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Critical behavior of a photodisordered spin system in doped manganite

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Dynamics of the spin system has been investigated in a ferromagnetic $La_{0.7}Ca_{0.3}MnO_3$ film by means of a time-resolved pump-probe method. In a weak excitation condition, the relaxation time τ increases critically on approaching the critical temperature T_C ($=262$ K) from the low-temperature side as $\tau \propto |T/T_C - 1|^{-1.39}$ for $T \gtrsim 200$ K. Surprisingly, the same scaling relation holds even after strong excitation in a much wider temperature range down to ~ 10 K. We will discuss these behaviors in terms of photoinduced growth of the charge-ordering fluctuations.

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Critical behavior near a phase transition, e.g., critical slowing down of the relaxation time, has been awarded great attention. So far, many theoretical and experimental studies[1–4] have been carried out on the critical behavior to describe the fluctuations near the phase transition. Recently, Kise *et al.*[5] investigated temperature dependence of the relaxation time τ on Sr_2FeMoO_6 with ferrimagnetic spin structure after photoirradiation: they found that τ increases critically with temperature as $\propto |T/T_C - 1|^{-1.22}$ near below T_C. Thus, the time-resolved pump-probe technique is a powerful tool to investigate dynamical properties, especially near the critical temperature. Here, we chose another spin system, perovskite-type doped manganite, for detailed investigation on the critical behavior. This is because we can easily monitor the nearest-neighboring spin correlation $\langle S_i S_{i+1} \rangle$ by transmittance of the exchange-split band at ~ 3 eV:[6–8] $T \propto 1 - \langle S_i S_{i+1} \rangle / S^2$ or $\Delta T \propto -\Delta \langle S_i S_{i+1} \rangle$. Similarly to the case of Sr_2FeMoO_6, we observed a similar scaling relation between τ and $|T/T_C - 1|$ near T_C. We further have found that the τ value shows a characteristic photon density dependence, and interpreted the behavior in terms of the photoinduced charge-ordering fluctuations.

The perovskite-type doped manganite becomes ferromagnetic metallic below T_C. The generic features of the magnetic and transport properties of doped manganites are well understood in the framework of the double-exchange mechanism,[9] which includes the transfer integral t of the e_g electrons and the Hund's rule coupling J between the local t_{2g} spins and the e_g electrons. The peculiar feature of the system is the existence of the charge-ordering fluctuations in the paramagnetic phase ($\geqslant T_C$), as is suggested by diffuse x-ray scattering,[10,11] optical absorption,[12] Raman scattering,[13] and electron diffraction[12] measurements. For example, Shimomura *et al.*[10] 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 charge-ordering fluctuations. Machida *et al.*[12] reported a temperature-dependent absorption band at ~ 1.5 eV in manganite films above T_C, which they ascribed to the formation of charge-ordering clusters. Recently, Liu *et al.*[14] have investigated temperature variation of the photoinduced effects in a film of $La_{0.7}Ca_{0.3}MnO_3$, and have found a characteristic photoinduced signal at ~ 1.5 eV in the ferromagnetic phase ($\leqslant T_C$). This observation suggests photoinduced formation of the charge-ordering clusters in the ferromagnetic phase.

In this paper, we have investigated dynamical behavior of the spin system near T_C with changing temperature T and total pulse energy P per one shot in a film of $La_{0.7}Ca_{0.3}MnO_3$ ($T_C = 262$ K), by means of a time-resolved pump-probe method. In a weak excitation limit, we found an elongation of τ on approaching T_C ($=262$ K) as $\propto |T/T_C - 1|^{-1.39}$ for $T \gtrsim 200$ K. This empirical relation is well reproduced by the three-dimensional Heisenberg model.[1] We further have found anomalous photon density dependence of the relaxation process, and have interpreted these behaviors in terms of photoinduced growth of the charge-ordering fluctuations.

A $La_{0.7}Ca_{0.3}MnO_3$ film with a thickness of 1700 Å was fabricated using a laser molecular beam epitaxy.[15] Sintered $La_{0.7}Ca_{0.3}MnO_3$ pellets were used as a target. A pulsed laser beam (ArF excimer laser with wavelength 193 nm) was used for ablation. The distance between the substrate and the target was 40 mm. The repetition rate was 5 Hz. The $La_{0.7}Ca_{0.3}MnO_3$ was stacked on the $SrTiO_3$ (001) substrate in an NO_2 atmosphere with a pressure of 1.0×10^{-8} bar. The film was grown at a substrate temperature of 700 °C. The formed film was kept for 30 min at the substrate temperature (700 °C) and in NO_2 pressure of 1.0×10^{-5} bar. X-ray diffraction measurements revealed that the obtained films were

