Photoinduced formation of charge-ordering clusters in a manganite film

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Effects of pulse-laser irradiation on $La_{0.7}Ca_{0.3}MnO_3$ film ($T_C=260$ K) are investigated by the pump and probe technique as a function of temperature (5 K$\leqslant T \leqslant$470 K). We find that the photo-induced transmission changes (ΔT) at $E_{probe}=1.55$ eV and 2.54 eV show significant temperature dependence. These transmission changes are interpreted in terms of photoinduced formation of the charge-ordering clusters.

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I. INTRODUCTION

In perovskite-type doped manganites, the subtle competition between charge-ordering instability and the double-exchange[1] interaction produces a variety of phenomena. Among them, a phase separation phenomenon attracts considerable attention as a strong candidate for the origin for the colossal magnetoresistance (CMR). So far, many experimental[2–6] and theoretical[7–10] studies on the phase separation problem have been carried out to clarify the origin of the CMR effects. In particular, substitution of the perovskite *B*-site induces the coexistence of the ferromagnetic metallic (FM) and charge-ordering (CO) clusters of the order of ~10 nm, as confirmed by the dark field image of the superlattice spot in $La_{0.375}Ca_{0.625}(Mn_{0.97}Cr_{0.03})O_3$ (Ref. 11) and $Nd_{1/2}Ca_{1/2}(Mn_{0.97}Cr_{0.03})O_3$.[12] Such microstructures have been ascribed to the destruction of the coherence of the charge/orbital ordering.[11] From Monte Carlo simulations, Moreo *et al.*[10] indicated that randomness of the exchange and hopping amplitudes can cause the phase separation. Thus, phase separation effects are enhanced by the introduction of randomness. Then, photoirradiation, which transiently destroys the ferromagnetic correlation between the local t_{2g}-spins in the FM state,[13,14] can trigger the formation of the CO clusters.

In the paramagnetic phase ($\geqslant T_C$), a more dynamical aspect of the CO clusters is suggested by diffuse x-ray scattering,[15,16] optical absorption,[17] Raman scattering[18] and electron diffraction[17] measurements. For example, Shimomura *et al.*[15] found a (−0.3,10,0) diffuse reflection in $(Nd_{0.125}Sm_{0.875})_{1/2}Sr_{1/2}MnO_3$, and interpreted it in terms of the CO fluctuation. Interestingly, the intensity of the diffuse reflection increases on approaching the Curie temperature T_C (=130 K) from the high temperature side, and then drops precipitously below T_C. A similar diffuse reflection has been observed as well in the paramagnetic phase ($\geqslant T_C=120$ K) of $La_{1.2}Sr_{1.8}Mn_2O_7$ with bilayer structure.[16] Machida *et al.*[17] reported a temperature-dependent absorption band at ~1.5 eV in manganite films, that they ascribed to the formation of CO clusters.

In this paper, we investigate the temperature variation of the photoinduced transmission change (ΔT) on a $La_{0.7}Ca_{0.3}MnO_3$ film ($T_C=260$ K) at $E_{probe}=1.55$ eV and 2.54 eV. We interpret ΔT at 1.55 eV in terms of the formation of CO clusters. This interpretation is consistent with the negative ΔT value at 2.54 eV due to the photoinduced suppression of the ferromagnetic correlation,[13,14] because the antiferromagentic charge-exchange-type (CE-type) spin correlation couples with the CO fluctuation.

II. EXPERIMENT

A. Sample preparation

A $La_{0.7}Ca_{0.3}MnO_3$ film with a thickness of ≈1700 Å was fabricated by a laser-molecular beam epitaxy.[22] Sintered $La_{0.7}Ca_{0.3}MnO_3$ pellets were used as target. A pulsed-laser beam (193-nm ArF excimer laser) with 5-Hz repetition ratio was used for ablation. The distance between the substrate and the target was 40 mm. The $La_{0.7}Ca_{0.3}MnO_3$ film was grown on a $SrTiO_3$ (001) substrate in an NO_2 atmosphere at a pressure of 1.0×10^{-5} mbar and at a substrate temperature of 700 °C. After film formation, the substrate temperature was kept for 30 min in NO_2 pressure of 1.0×10^{-2} mbar.

