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Persistent photoconductivity in a ferromagnetic-metallic state of a Cr-doped manganite thin film

Hirotaka Oshima,[1,2] Masao Nakamura,[1] and Kenjiro Miyano[1,2]
[1]*Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*
[2]*Japan Science and Technology Corporation (JST), Tokyo 171-0031, Japan*

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Photoinduced persistent conductance has been observed in a Cr-doped $Pr_{0.5}Ca_{0.5}MnO_3$ thin film. The film shows a diffuse phase transition and phase separation that arise from the quenched random fields produced by the Cr ions. Photoexcitation of the sample with a continuous-wave–yttrium-aluminum-garnet laser causes a gradual increase of the conductance in the ferromagnetic-metallic (FM) state, whereas the magnetization and absorption spectra show little change. The persistent conduction is ascribed to the increase in the conducting paths by the optical excitation in the percolative conduction through FM regions, without significant overall growth of the FM regions. The heating effect and the permanent damage to the sample are absent. The temperature dependence of the absorption spectra and the phonon modes were studied and have presented consistent results with the diffuse transition from a charge-orbital ordered insulating to FM phase.

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I. INTRODUCTION

As with many compounds of the correlated electron systems, perovskite manganites $R_{1-x}A_x\mathrm{MnO}_3$ (R=trivalent rare-earth element and A= divalent alkaline-earth element) show various phases in the phase diagrams upon doping x. The doping dependence of their properties is still an open problem in the physics of these compounds, attracting much current interest. An interplay between spin, charge, orbital, and lattice degrees of freedom has now become a basic research problem in transition-metal oxides.[1] From the technological point of view, their peculiar properties, such as the colossal magnetoresistance (CMR) effect, may find applications in sensor and storage devices.

One of the most important issues in manganites is the intrinsic phase separation, especially in the neighborhood of the insulator-metal (IM) transition.[2–4] The ferromagnetic-metallic (FM) phase promoted by the double-exchange mechanism[5] coexists with the insulating phase. Percolative conduction through metallic regions in the insulating matrix often plays a key role in the IM transitions, particularly in the CMR effect. The origin of the phase coexistence, however, is still unclear. The intermediate one-electron bandwidth is clearly an important factor for the phase separation. Besides, a new factor was recently discovered by Raveau *et al.*[6]; a few percent replacement of Mn atoms by Cr in the charge-orbital ordered (CO-OO) manganites results in the emergence of the FM phase and the coexistence of those two phases.[7,8] This discovery added a new dimension in investigating the phase control of the correlated electron systems; the mechanism as well as the interesting properties deserve to be studied.

The localized holes and orbital deficiencies produced by Cr^{3+} ions ($t_{2g}^3 e_g^0$, $S=\frac{3}{2}$) are the essence of the consideration of the physics of the IM transition in Cr-doped manganites.[9] They act as pinning centers of the ordering patterns, and bring about *frustration* because of the randomness of the Cr positions (Fig. 1). Thus it can be regarded as quenched random fields in the CO-OO phase. The frustration forces the order to diminish and give way to the FM state. In the ferroelectric oxides, it is known that quenched random electric fields originating from charged compositional fluctuations cause the so-called relaxor behavior, such as diffuse phase transition and slow relaxation.[10] The random fields break the symmetry of the long-range ferroelectric order, and are responsible for the freezing into a nanometric ferroelectric domain. Intriguingly, it is revealed that the Cr-doped manganites behave just as the ''ferromagnetic'' relaxors.[8,11] The physics is not fully comprehended, but the origin is probably explained in the same way by analogy with the ferroelectric relaxor materials.

The subtle balance of the phases, on the other hand, leads us to speculate on the new possibility of the phase control in these manganites by external fields or stimuli.[12–15] Especially when the system is frustrated and thus glassy, changes of the configuration between a number of metastable states by, for instance, optical excitation is expected. The quest for those phenomena is important not only for fundamental interest, but also for the practical utilities for applications.

