_3$O$_4$ [23], it could be attributed to the local orbital fluctuation without a long range CE-type AFM ordering or charge ordering.

In summary, we investigated the orbital ordering in La$_{1/2}$Sr$_{3/2}$MnO$_4$ using the optical conductivity analyses. With decreasing temperature, the peak corresponding to bonding $\rightarrow$ non-bonding transition shifts to the high frequency and becomes narrower. Comparing with optical conductivity of Nd$_{1/2}$Sr$_{3/2}$MnO$_4$ and theoretical results, we conclude that such behaviors could be explained by the CE-type orbital ordering within the MnO$_2$ layers stabilized by the Jahn-Teller distortion.

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    but failed. The fitting became much better with a small peak near 2.0 eV.

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FIGURES

FIG. 1. $\sigma(\omega)$ of (a) LSMO and (b) NSMO for $E \parallel ab$ and $E \parallel c$ at 290 K.

FIG. 2. $T$-dependent $\sigma(\omega)$ for $E \parallel ab$ of (a) LSMO and (b) NSMO. In the insets of (a) and (b), values of $\Delta$ were also shown.

FIG. 3. Polarization dependent $\sigma(\omega)$ of $Y_{1/2}Sr_{3/2}MnO_4$ obtained by the LMTO calculation.

FIG. 4. (a) Energy band diagram for B, N, and A of hybridized Mn(1) and Mn(2) orbitals. (b) JDOS projected on Mn(2) site without any JT distortion (solid line) and with JT distortion (dashed line).