X-ray diffraction measurements revealed that the obtained films were ⟨001⟩-oriented in the pseudocubic setting. The Curie temperature T_C (=260 K) was determined from the

temperature dependence of the magnetization M measured at 0.05 T after cooling down to 5 K at zero field (ZFC).

B. Optical measurements

Absorption coefficient $\alpha(\omega)$ was determined from transmission spectra using the standard formula neglecting the multireflection effect, since the optical density of our films is larger than 0.7 in the spectral region investigated. Reflectance correction is not performed, since the reflectivity is low and nearly constant ($R \sim 0.15$) in the spectral region investigated (0.6–3.0 eV). Here, note that experiment above 3.0 eV is impossible due to the intense absorbance of the $SrTiO_3$ substrate.

Photoirradiation effects were measured by means of the pump and probe method using a dye laser system as a pump source. The pulse duration and frequency are 20 ns and 10 Hz, respectively. The photon energy is fixed at $E_{\rm exc} = 3.05$ eV, below the absorption edge of the $SrTiO_3$ (001) substrate. We confirmed that the substrate does not show any photoinduced signal. We used a cw Ar^+ laser ($E_{\rm probe} = 2.54$ eV) and a cw $Ti:Al_2O_3$ laser (1.55 eV) as probe light sources. The transient data were accumulated for 5 min. with a digital oscilloscope.

III. RESULTS AND DISCUSSION

A. Temperature variation of absorption spectra

Before describing the photoinduced effects on the manganite film, let us survey the temperature variation of the absorption spectra of $La_{0.7}Ca_{0.3}MnO_3$ used in the present experiment. Figure 1 shows absorption spectra $\alpha(\omega)$ of $La_{0.7}Ca_{0.3}MnO_3$ film (a) at 5 K ($\ll T_C = 260$ K), (b) at 265 K ($\sim T_C$), and (c) at 410 K ($\gg T_C$). As indicated in the figure, the absorption spectra can be divided into six components: three *temperature-independent* charge-transfer transitions (broken curves) and three *temperature-dependent* transitions (solid curves). The three charge-transfer components correspond to the transitions from O $2p$ band to Mn$e_{g\uparrow}$, Mn$t_{2g\downarrow}$, and Mn$e_{g\downarrow}$ levels, respectively.[14,19–21] In the following, we will discuss the origin for the three temperature-dependent components.

In the double-exchange doped manganites, it is well established that the e_g band *a priori* splits into two bands,[23] since the one-electron bandwidth W (~ 1 eV) is much smaller than the on-site exchange coupling ($J \sim 3$ eV) between the local t_{2g} spins and the itinerant e_g-electrons. Actually, Moritomo *et al.*[24] have found a characteristic excitation (J-gap transition) at ~ 3 eV between the exchange-split bands; the spectral weight increases with decrease of the ferromagnetic correlation between the local t_{2g} spins. Looking at Fig. 1, one may find the corresponding transition at ~ 3 eV, whose spectral weight S_J increases with temperature due to the suppressed nearest-neighboring spin-correlation (see also filled circles in Fig. 2). Inset of Fig. 2 shows the linear relation between S_J and $1-(M/M_s)^2$, where M and M_s are the temperature-induced magnetization and the saturation magnetization, respectively. Thus, we can monitor the spin correlation by the transmission change ΔT at

