Electronic structure and photoinduced effect of LaMnO$_3$ film

Murakami K., Yamauchi T., Nakamura A., Moritomo Y., Tanaka H., Kawai T.

journal or publication title Physical review B

volume 73

number 18

page range 180403

year 2006-05

(C)2006 The American Physical Society

URL http://hdl.handle.net/2241/101631

doi: 10.1103/PhysRevB.73.180403
Electronic structure and photoinduced effect of LaMnO₃ 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 LaMnO₃ film. We found characteristic spin-dependent absorption bands at ≈1.6 eV and ≈3 eV, and ascribed them to the d-d transitions into the adjacent Mn³⁺ 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 Mn³⁺ spins.

DOI: 10.1103/PhysRevB.73.180403 PACS number(s): 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. They ascribed the photoinduced effect to the strong on-site exchange coupling mediated by the cooperative Jahn-Teller distortion of the MnO₆ octahedron. This orbital alternation mediates the ferromagnetic exchange coupling within the layer, and causes the layer-type spin structure below T_N (=140 K). The hole-doping process in LaMnO₃ induces the ferromagnetism, which is mediated by strong on-site exchange coupling J_H between the local t₂_g spins and itinerant e_g carriers (double-exchange interaction). This strong coupling a priori splits the e_g band into the parallel spin state and the antiparallel spin state. Actually, Moritomo et al. have observed the spin-dependent absorption band at J_H (=3 eV) in several ferromagnetic manganites, and ascribed the band to the d-d transition between the exchange-split bands (J-gap transition). The corresponding absorption band is also expected in the insulating LaMnO₃. The interpretation of the electronic structure of LaMnO₃, however, is still controversial, even though there exists a long list of experimental and theoretical investigations. Quijada et al. investigated the optical conductivity spectrum of crystalline LaMnO₃ against temperature, and found a characteristic transfer of the spectral weight from the ultraviolet region (≈3 eV) to the visible region (≈2 eV). They ascribed the former (latter) absorption to the d-d transition into the Mn³⁺ site with the parallel (antiparallel) spin. Contrary to this argument, Tobe et al. reported that the anisotropic optical conductivity spectrum of LaMnO₃ crystal shows negligible change at T_N. Recently, Kovaleva et al. reported spin-dependent transition at ≈2 eV in untwinned LaMnO₃ crystal, and Kim et al. observed distinct suppression of the absorption band at ≈2 eV around T_N in the epitaxial LaMnO₃ film. In addition, several researchers observed spin-dependent excitation around 2 eV in doped and nondoped manganites by means of the resonant inelastic x-ray scattering experiments.

In this paper, we have investigated electronic structure as well as the photoinduced effect of LaMnO₃ film. We observed temperature-dependent absorption bands at ≈1.6 eV and ≈3 eV. We further observed that the photoexcitation of the down-spin d electrons significantly enhances (suppresses) the lower-lying (higher-lying) d-d band, and ascribed the behavior to the photoinduced disorder of the Mn³⁺ spins.

A LaMnO₃ film was fabricated using a laser molecular-beam epitaxy method on a SrTiO₃ (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 (=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 α(ω) 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~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 absorption of the SrTiO₃ substrate.
components by Gaussians, that is, temperature-dependence. So, we expressed the 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, \( \Gamma \) and the spectral weight \( S \), are adjusted so that the sum of the Gaussians reproduce the temperature-independent component except around \( \sim 1.6 \) eV and \( \sim 3 \) eV: \( \Gamma = 1.20 \) eV and \( S = 1.22 \times 10^5 \) eV cm\(^{-1} \) for the 1.47 eV component, \( \Gamma = 0.93 \) eV and \( S = 0.72 \times 10^5 \) eV cm\(^{-1} \) for the 2.44 eV component, and \( \Gamma = 1.93 \) eV and \( S = 1.08 \times 10^5 \) 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 \( S_{up} \) and \( S_{down} \) 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 \( \text{Mn}^{3+/-}, \text{Mn}^{2+/-} \) and \( \text{Mn}^{2+/-} \)-levels, respectively. \( ^{19} \)