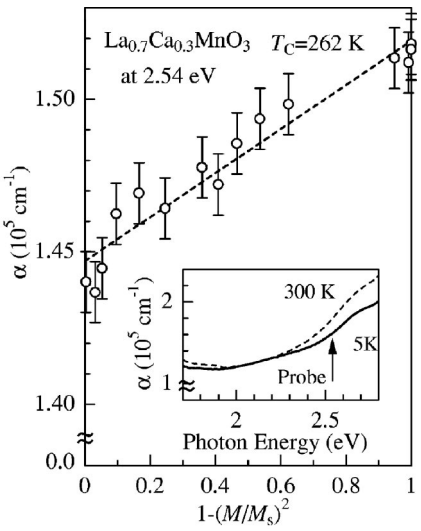

FIG. 1. Magnetization (M) dependence of absorption coefficient α of $La_{0.7}Ca_{0.3}MnO_3$ film at 2.54 eV (upward arrow in the inset). M_s is the saturation magnetization. Broken line is the least-square-fitted result. Inset shows the absorption spectra at 5 K (solid curve) and 300 K (broken curve).

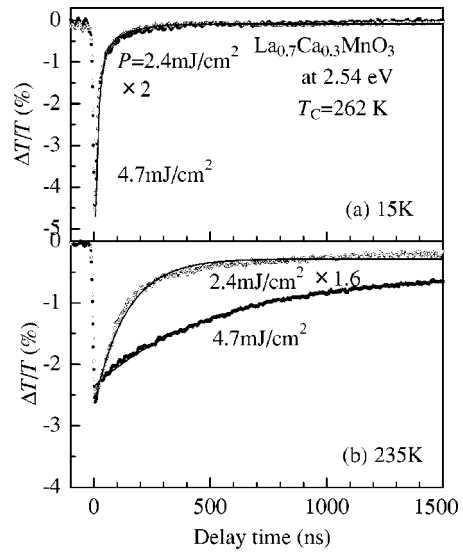

FIG. 2. Temporal evolution of the transmission change $\Delta T/T$ at $E_{probe}=2.54$ eV of $La_{0.7}Ca_{0.3}MnO_3$ film at (a) 15 K ($\leqslant T_C=262$ K) and (b) 235 K ($\sim T_C$). Open and filled marks represent the data obtained at 2.4 mJ/cm^2 and 4.7 mJ/cm^2, respectively. The pump pulse duration, frequency, and photon energy E_{exc} are 20 ns, 10 Hz, and 3.05 eV, respectively. The solid curves are the best-fitted results with single exponential function (see text).

(001)-oriented in the pseudocubic setting. The Curie temperature T_C ($=262$ K) was determined from the temperature dependence of the magnetization M measured at 0.05 T after cooling down to 5 K in the zero field. 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 of the pump pulse is fixed at $E_{exc}=3.05$ eV, below the absorption edge of the $SrTiO_3$ (001) substrate. We confirmed that the substrate does not show any photoinduced signal. We used an Ar^+ laser ($E_{probe}=2.54$ eV) as a probe light source. The transient data were accumulated for 5 min with a digital oscilloscope. The response of both the detector (PIN photodiode) and digital oscilloscope is ~ 10 ns. So, time resolution of our system is ~ 20 ns.

Before describing the photoinduced effects of the $La_{0.7}Ca_{0.3}MnO_3$ film, let us survey the temperature variation of the absorption spectra. The inset of Fig. 1 shows the absorption spectra $\alpha(\omega)$ of the same film used for the pump-probe experiments: solid curve and broken curve are at 300 K ($\geqslant T_C=262$ K) and at 5 K ($\ll T_C$). α significantly increases above ~ 2.2 eV at 300 K as compared with the value at 5 K. This is due to *the interband transition between the exchange-split bands*, or due to the transition of an e_g electron to the neighboring Mn site with opposite spin direction, which strongly depends on the net magnetization M.[7] As shown in Fig. 1, we observed a scaling relation between α at 2.45 eV (probe photon energy) and $1-(M/M_s)^2$. Here, note that variation of $(M/M_s)^2$ scales that of nearest-neighbor spin correlation $\langle S_i S_{i+1}\rangle$. Thus, we can easily monitor the spin correlation by transmittance at $E_{probe}=2.54$ eV.