Accordingly, for the studies of the phase separation and the phase control, we have studied photoexcitation effects in the Cr-doped manganite. We prepared thin films of $Pr_{0.5}Ca_{0.5}Mn_{0.96}Cr_{0.04}O_3$ that exhibit relaxor behavior. Thin-

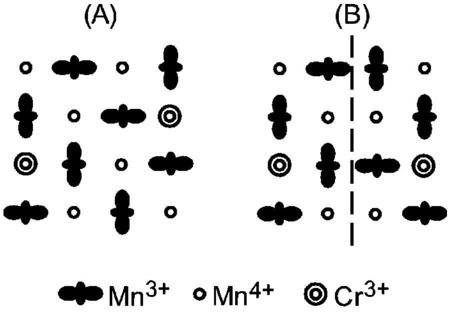

FIG. 1. Schematic diagrams of the charge-orbital order in Cr-doped $Pr_{0.5}Ca_{0.5}MnO_3$. $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals at Mn^{3+} sites and holes at Mn^{4+} and Cr^{3+} sites are denoted. (a) Cr ions are in phase with the ordering pattern. (b) Cr ions are out of phase. Frustration occurs at the phase boundary indicated by the dashed line.

film form is suitable for the optical measurements; it transmits light and no polishing is required, which might cause surface damage. In the present paper, we show a gradual increase of the conductance by irradiation of a continuous-wave (cw) YAG (yttrium-aluminum-garnet) laser in the FM state at low temperature. The conductance is stable after the light is switched off, suggesting controllable conductance by optical excitation.

The outline of this paper is as follows. In Sec. II, experimental details are described, including the procedure of thin-film fabrication. Characterization of the sample and results of the experiments are shown in Sec. III. Photoexcitation effects have been investigated in conductance, magnetization, and reflectivity and transmissivity spectra measurements. Section IV is devoted to a discussion about the origin of the experimental results and about the electronic structure of the sample, and the paper is concluded in Sec. V.

II. EXPERIMENT

$Pr_{0.5}Ca_{0.5}Mn_{0.96}Cr_{0.04}O_3$ thin films with a thickness of 350 nm on a MgO (001) substrate were fabricated by pulsed-laser deposition. A pellet of a sintered stoichiometric mixture of Pr_2O_3, $CaCO_3$, Mn_3O_4, and Cr_2O_3 was checked by x-ray diffraction and revealed as a single phase; it was used for the target onto which ArF excimer laser pulses of about 100 mJ with a repetition rate of 10 Hz were focused. The substrate was held at 800°C in an atmosphere of 1 mTorr oxygen during deposition. The deposited film was postannealed for 30 min at 700°C in a 760-Torr oxygen atmosphere, and then cooled to room temperature in 1 h. X-ray diffraction indicates that the sample is polycrystalline partially oriented with pseudocubic (001) and (011) along the film normal; there is little stress effect by the substrate.

Resistivity under magnetic fields (up to 9 T) was measured by the standard four-probe method. Magnetization data were obtained with a superconducting quantum interference device (SQUID) magnetometer. For the resistivity measurements with laser irradiation, the sample was mounted in a continuous-flow helium cryostat. As a light source, a cw-YAG laser at a photon energy of 1.17 eV was used. The laser beam was focused onto the sample in a spot size of 2 mm in diameter. Intensity of the light was controlled with neutral density filters. The position and the shape of the focused laser spot were checked with a CCD camera. The gap of silver electrodes for resistivity measurements was 500 μm, and the width of the sample was 2 mm. When the photoexcitation effect on magnetization was measured, the laser light was introduced via an optical fiber into the SQUID magnetometer. The spot size was about 2 mm diam on the sample whose size was 2.7 mm×3.9 mm. Near-normal incidence reflectivity $R(\omega)$ and transmissivity $T(\omega)$ spectra were measured in the midinfrared and near-infrared range. A Fourier transform spectrometer (0.05–0.8 eV) and grating monochromators (higher than 0.6 eV) were used. A gold mirror and a MgO substrate were adopted as references in each experiment. The absorption coefficient $\alpha(\omega)$ was calculated as