In Fig. 2, we plotted the spectral weights of the \( S_{up} \) component (open circles) and the \( S_{down} \) component (filled circles). As temperature increases beyond \( T_N \), the spectral weight of the \( S_{up} \) component gradually transfers to the \( S_{down} \) component. These temperature dependencies are well explained if we ascribe the \( S_{up} (S_{down}) \) component to the \( d-d \) transition into the adjacent \( \text{Mn}^{3+/-} \) site with the parallel (antiparallel) spin. With increases of temperature above \( T_N \), the probability of finding a parallel (antiparallel) spin pair within the \( ab \) plane decreases (increases), and eventually becomes the same (= \( \frac{1}{2} \)) in the paramagnetic phase. The rather gradual spectral weight transfer above \( T_N \) 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 \( S_{up} \) component. \( ^{32} \) The magnitude of \( f_{dd} \) (\( \approx 0.04 e^2 \) electron) is comparable with that of (\( f_{dd} \)) of the ferromagnetic \( \text{Sm}^{3+/-}\text{Sr}^{2+/-}_2\text{MnO}_3 \) film.

Figure 3(a) shows the differential absorption spectra \( \Delta \alpha \) 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 \( \sim 1.6 \) eV (at \( \sim 3 \) eV), which is close to the \( S_{up} (S_{down}) \) 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 \( S_{up} \) component and plotted them in Fig. 3(b), taking account of the reflectivity and transmittance at \( E_{pump} \). Magnitude of \( \Phi \) is nearly constant (\( \sim 3 \) site/photon) below 2 eV, but jumps to \( \sim 8 \) site/photon when \( E_{pump} \) exceeds \( \sim 2 \) eV. This observation excludes the conventional heating effects as the origin for the photoinduced spectral change.

Matsuda et al.\(^3\) reported a similar excitation photon energy dependence in the photoinduced absorption at the \( J \)-gap transition (\( \sim 3 \) 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.

FIG. 3. (a) Differential absorption spectra \( \Delta \alpha \) (at \( \Delta \tau = 0 \text{ ns} \)) of LaMnO\(_3\) film at 30 K. Arrows represent the excitation photon energy \( E_{pump} \). The excitation intensity \( I \) is 4 mJ/cm\(^2\). (b) Quantum efficiency \( \Phi \) for the \( S_{up} \) component. A solid curve represents the absorption spectrum of LaMnO\(_3\) film at 4 K.

Finally, let us discuss temperature dependence of the photoinduced signal. Figure 4(a) shows prototypical examples of temporal behavior of \( \frac{\Delta T}{T} \) at \( E_{probe} = 1.95 \text{ eV} \), which is equivalent to \( \frac{\Delta \alpha}{\alpha} \), where \( I_b \) represent the intensity of the transmitted light without photoexcitation. Base on the above interpretation, the magnitude of \( \frac{\Delta T}{T} \) is equivalent to the degree of photoinduced spin disorder. The \( \frac{\Delta T}{T} - t \) 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 \( S_{up} \) 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,\(^4\) in which \( \tau \) critically slows down on approaching the Curie temperature \( T_C \). Similar behaviors of \( A \) and \( \tau \) are observed for the \( S_{down} \) 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.\(^5\) observed ferromagnetic spin-wave-like dispersion for \( E \approx 10 \text{ meV} \) 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.


$T_N$ of our LaMnO$_3$ film is lower than that ($\approx$140 K) of the LaMnO$_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.

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 $\pm0.01 \times 10^4$ cm$^{-1}$, which is much smaller than $\alpha$ and $\Delta\alpha$ (see Fig. 1).

The absolute magnitude of $S_{\text{down}}$ has ambiguity due to the limitation of the spectral range.

The refractive index $n$ of LaMnO$_3$ is $\sim$2 in the visible region.19