著者別名	守友 浩

DOI	10.1103/PhysRevB.73.180403
Electronic structure and photoinduced effect of LaMnO$_3$ film

K. Murakami, T. Yamauchi, and A. Nakamura
Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

Y. Moritomo*
Department of Physics, University of Tsukuba, Tsukuba 305-8571, Japan

H. Tanaka and T. Kawai
Institute of Scientific and Industrial Research, Osaka University, Osaka 567-0047, Japan

(Received 1 May 2006; published 23 May 2006)

The electronic structure as well as the photoinduced effect were investigated in an antiferromagnetic LaMnO$_3$ film. We found characteristic spin-dependent absorption bands at $\sim 1.6$ eV and $\sim 3$ eV, and ascribed them to the $d$-$d$ transitions into the adjacent Mn$^{3+}$ sites with the parallel and antiparallel spins, respectively. We further observed that the photoexcitation of the down-spin $d$ electrons significantly influences these $d$-$d$ bands, and ascribed the behavior to the photoinduced disorder of the Mn$^{3+}$ spins.

DOI: 10.1103/PhysRevB.73.180403  PACS number: 68.35.Rh, 75.40.–s

The photoinduced effects on the strongly correlated electron system is one of the hottest topics in solid state physics both from the fundamental and technical points of view. Especially in the perovskite-type doped manganites, the strong coupling between the spin, charge and orbital degree of freedoms causes a variety of magnetic/electronic phases.  

Especially in the perovskite-type doped manganites, the electronic structure as well as the photoinduced effect were investigated in an antiferromagnetic LaMnO$_3$ film. We found characteristic spin-dependent absorption bands at $\sim 1.6$ eV and $\sim 3$ eV, and ascribed them to the $d$-$d$ transitions into the adjacent Mn$^{3+}$ sites with the parallel and antiparallel spins, respectively. We further observed that the photoexcitation of the down-spin $d$ electrons significantly influences these $d$-$d$ bands, and ascribed the behavior to the photoinduced disorder of the Mn$^{3+}$ spins.

A LaMnO$_3$ film was fabricated using a laser molecular-beam epitaxy method on a SrTiO$_3$ (100) substrate. Details of the synthesis process were described elsewhere. An x-ray diffraction measurement revealed that the obtained films were (001) oriented in the pseudo-tetragonal setting. That is, the ferromagnetic $ab$ plane is parallel to the film surface. The Néel temperature $T_N$ ($\sim 60$ K) was determined from the inflection point of the temperature dependence of the magnetization $M$, which was measured at $0.1$ T after cooling down to $5$ K in the zero field. The absorption coefficient $\alpha(\omega)$ was determined from transmission spectra using the standard formula neglecting the multi-reflection effect. The film thickness was $1790$ Å. The transmission spectra were measured with a grating-type spectrometer. Reflectance correction is not performed, since the reflectivity ($R \sim 0.15$) is low and nearly constant in the spectral region investigated ($0.6$–$3.1$ eV). Here, note that the spectral region is limited by the absorption of the SrTiO$_3$ substrate.
components by Gaussians, that is, negligible temperature-dependence. So, we expressed the two

prototypical example of the absorption spectra at

induced absorption change, we used continuous wave lasers,

In order to obtain the overall temporal behavior of the photoexcitation light. The time resolution of the system was 12 ns.

We used a nanosecond optical parametric oscillator system pumped by a yttrium-aluminum-garnet (YAG) laser (355 nm, 10 Hz) as an excitation source. The pulse width was 3–5 ns. We confirmed that the SrTiO3 (100) substrate does not show any photoinduced signal, when the excitation photon energy was set below the absorption edge (~3.1 eV) of the SrTiO3 substrate. In the time-resolved spectroscopy, a xenon flash lamp was synchronized with the YAG laser. The transmitted light was detected with a gated charge-coupled device camera attached at the output stage of a grating monochromator. We put a polarizer in front of the monochromator to eliminate the intense scattering from the excitation light. The time resolution of the system was 12 ns.