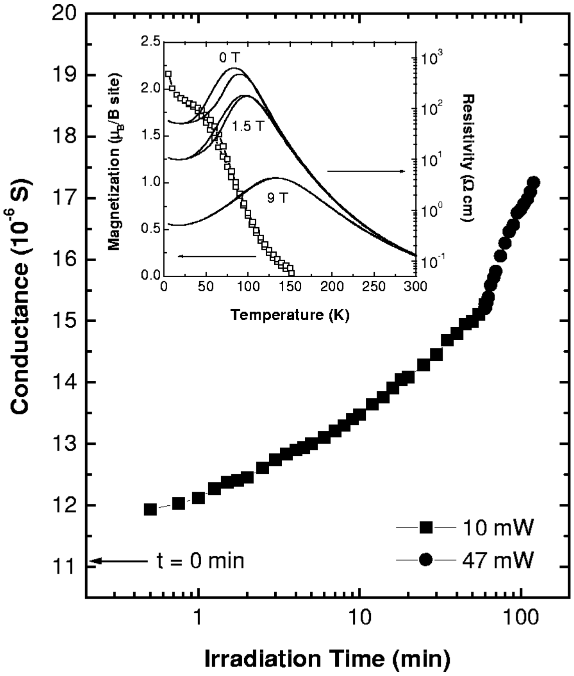

FIG. 2. Conductance as a function of irradiation time at 20 K. $Pr_{0.5}Ca_{0.5}Mn_{0.96}Cr_{0.04}O_3$ thin film on a MgO (001) substrate was irradiated at the laser power of 10 mW for 1 h, then the laser was turned off for 15 min. The sample was irradiated again at the power of 47 mW for the subsequent 1 h after the suspension. Inset shows temperature dependence of the resistivity of the sample under 0, 1.5, and 9 T (solid lines) and the magnetization under 1.5 T (open squares).

$$e^{-\alpha(\omega)d}=1-[R(\omega)+T(\omega)], \tag{1}$$

where d is the thickness of the film.

III. RESULTS

A. Resistivity and magnetization

Diffuse phase transition of the sample[11] is depicted in the inset of Fig. 2. Magnetization appears gradually accompanied by the decrease of the resistivity. The FM ground state is confirmed. However, there is no clear transition temperature nor discontinuous change in the observed property. Large residual resistance, less magnetization than the full polarization, and the CMR effect over a wide range of temperature strongly suggest the phase separation between CO-OO insulating and FM states. All these characters are appropriate for the system to be termed a relaxor.

B. Persistent photoconductivity

Figure 2 shows the conductance increase by photoexcitation as a function of irradiation time at 20 K. The sample was irradiated for 1 h at the laser power of 10 mW, left for 15 min with no light, and then irradiated again at the power of 47 mW for the subsequent 1 h. The conductance increased gradually by the photoexcitation; total increase ($\Delta G/G_0$) of the conductance was 55% (the resistance decreased from 90 kΩ to 58 kΩ), where ΔG is the conductance change

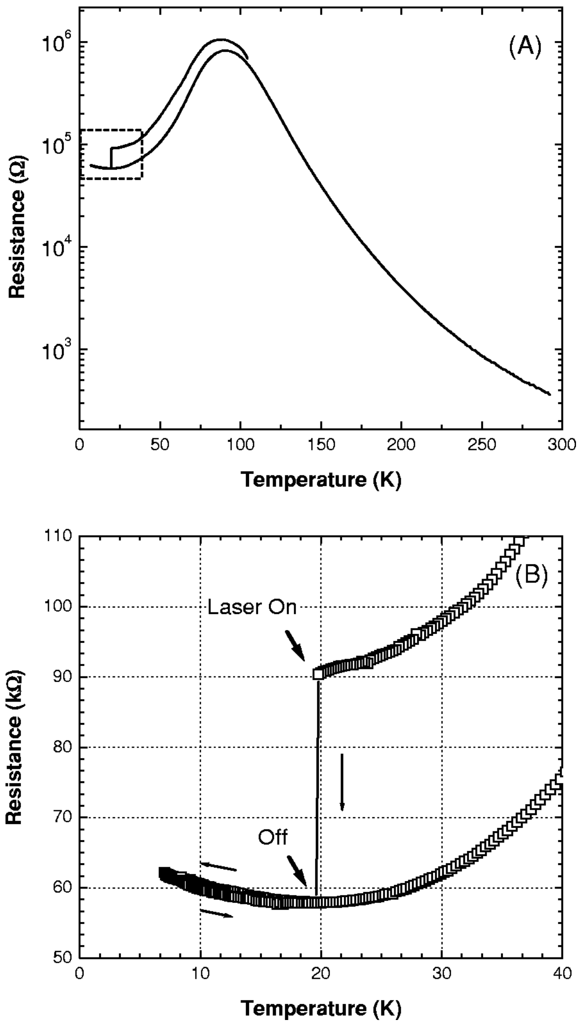

FIG. 3. (a) Temperature dependence of the resistance before and after the photoexcitation at 20 K. (b) The behavior around 20 K presented by the dashed square in (a) is magnified.

and G_0 is the conductance before irradiation. The conductance was stable before the irradiation and during the 15-min period in which the laser was switched off. The resistivity of the sample is minimum at 20 K in the FM state (Fig. 2, inset). Thus, the heating effect cannot be the cause of the conductance increase.

In order to identify that this is not due to damage of the sample, we measured the temperature dependence of the resistance before and after irradiation (Fig. 3). The sample was cooled down to 20 K, photoexcited by the laser as in Fig. 2, cooled further down to 7 K, then heated up to 300 K. The resistance in the heating run in the temperature region higher than the resistance peak is identical with that of the first cooling run. Furthermore, the behavior of the resistance in this whole procedure is reproducible, which excludes the possibility of any damage to the sample.