Figure 2(a) shows prototypical examples of the temporal evolution of $\Delta T/T$ ($E_{probe}=2.54$ eV) at 15 K ($\ll T_C=262$ K) after photoirradiation: open and filled marks are the data obtained at $P=2.4$ mJ/cm^2 and 4.7 mJ/cm^2, respectively. P is the total pulse energy per one shot. The excitation photon energy E_{exc} is 3.05 eV, which corresponds to the charge transfer transition (~ 4 eV) from the O $2p$ level to Mn $e_{g\downarrow}$ state.[6,16] After photoirradiation, the absolute magnitude of $\Delta T/T$ soon reaches a maximum, and then monotonously decreases. The observed negative $\Delta T/T$ value indicates that the photoexcited $e_{g\downarrow}$ electrons suppress the spin correlation, or cause the spin disorder, via the strong on-site exchange coupling J. The relaxation processes from the photodisordered spin state are well reproduced by the following single exponential function:

$$-\Delta T/T = A\exp(-t/\tau) + C, \tag{1}$$

where τ is the relaxation time. The constant term (C) is probably due to the heating effect, lasting for much longer time than the time range concerned here. A solid curve in Fig. 2(a) is the best-fitted result. At 15 K, the τ value (≈ 25 ns) is independent of P.

The relaxation process becomes significantly P dependent on approaching T_C. Figure 2(b) shows the temporal evolution of $\Delta T/T$ ($E_{probe}=2.54$ eV) at 235 K ($\sim T_C$) after photoirradiation. The τ value increases from ≈ 150 ns at 2.4 mJ/cm^2 to ≈ 550 ns at 4.7 mJ/cm^2. Nevertheless, the relaxation processes are well reproduced by the single exponential functions, as shown by the solid curve in Fig. 2(b). We plotted in Fig. 3 the P dependence of (a) τ and (b) A of the photoinduced signal at various T. The photoinduced signal almost disappears above T_C.[14] The τ value increases nonlinearly as $\sim P^2$ [see the broken lines in Fig. 3(a)]. On the other hand, the A value increases linearly with P, as indicated by

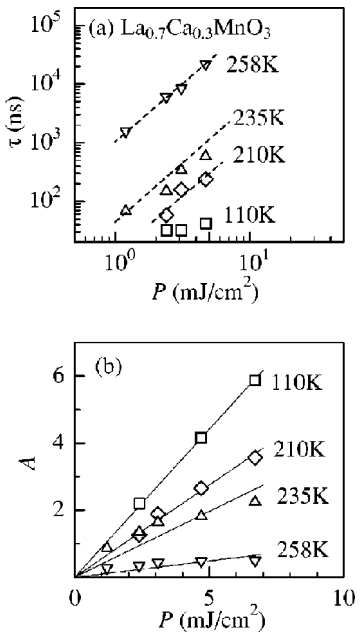

FIG. 3. Pulse energy (P) dependence of (a) relaxation time τ and (b) magnitude A of the photoinduced signals of $La_{0.7}Ca_{0.3}MnO_3$ film at various temperatures. Broken straight line in (a) is the guide to the eyes. Solid lines in (b) represent linear relation between A and P.

the straight line in Fig. 3(b). With increase of temperature, the A value decreases due to the suppressed net magnetization.

In Fig. 4, we plotted thus obtained τ against reduced temperature $|T/T_C-1|$ for various P. In a weak excitation limit (for example, see filled and open circles), τ critically increases on approaching T_C ($=262$ K) from the low-temperature side. We found an empirical power law between τ and $|T/T_C-1|$, and determined the exponent to be $\sim -1.39\pm 0.06$ (broken straight line). The inset of Fig. 4 shows τ against T at 2.4 mJ/cm^2: the data points obey the empirical relation for $T \gtrsim 200$ K. This enhancement of τ can be ascribed to the critical slowing down. The dynamical scaling theory for the second-order phase transition[3,4] predicts that τ obeys the power law as $|T/T_C-1|^{-z\nu}$ in the vicinity of T_C, where the correlation length ξ ($\propto|T/T_C-1|^{-\nu}$) of fluctuations is much longer than the atomic interval. z and ν denote the dynamical critical exponent and the critical exponent of the correlation length, respectively. The three-dimensional Heisenberg model gives $z\nu=1.38$,[1] and well reproduces the empirical relation ($\tau\propto|T/T_C-1|^{-1.39}$). This is consistent with the three-dimensional spin structure of $La_{0.7}Ca_{0.3}MnO_3$.

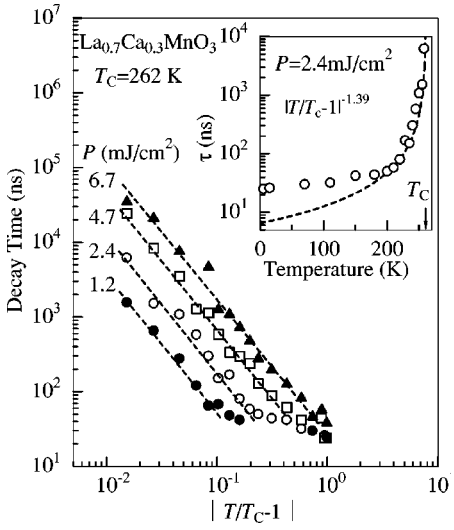

FIG. 4. Temperature variation of the relaxation time τ of the photoinduced signals of a $La_{0.7}Ca_{0.3}MnO_3$ film for various pulse energies (P). The broken straight lines are the best-fitted results. Inset shows the temperature dependence of τ at 2.4 mJ/cm^2. Broken curve shows the empirical relation ($\tau\propto|T/T_c-1|^{-1.39}$) between τ and the reduced temperature.