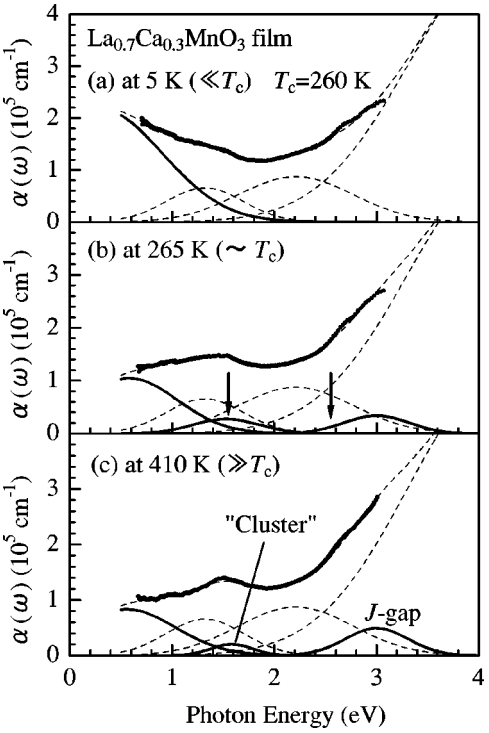

FIG. 1. Absorption spectra $\alpha(\omega)$ of $La_{0.7}Ca_{0.3}MnO_3$ film at (a) 5 K ($\ll T_C = 260$ K), (b) at 265 K ($\sim T_C$), and (c) at 410 K ($\gg T_C$). Each spectrum consists of six components, that is, three temperature-independent charge-transfer transitions (broken curves), and three temperature-dependent transitions (solid curves). The three charge-transfer components correspond to the transitions from O $2p$ band to Mn$e_{g\uparrow}$, Mn$t_{2g\downarrow}$, and Mn$e_{g\downarrow}$ levels, respectively. The temperature dependent ~ 1.5 eV and ~ 3.0 eV transitions are called as ''cluster'' and J-gap transitions, respectively. Downward arrows in (b) represent the probe photon energies $E_{\rm probe}$.

$E_{\rm probe} = 2.54$ eV.[13,14] Within this picture, the lowest-lying component can be ascribed to the intraband transition within the exchange-split band, or the so-called Drude-like component. Here, we only notice that the e_g carriers of doped manganites are amenable to the polaron formation, and the assignments of the low energy region ($\leqslant 1$ eV) is still controversial.[25,26]

Now, let us proceed to the origin for the ~ 1.5-eV component. This ~ 1.5-eV component has been reported in $R_{0.6}Sr_{0.4}MnO_3$ ($R = $ Sm, $Nd_{0.25}Sm_{0.75}$, and $Nd_{0.5}Sm_{0.5}$) film[17] and in $Nd_{0.7}Sr_{0.3}MnO_3$ single crystal.[25] In Fig. 2, we plotted the spectral weight S_c of the component against temperature. With increase of temperature, S_c suddenly jumps at T_C and then gradually decreases. This temperature-dependent behavior scales well with the diffuse x-ray scattering due to the *intrinsic* CO clusters.[15,16] Therefore, we ascribe the ~ 1.5-eV component to the optical transition within the CO cluster, and will use it as a monitor of the clusters. This assignment is further supported by the fact that the ~ 1.5-eV component is significantly enhanced in the charge-ordered insulating state of $Nd_{1/2}Sr_{1/2}MnO_3$ (Ref. 27) and $Pr_{0.7}Ca_{0.3}MnO_3$.[28]

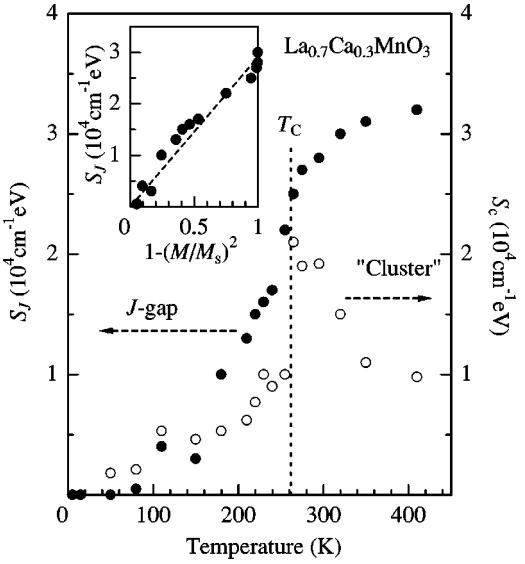

FIG. 2. Spectral weight of the ''cluster'' (S_c; open circles) and J-gap (S_J; filled circles) transitions against temperature. T_C means the Curie temperature. Inset shows linear relation between S_J and $1-(M/M_s)^2$, where M and M_s are the temperature-induced magnetization and the saturation magnetization, respectively.