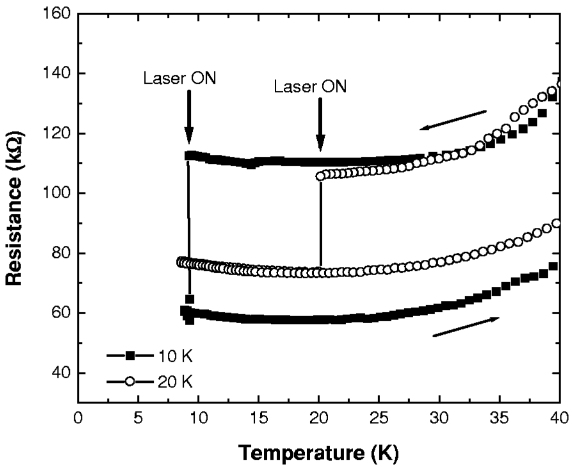

FIG. 4. Temperature dependence of the resistance before and after the photoexcitation at 10 K and 20 K. The sample was irradiated at the laser power of 210 mW for 1 h at 10 K and 20 K, after it was cooled from room temperature.

The conductance increase by photoexcitation is larger at lower temperature. The temperature dependence of the resistance before and after the irradiation at 10 K and 20 K is depicted in Fig. 4. The laser power was 210 mW, and the irradiation time was for 1 h. The increase at 20 K was 43%, and 85% at 10 K. Slight deviations observed after the laser was turned off are due to the heating effect; high intensity contributes to the heating. Even when the laser power is 21 times larger (210 mW/10 mW = 21) compared with the result in Fig. 2, the conductance increase is much less (43%/38% = 1.1). When the laser power is very high, it causes the temperature rise of the sample resulting in the lower conductance increase. The resistance at low temperature before the photoexcitation is a little different (several percent) in each temperature scan. The slight difference of the resistance in the FM region probably reflects the different connectivity of FM clusters in every scan.

Photoexcitation at 70 K and 90 K was examined only to find nothing but the heating effect. 70 K is the temperature in the hysteresis region at which about half of the saturated magnetization appears (Fig. 2, inset), and 90 K is a temperature slightly higher than the resistivity peak. The conductance varies in the same way as the temperature increase would cause, and returns to the original value when the laser irradiation is discontinued.

Organizing the results up to this point, we can remark that the persistent photoconductivity occurs merely in the temperature region much lower than the resistivity peak and is not due to heating. Also, it should be added that the applied electric field to measure the resistivity is not the substantial driving force, as we observed an increase of the conductance after the irradiation even when there was no applied field during photoexcitation. The increase of the conductance by photoexcitation depends on the intensity of the light, the duration of the irradiation time, and the temperature of the sample: the lower the temperature, the more the conductance increases.

C. Photoexcitation effect in magnetization

The IM transition of this relaxor manganite is accompanied by the appearance of ferromagnetism (Fig. 2, inset); diffuse phase transition comes from the diffuse emergence of the FM clusters and the percolative conduction through