We first carefully investigated the temperature dependence of the absorption spectra of the LaMnO3 film. Figure 1 shows a prototypical example of the absorption spectra at (a) 4K (≤TN) and at (b) 300 K (≥TN). Consistent with the work done by Quijada et al.,18 we observed a characteristic transfer of the spectral weight from the ultraviolet region to the visible region. Figure 1(c) shows temperature differential spectrum of the LaMnO3 film, which shows negative (positive) component at ~1.6 eV and (~3.0 eV), even though the spectral region was limited below 3.1 eV. For convenience of explanation, we will call the lower-lying (higher-lying) component S↑ (S↓) component. The peak position hω0 and the full width at half maximum Γ of the S↑ component show negligible temperature-dependence. So, we expressed the two components by Gaussians, that is, \[\alpha \propto \exp\left[-4 \ln 2 \left(\frac{\hbar - \hbar_{\omega_0}}{\Gamma} \right)^2\right],\]

where \(\hbar\omega_0\) and Γ are the fixed values: \(\hbar\omega_0=1.62\) eV (3.5 eV) and Γ=0.79 eV (0.70 eV) for the S↑ (S↓) component. Keeping these two components in mind, we decomposed the overall spectra into two temperature-dependent components (thin solid curves in Fig. 1) and three temperature-independent components (thin broken curves). The positions of the latter three components were chosen at \(\hbar\omega_0=1.47, 2.44, \) and 4.5 eV so as to cover the spectra. The residual parameters, Γ and the spectral weight S, are adjusted so that the sum of the Gaussians reproduce the temperature-independent component except around ~1.6 eV and ~3 eV: Γ=1.20 eV and S=1.22×10^5 eV cm\(^{-1}\) for the 1.47 eV component, Γ=0.93 eV and S=0.72×10^5 eV cm\(^{-1}\) for the 2.44 eV component, and Γ=1.93 eV and S=1.08×10^5 eV cm\(^{-1}\) for the 4.5 eV component. The temperature variation of the spectra can be reproduced only by the spectral weights of the S↑ and S↓ components.31 The three temperature-independent components located at 1.5, 2.4, and 4.5 eV are reasonably ascribed to the CT transitions into the Mn\(_{\uparrow}\)↑, Mn\(_{2\uparrow}\)↑ and Mn\(_{\downarrow}\)↑-levels, respectively.19

In Fig. 2, we plotted the spectral weights of the S↑ component (open circles) and the S↓ component (filled circles). As temperature increases beyond TN, the spectral weight of the S↑ component gradually transfers to the S↓ component. These temperature dependencies are well explained if we ascribe the S↑ (S↓) component to the d-d transition into the adjacent Mn\(^{3+}\) site with the parallel (antiparallel) spin. With increases of temperature above TN, the probability of finding a parallel (antiparallel) spin pair within the ab plane decreases (increases), and eventually becomes the same (~0.5) in the paramagnetic phase. The rather gradual spectral weight transfer above TN may be ascribed to the residual short-range ferromagnetic correlation. Here, we roughly estimated the oscillator strength f\(_{dd}\) of the d-d transition from the spectral weight of the S↑ component.32 The magnitude of f\(_{dd}\) (0.04/e\(_{0}\) electron) is comparable with that (0.051/e\(_{0}\)) of the ferromagnetic Sm\(_{\downarrow}\)Sr\(_{2}\)MnO\(_3\) film.

Figure 3(a) shows the differential absorption spectra Δ\(\alpha\) soon after the photoexcitation at 1.5 eV (gray spectrum) and at 2.3 eV (black spectrum). In both spectra, negative (positive) signal is observed at ~1.6 eV (at ~3 eV), which is close to the S↑ (S↓) component. So, we concluded that the photoexcitation modifies the spectral weights of the d-d tran-
sitions. The magnitude of the photoinduced spectral change is proportional to $I$ up to $I=4\text{ mJ/cm}^2$. We further estimated the quantum efficiency $\Phi$ for the $S_{\text{up}}$ component and plotted them in Fig. 3(b), taking account of the reflectivity and transmittance at $E_{\text{pump}}$. Magnitude of $\Phi$ is nearly constant ($\sim 3$ site/photon) below $2\text{ eV}$, but jumps to $\sim 8$ site/photon when $E_{\text{pump}}$ exceeds $\sim 2\text{ eV}$. This observation excludes the conventional heating effects as the origin for the photinduced spectral change.