How does the relation between τ and T change as P increases? Looking at Fig. 4, one may notice that the scaling relation, i.e., $\tau\propto|T/T_C-1|^{-1.39}$, holds even after strong excitation, but *in much wider temperature range* down to ~ 10 K. In addition, *the magnitude of τ increases* significantly. For example, the τ value at 258 K increases more than one order: ≈ 1500 ns at 1.2 mJ/cm^2 and ≈ 24000 ns at 4.7 mJ/cm^2. Note that this P dependence of τ cannot be ascribed to a conventional heating effect, because the *τ value diverges at T_C* even after strong excitation.

Here, let us argue the photoinduced effect on the spin system of doped manganites, considering the pulse energy dependent behavior. The photoirradiation at $E_{exc}=3.05$ eV excites the $e_{g\downarrow}$ electrons from the O $2p$ band. Then, the $e_{g\downarrow}$ electrons relax within ~ 1 ps (Ref. 17) with creating spin waves via the strong on-site Hund's-rule coupling J. As a result, the spin correlation is destroyed, which causes the photoinduced signal at $E_{prob}=2.54$ eV.[18] Here, the number of the created spin waves, and hence the photoinduced signal, is proportional to P [see Fig. 3(b)]. In a weak excitation limit, the spin system is nearly the same as before photoexcitation. In this sense, the weak photoexcitation only perturbs the spin system, and hence we can observe the critical slowing down of τ only near T_C (see inset of Fig. 4).

By contrast, after the strong excitation, a large number of spin waves fairly alter the distribution of the spin alignments. Judging from the magnitude of the photoinduced signal, the nearest-neighboring spin correlation almost disappears after photoexcitation with pulse energy of 6.7 mJ/cm^2. In this heavily photodisordered spin state, the charge-ordering fluctuations, which strongly compete with the ferromagnetic ground state,[19–22] are considered to grow. From Monte Carlo simulations, Moreo *et al.*[23] indicated that randomness of the exchange and hopping amplitudes can cause the charge-ordering fluctuations. Then, photoirradiation, which transiently destroys the ferromagnetic spin correlation and hence suppresses the hopping amplitude [$\propto t_0\cos(\theta/2)$,[9] where t_0 and θ are the bare value and the relative angle of the neighboring local spins, respectively], can trigger the charge-ordering fluctuations.[24] Actually, Liu *et al.*[14] observed a characteristic photoinduced signal at ~ 1.5 eV, and ascribed it to photoinduced growth of the charge-ordering fluctuations.

According to this scenario, the nonlinear enhancement of τ with P is interpreted as follows. After strong excitation, the heavily photodisordered spin state triggers charge-ordering fluctuations with charge-exchange (CE) -type antiferromagnetic spin correlation. The stronger P becomes, the longer correlation length ξ of the fluctuations (the larger size of the charge-ordering clusters) becomes, perhaps due to combination of the neighboring fluctuation regions (charge-ordering clusters) into one large fluctuation region (cluster). Since the relaxation time τ increases as $\sim\xi^z$ ($z=1.94$ for the three-dimensional Heisenberg model[1]), our results ($\tau\propto P^2$) suggest that the correlation length (cluster size) ξ increases as $\sim P$.[25] The lengthened correlation length ξ, further, enlarges the temperature range where ξ is much longer than the atomic interval. This is why the scaling relation, i.e., $\tau\propto|T/T_C-1|^{-1.39}$, is observed in much wider temperature range after strong excitation.

In summary, we have investigated dynamics of the spin system in a ferromagnetic $La_{0.7}Ca_{0.3}MnO_3$ film by means of time-resolved pump-probe method. In a weak excitation limit, the relaxation time τ critically slows down as $\tau\propto|T/T_C-1|^{-1.39}$ near T_C ($=262$ K). We have found that this scaling relation holds even from the heavily photodisordered spin state, and interpreted it in terms of the charge-ordering fluctuations induced by the photoexcitation. Thus, the time-resolved pump-probe technique gives us a good opportunity to investigate the critical behaviors of the spin fluctuations.

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[24] Note that the charge-ordering clusters prefer the antiferromagnetic (CE-type) spin fluctuation, and could cause the negative signal at 2.54 eV.
[25] Note that the cluster size increases as $\sim P^{1/3}$, if the number of the clusters is constant without combination of the neighboring clusters.