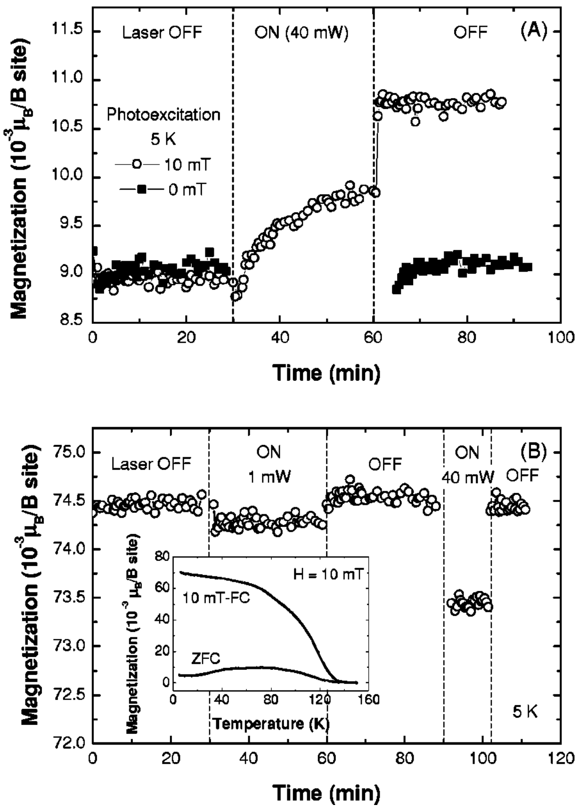

FIG. 5. Magnetization as a function of time at 5 K. (a) After the magnetization measurement of the zero-field-cooled (ZFC) sample for 30 min in 10 mT, the sample was irradiated at the laser power of 40 mW for 30 min in 0 mT (filled squares) and in 10 mT (open circles), then the magnetization was measured for 30 min again. (b) The 10 mT–field-cooled (10 mT-FC) sample was irradiated at the power of 1 and 40 mW according to the time schedule shown. Inset in (b) shows the temperature dependence of the magnetization of the ZFC and 10 mT-FC sample in 10 mT.

them. As the metallic conductivity is associated with the ferromagnetism, we have investigated the photoexcitation effect on magnetization of the sample.

Figure 5(a) shows the magnetization before and after the photoexcitation. The sample was zero-field-cooled (ZFC) down to 5 K, and the magnetization was monitored in 10 mT of the magnetic field perpendicular to the film for 30 min. Confirming that the magnetization was stable, the sample was irradiated with 40 mW of cw-YAG laser light for 30 min with no field. During the irradiation with no field, the spontaneous magnetization was too small to be measured. We measured the magnetization again in 10 mT after the photoexcitation for 30 min (filled squares). There was little change in the magnetization before and after the photoexcitation.

Photoexcitation in 10 mT, on the other hand, increased the magnetization (open circles). However, this does not mean the volume fraction change of the FM clusters. This is the field-heating effect of the ZFC sample by heating and cooling in the 10 mT field, judging from the experiments below. As shown in the inset of Fig. 5(b), magnetization of the ZFC and field-cooled (FC) sample is completely different; the magnetization of the ZFC sample is much smaller than that of the 10 mT-FC sample.[11] The difference between ZFC and FC measurements is not due to the change of the volume fraction of the FM regions by the magnetic field, but is probably due to the freezing of the magnetization of the FM clusters. This view is justified from the result of the resistivity measurement as a function of temperature under 0 and 10 mT, which showed identical values in both cooling and heating runs (data not shown). Furthermore, when the 10 mT-FC sample was photoexcited in the field of 10 mT, no increase but a decrease due to heating was observed [Fig. 5(b)] without any net increase of the magnetization after the laser was turned off. Thus, photoexcitation has been revealed to act on the magnetic properties only through heating by photoabsorption. The temperature rise in the sample is estimated to be 1 K and 4 K under 1 mW and 40 mW laser irradiation, respectively. No increase of the magnetization corresponding to the increase of the conductance by photoexcitation has been detected even at the lowest temperature of 5 K.

D. Optical spectra

To explore the electronic structure of the system and, if it exists, its modification by the photoexcitation, we studied reflectivity and transmissivity in the midinfrared and near-infrared regions from room temperature to 9 K. Figure 6 shows spectra, at 298 K, 130 K, and 9 K before and after the

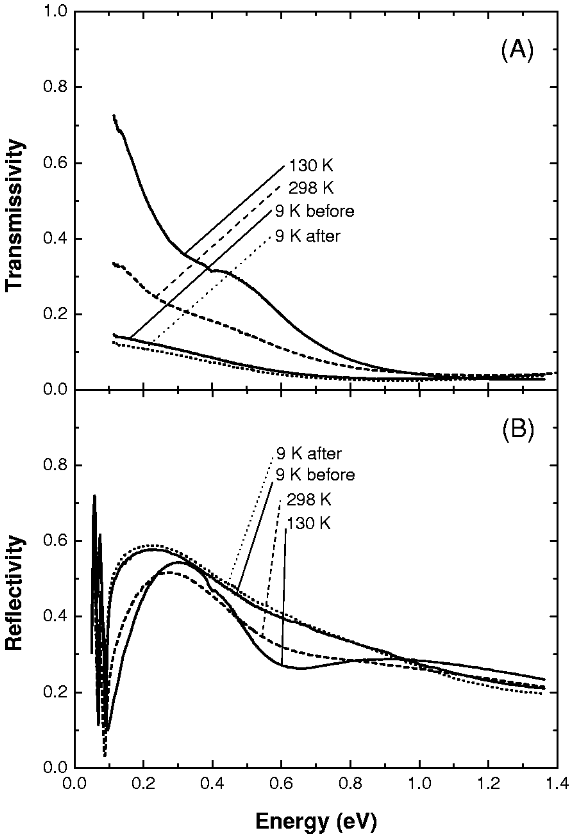

FIG. 6. Transmissivity (a) and reflectivity (b) spectra measured in a cooling run. The spectra in the midinfrared and near-infrared regions at 298 K, 130 K, and 9 K before and after the photoexcitation are shown.