Matsuda et al.\textsuperscript{3} reported a similar excitation photon energy dependence in the photoinduced absorption at the $J$-gap transition ($\sim 3\text{ eV}$) in a ferromagnetic (Nd,Sm)$_{0.6}$Sr$_{0.4}$MnO$_3$ film. In this system, the profile of $\Delta\alpha$ is analogous to the spectral change between the ferromagnetic and paramagnetic phases. In addition, the photoinduced signal disappears in the spin-disordered paramagnetic phase. Based on these observations, they concluded that the observed photoinduced effect is originated in the photoinduced spin disorder, which is much enhanced by the excitation of the down-spin $d$ electrons.

We think that the presently observed photoinduced effect is also ascribed to photoinduced disorder of the Mn$^{3+}$ spins, because the enhancement of $\Phi$ [Fig. 3(b)] appears to correlate with the CT excitation of the down-spin $d$ electrons. In addition, the photoinduced spectral change [Fig. 3(a)] was analogous to the spectral change [Fig. 1(c)] between the spin-ordered and spin-disordered phases.

Finally, let us discuss temperature dependence of the photoinduced signal. Figure 4(a) shows prototypical examples of temporal behavior of $\Delta T/T$ at $E_{\text{probe}}=1.95\text{ eV}$, which is equivalent to $I_{\text{pump}}^{10-8}$, where $I_{\text{pump}}$ represent the intensity of the transmitted light without photoexcitation. Base on the above interpretation, the magnitude of $\Delta T/T$ is equivalent to the degree of photoinduced spin disorder. The $\Delta T/T - t$ curves are well reproduced by the single exponential function: $\Delta T/T = A \cdot \exp(-t/\tau) + C$, where $A$ and $\tau$ are the amplitude and the lifetime, respectively. The constant term ($C$) is probably due to the heating effect, lasting for much longer time than the time range concerned here. Open circles in Fig. 4(b) represent $A$ and $\tau$ for the $S_{\text{up}}$ component. Magnitude of $A$ is nearly constant below $T_N$, but gradually decreases as temperature increases beyond $T_N$. On the other hand, $\tau$ is almost temperature independent even near $T_N$. This is in sharp contrast with the La$_{0.7}$Ca$_{0.3}$MnO$_3$ film,\textsuperscript{4} in which $\tau$ critically slows down on approaching the Curie temperature $T_C$. Similar behaviors of $A$ and $\tau$ are observed for the $S_{\text{down}}$ component (indicated by filled circles), though the data points are rather scattered.

These observations suggest that the local spin correlation does not change much even around $T_N$. Actually, Hirota et al.\textsuperscript{33} observed ferromagnetic spin-wave-like dispersion for $E \gtrapprox 10\text{ meV}$ even near $T_N$, indicating residual short-range ferromagnetic spin correlation due to two-dimensional exchange coupling. Here, note that the optical probe mainly detects the nearest-neighboring spin correlation. Then, it is plausible that the optical probe does not feel the long-range antiferromagnetic-paramagnetic phase transition of LaMnO$_3$.

In summary, we have investigated the electronic structure as well as the photoinduced effect in an antiferromagnetic LaMnO$_3$ film. We decomposed the absorption spectra into three spin-independent CT components and two spin-dependent $d$-$d$ components, and concluded that the charge gap has the CT character. We further observed that the photoexcitation significantly influences the spin-dependent $d$-$d$ components due to the photoinduced disorder of the Mn$^{3+}$ spins.

Temperature dependence of the photoinduced signal of LaMnO$_3$ is qualitatively different from that of the ferromagnetic La$_{0.7}$Ca$_{0.3}$MnO$_3$.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and from the Ookura Foundation.
MURAKAMI et al.

PHYSICAL REVIEW B 73, 180403(R) (2006)

64, 224426 (2001).
29 $T_N$ of our LaMnO$_3$ film is lower than that (=140 K) of the LaMnO$_3$ bulk. This may be due to the slight oxygen deficiency, because the film was synthesized in a moderate oxidizing atmosphere in order to avoid the cation deficiencies.
30 The temperature change of the absolute reflectivity was less than 1.5% in the spectral range of 0.7–3.0 eV. The resultant error in the absorption coefficient $\alpha$ is $\pm 0.01 \times 10^5$ cm$^{-1}$, which is much smaller than $\alpha$ and $\Delta \alpha$ (see Fig. 1).
31 The absolute magnitude of $S_{\text{down}}$ has ambiguity due to the limitation of the spectral range.
32 The refractive index $n$ of LaMnO$_3$ is ~2 in the visible region.19