B. Photoinduced spin-disorder

Figure 3 shows prototypical examples of the temporal evolution of ΔT of the $La_{0.7}Ca_{0.3}MnO_3$ film at various temperatures: squares, triangles, and circles are at 5 K ($\ll T_C = 260$ K), 210 K ($\leqslant T_C$), and 290 K ($\geqslant T_C$), respectively. The excitation photon energy E_{exc} and pulse energy density I are 3.05 eV and 4 mJ/cm^2, respectively. With this E_{exc}, the $e_{g\downarrow}$ electrons are excited from the O $2p$ band (see Fig. 1). We have confirmed that the photoinduced signal is proportional to I up to 4 mJ/cm^2 at 5 K and 300 K. First of all, let us investigate the $\Delta T-t$ curves in the ferromagnetic state with perfect spin polarization (at 5 K; open squares). In this state, the photoirradiation induces negative ΔT both at 2.54 eV and 1.55 eV, which monitor the nearest-neighboring spin correlation and the CO clusters, respectively. This indicates that the photoexcited down-spin carriers create the spin waves via the strong on-site exchange coupling J, and cause the spin disorder. We think only a part of energy is transformed to the spin waves. Other parts of the energy may be transformed to the phonon system, or be converted into photon again and emitted as luminescence. Matsuda *et al.*[13] have estimated the efficiency of the photoinduced effect in doped manganites; one photon affects ~10–50 spin sites. This implies that at least several spin waves are excited by one photon. The ferromagnetic ordering recovers in ~30 ns. This fast recovery process rules out conventional heating effect as the source of the photoinduced ΔT. Interestingly, the spin disorder accompanies negative ΔT at 1.55 eV, suggesting the formation of the CO clusters. It is probable that photoinduced disorder of the transfer integral t [$=t_0\cos(\theta/2)$, where θ is the relative angle between the neighboring t_{2g} spins] causes the formation of the CO clusters.[10,29]

How does the $\Delta T-t$ curve change with increase of temperature? At 210 K near below T_C (=260 K), the decay time

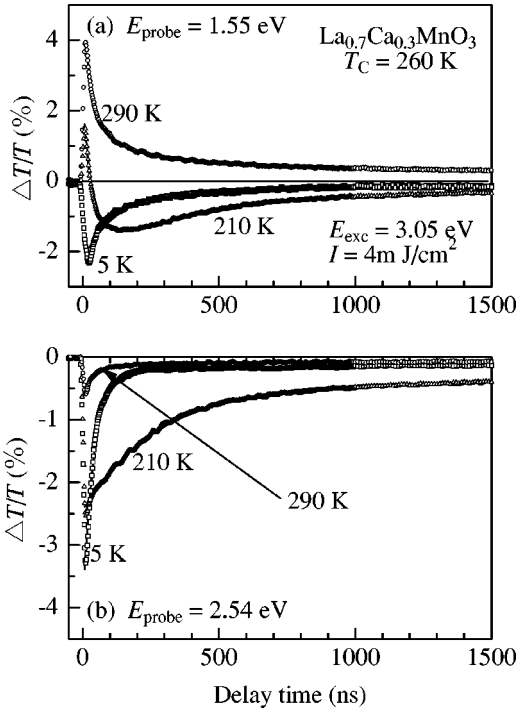

FIG. 3. Temporal evolution of the transmission change ΔT of $La_{0.7}Ca_{0.3}MnO_3$ film at various temperatures: squares, triangles, and circles are at 5 K ($\ll T_C = 260$ K), 210 K ($\leqslant T_C$), and 290 K ($\geqslant T_C$), respectively. The probe photon energies E_{probe} are (a) 1.55 eV and (b) 2.54 eV. The pump-pulse duration, frequency, photon energy E_{exc}, and pulse energy density I are 20 ns, 3.05 eV, 10 Hz, and 4 mJ/cm^2, respectively. The thin solid curves are the best-fitted results with exponential functions (see text).