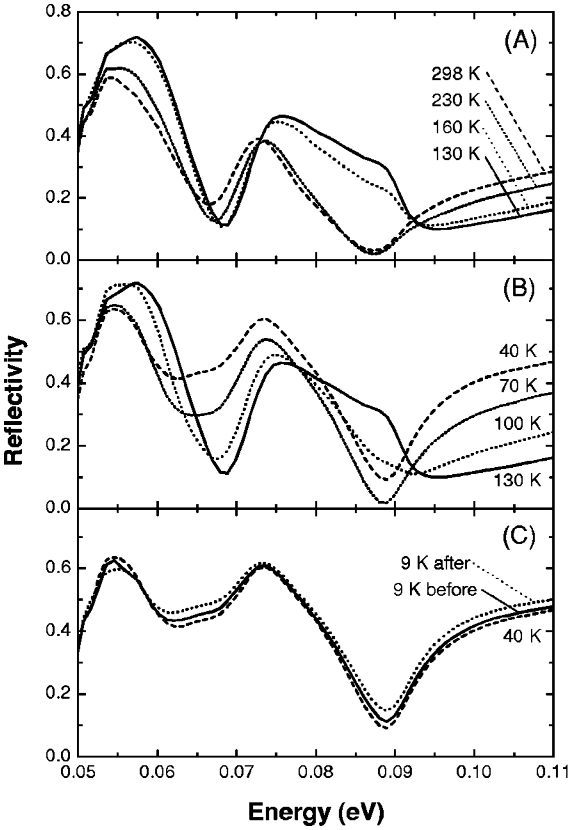

FIG. 7. Infrared optical-phonon spectra at various temperatures in a cooling run. (a) 298–130 K, (b) 130–40 K, (c) 40–9 K.

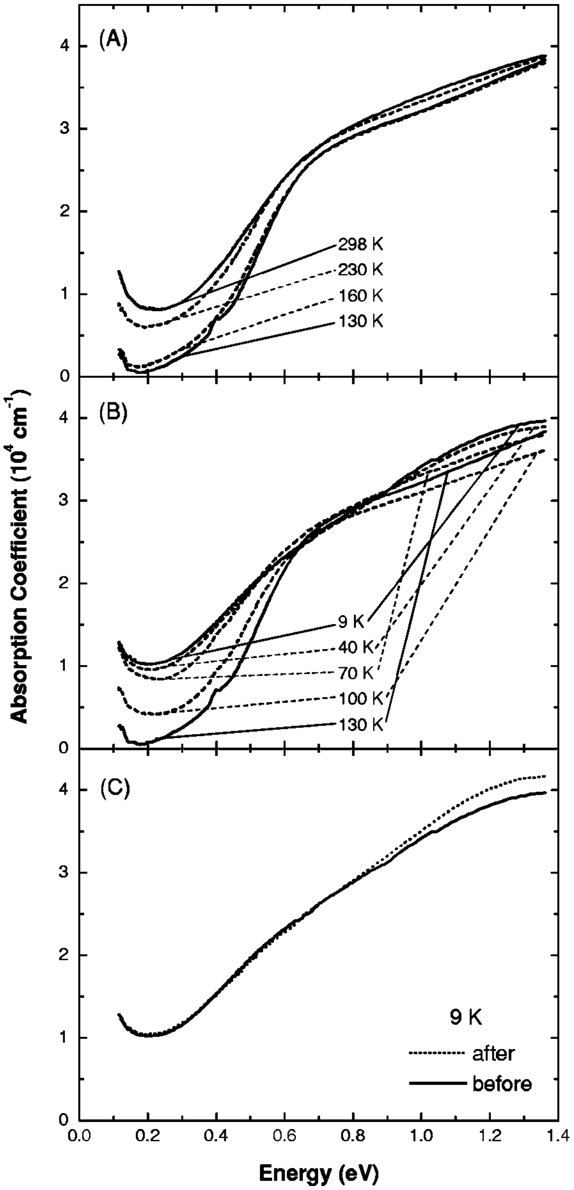

FIG. 8. Absorption spectra at various temperatures in a cooling run. (a) 298–130 K, (b) 130–9 K, (c) 9 K before and after the photoexcitation. The sample was irradiated with a cw-YAG laser light at 65 mW for 30 min.

photoexcitation. The cw-YAG laser intensity was 65 mW, and the spot size was about 2 mm in diameter. The difference in the spectral ranges shown for reflectivity and transmissivity is due to the transmissivity of the substrate and windows of the cryostats used in these experiments. Strong temperature dependence has been observed in both of the spectra. The transmissivity increased from 298 K down to 130 K, and decreased from 130 K to 9 K. The reflectivity, on the other hand, decreased down to 130 K with some structured increase near 0.3 and 1.0 eV, and increased from 130 K to 9 K. There is a small change of the spectra by photoexcitation. The transmissivity decrease as well as the reflectivity increase by photoexcitation were found, but they were less than a few percent.

Optical-phonon spectra shown in Fig. 7 also present a characteristic change corresponding to the electronic phases of the relaxor system. There are two phonon peaks at 0.054 eV (440 cm^{-1}) and at 0.073 eV (590 cm^{-1}) at 298 K. Around 130 K, there gradually appears an additional peak at 0.088 eV (710 cm^{-1}) and disappears again at lower temperatures. The peak at 0.073 eV shifts to higher energy around 130 K. It goes back to 0.073 eV again at lower temperatures with a broad shoulder. In addition, a ravine between those two peaks is gradually filled in below 70 K. The results of these optical spectroscopic measurements will be discussed in the next section.

Figure 8 shows the absorption spectra at various temperatures calculated using Eq. (1). The spectral weight of the lower-energy part is suppressed from 298 K down to 130 K indicating the evolution of the CO-OO insulating state [Fig. 8(a)]. There can be seen a clear gaplike feature at 130 K. At all temperatures, small upturn exists below 0.2 eV, probably due to a tail of the phonon mode[16] which can be observed also in the reflectivity spectra (Fig. 6). Below 130 K, the lower-energy weight increases again [Fig. 8(b)]. Although this behavior is consistent with the appearance of the FM phase at low temperature, little Drude weight (coherent part) except for the small upturn below 0.2 eV mainly due to the phonon mode appears even at the lowest temperature 9 K. Furthermore, the spectral change between 40 K and 9 K is small, which suggests only a slight change in the electronic structure below 40 K.

Comparing the absorption coefficient before and after the photoexcitation, little change in the spectral weight of the lower-energy part can be found [Fig. 8(c)]. The small changes of the reflectivity and the transmissivity by photoexcitation (Fig. 6) negate each other; there is little change in absorption spectra as a result. In the range above 1 eV, on the other hand, the spectral weight increased by 5% by the laser irradiation.

IV. DISCUSSION

A. Possible origin and percolative conduction

The experimental results are first summarized below from a standpoint of the photoexcitation effects in the $Pr_{0.5}Ca_{0.5}Mn_{0.96}Cr_{0.04}O_3$ thin film.

(i) Persistent photoconductivity in the FM state. Photoexcitation with a cw-YAG laser causes an increase of the conductance in the FM state at low temperature. The increased conductance by the photoexcitation is stable after the termination of the laser irradiation.

(ii) No photoinduced magnetism. No magnetization arises from photoexcitation even at the lowest temperature. Only the field-heating effect has been observed.

(iii) No photoinduced absorption. The absorption coefficient spectra hardly varied in the lower-energy part.

Taking these results into consideration, the persistent photoconductivity cannot be ascribed to the proportionate increase of the metallic state by photoinduced IM transition, which has been observed in other perovskite manganites.[14,17] Little change by photoexcitation in the magnetization and the midinfrared absorption spectra, which is an index of the metallicity, indicates that few FM clusters are created.

The mechanism is again different from that of the persistent photoconductivity observed in a variety of semiconductors; its common origin is certain types of impurities, the so-called *DX* centers. Large relaxation of the lattice around the impurities prevents recapture of the electron by photon emission, because it needs substantial momentum transfer.[18] Therefore, photogenerated carriers live long; the lifetimes reach easily more than days or weeks. In manganites, however, carriers in the conduction band align the spin direction by a double-exchange mechanism, which involves ferromagnetism. Little change in the magnetization by the photoexcitation indicates that the long-lived carriers have not been generated in our sample. Also, illumination of the related compound $Pr_{0.7}Ca_{0.3}MnO_3$ by x rays induces persistent change in conductivity by several orders of magnitude.[13] Keimer *et al.* argued that the observed behavior is caused by a ferromagnetic polarization of local spins by hot electrons generated by x rays.[19] The mechanism is then probably different from ours as well.