is longer: ~400 ns at 1.55 eV and ~300 ns at 2.54 eV (open triangles in Fig. 3). In addition, a fast positive signal overlaps with a slow negative component at 1.55 eV. With further increase of temperature above T_C, the signal intensity at 2.54 eV is fairly reduced, while the $\Delta T-t$ curve at 1.55 eV is dominated by the positive component (open circles at 290 K). To quantitatively analyze the $\Delta T-t$ curve, we fitted our data using the following exponential functions:

$$\Delta T = -Ae^{-t/\tau_A} + C \tag{1}$$

for $E_{probe}=2.54$ eV,

$$\Delta T = Be^{-t/\tau_B} + C \tag{2}$$

for $E_{probe}=1.55$ eV ($T\geqslant 270$ K),

$$\Delta T = -Ae^{-t/\tau_A}(1-e^{-t/\tau_{rise}}) + C \tag{3}$$

for $E_{probe}=1.55$ eV ($T\leqslant 130$ K), and

$$\Delta T = -Ae^{-t/\tau_A}(1-e^{-t/\tau_{rise}}) + Be^{-t/\tau_B} + C \tag{4}$$

for $E_{probe}=1.55$ eV (130 K$\leqslant T\leqslant$270 K). A and B are the magnitude of the negative and positive components, respectively. τ_A (τ_B) and τ_{rise} are the decay time for the negative (positive) component and the rise time for the negative component, respectively. C represents a long decay time ($\geqslant\sim$ ms) component due to the conventional heating effect. The

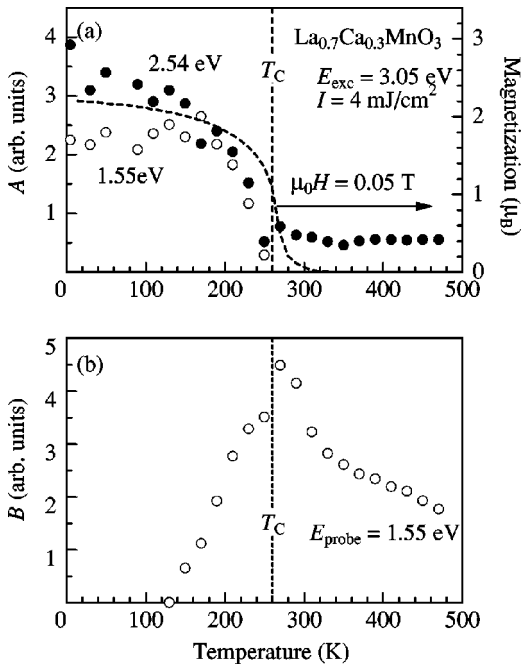

FIG. 4. Temperature dependence of magnitudes of (a) negative (A) and (b) positive (B) components of decay curve of transmission change ΔT. The pump pulse duration, frequency, photon energy E_{exc}, and pulse energy density I are 20 ns, 3.05 eV, 10 Hz, and 4 mJ/cm^2, respectively. Open and filled circles are data at E_{probe} = 1.55 eV and 2.54 eV, respectively. Broken curve in (a) is the magnetization measured at 0.05 T after cooling down to 5 K at zero field (ZFC). T_C is the Curie temperature.

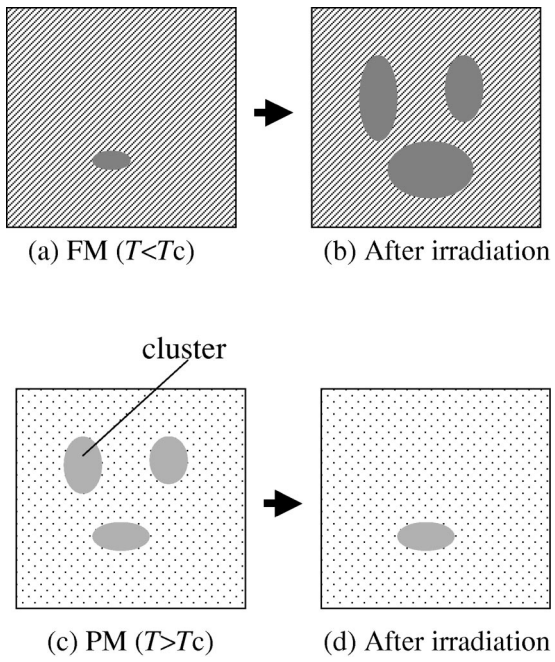

FIG. 5. Schematic pictures of photoirradiation effects: (a) before and (b) after photoirradiation in the ferromagnetic ($T \leqslant T_C$) state and, (c) before and (d) after photoirradiation in the paramagnetic ($T \geqslant T_C$) state.

solid thin curves in Fig. 3 are the best fitted results, taking the pulse duration (20 ns) into account. The τ_A-value critically increases on approaching T_C, e.g., ~ 1 μs at 250 K.[30] This behavior is qualitatively similar to that of ferromagnetic Sr_2FeMoO_6.[31] On the other hand, τ_B ($\approx$30 ns) and τ_{rise} ($\approx$10–20 ns) are nearly temperature independent.

C. Photoinduced formation of clusters in the ferromagnetic phase

Figures 4(a) and 4(b) show temperature variation of magnitudes of the negative (A) and positive (B) components, respectively. As seen in Fig. 4(a), the A value at 2.54 eV (filled circle) scales well to the magnetization (broken curve), consistently with our interpretation that photoinduced disorder of the spin system causes the signal. The finite A value observed above T_C is possibly ascribed to the photodestruction of the residual ferromagnetic short-range correlation. We found that the A value at 1.55 eV [open circles in Fig. 4(a)] shows similar temperature variation to that at 2.54 eV. In addition, the decay times τ_A at E_{probe}=1.55 eV and 2.54 eV are nearly the same in a wide temperature range of 5–240 K (not shown). These observations indicate that the origins for the two photoinduced signals are the same, i.e., photoinduced formation of the CO clusters [see schematics shown in Figs. 5(a) and 5(b)]. Note that the CO clusters prefer the antiferromagnetic (CE-type) spin fluctuation, and could cause the negative ΔT value at 2.54 eV.

Recently, Kise *et al.*[31] have investigated temperature dependence of the lifetime of the spin system in conductive ferromagnet Sr_2FeMoO_6: The lifetime is less than $\sim$0.2 ns even near T_C and further decreases with decrease of temperature. Presently observed lifetime (e.g., ~ 1 μs at 250 K) of the spin system of $La_{0.7}Ca_{0.3}MnO_3$ is much larger than the case of Sr_2FeMoO_6. We ascribe the longer lifetime to the formation of CO cluster domains. Because the cluster is expected to be metastable, due to the accompanied lattice distortion.

D. Photoinduced annihilation of clusters in the paramagnetic phase

On the other hand, the intensity B of the positive component [see Fig. 4(b)] shows a characteristic temperature dependence: the B value increases on approaching T_C from the high-temperature side, and then drops precipitously below T_C. This temperature-dependence is very similar to that of *intrinsic* CO clusters, as detected by the absorption spectroscopy (see open circles in Fig. 2) in the same $La_{0.7}Ca_{0.3}MnO_3$ film used in the present experiment. Therefore, we ascribe the positive signal to the direct annihilation of the inherent CO clusters [see schematics shown in Figs. 5(c) and 5(d)]. Note that the excitation photon energy E_{exc} (=3.05 eV) corresponds to the O $2p$–Mn$e_{g\downarrow}$ transition, and can destroy the charge-/orbital-ordering within the clusters.

IV. SUMMARY

We have observed temperature-dependent photoinduced transmission changes at E_{probe}=1.55 eV and 2.54 eV, and

have interpreted them in terms of creation ($T \leqslant T_C$) or annihilation ($T \geqslant T_C$) of the CO clusters. From the point of view of applications, such a creation/annihilation of the CO clusters could switch the conductivity of the film. Systematic research of the photoirradiation effect on the transient conductivity is now in progress.

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