A percolative conduction, on the other hand, can be a plausible scenario in which a very small change of the metallic fraction can induce a fairly large modification in conductance. A percolation theory gives the universal critical behavior of the percolative conductance,[20]

$$G \propto (p - p_c)^{\mu}, \qquad (2)$$

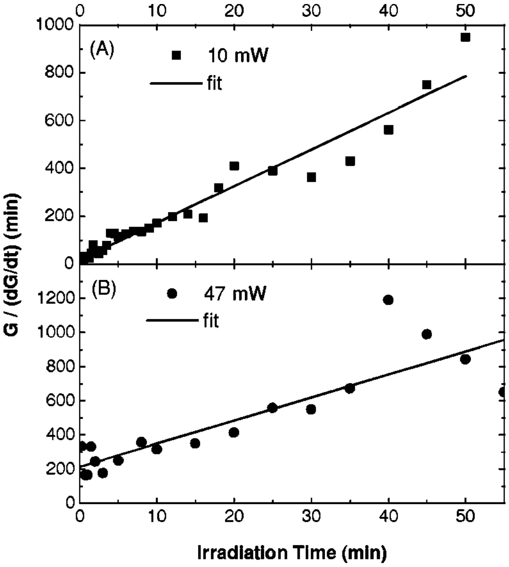

FIG. 9. Calculated $G(\partial G/\partial t)^{-1}$ from the results in Fig. 2, (a) 10 mW and (b) 47 mW. Their fits to the linear functions are also shown.

where G is the conductance, p is the occupation probability of the conducting sites or bonds while $1-p$ is that of the insulating ones, p_c is the critical value of p for the percolative conduction, and μ is the critical exponent that depends on the dimensionality of the system. Assuming that the probability p increases in proportion to the irradiation time t ($p = at + b$, where a and b are parameters), $G(\partial G/\partial t)^{-1}$ can be written as $t/\mu + c$, where $c = (b - p_c)/(\mu a)$. Therefore, it is possible to derive μ from plotting $G(\partial G/\partial t)^{-1}$ as a function of t irrespective of the initial conditions or the light intensity. In Fig. 9, the calculated $G(\partial G/\partial t)^{-1}$ from the experimental results depicted in Fig. 2 and their fits to the linear functions are shown. From the slopes, μ is estimated to be 0.065 and 0.076 under 10 mW and 47 mW laser irradiation, respectively.

The critical exponents μ of both fits are close. However, the theoretical value of the critical exponent μ is 1.3 in two dimensions (2D) and ~ 2 in three dimensions (3D) both in the site and bond percolation.[20] The theoretical values are much larger than the fitted parameters μ. The exponent μ less than unity implies that the photoinduced effect tends to saturate as a function of time. A homogeneous photoinduced promotion of the IM transition is thus not likely. A more elaborate model is needed.

Recently, a series of Monte Carlo simulations has been performed to describe the metal-insulator phase separation and the resulting percolative behavior in the conductance.[21,22] One peculiar aspect that the calculation revealed is that the FM clusters in the antiferromagnetic background are surrounded by thin paramagnetic insulating regions. They can be easily turned into the FM state. Hence, if FM clusters are separated by them, lowering the temperatures or application of the magnetic field link the clusters and cause a large resistivity change. It is not unreasonable to imagine that the light also acts on these unstable regions.

In a phase-separated system caused by the local random field, the phase boundary is inherently unstable. The photoexcitation can trigger the transition between metastable states of the frustrated system and reshuffle the configuration by the instantaneous disruption of the local order by the electronic excitation. The local path is established by chance and the overall conductance increases.

Under the scenario stated above, a number of observations can be explained. By acting only on the unstable regions, the effect of the light is rather limited. One can easily exhaust the parts favorable for the photoinduced transition. The conductance saturates quickly. The depth of the local potential minima of the metastable states should depend on the temperature. The lower the temperature is, the deeper the potential minima become. The stability of the photoinduced state is not strong enough at 70 K and no persistent effect results. The stability at 10 K is stronger than that at 20 K, hence the larger effect. While the percolative conduction is sensitive to a slight modification of the connectivity of the FM clusters, the other macroscopic properties such as magnetization and absorption spectra are not much influenced.

B. Optical spectra

The small spectral weight at the lower-energy part in the absorption spectra at all temperatures (Fig. 8) indicates its incoherent nature even in the temperature region where the FM phase appears; the coherent Drude part from the intraband transition, which is fairly large in the canonical double-exchange systems,[23,24] is not observed. Opening of the charge gap in lowering the temperature as well as the fully opened gap of about 0.2 eV are similar to those observed in the CO-OO insulator $Pr_{0.6}Ca_{0.4}MnO_3$ single crystal.[25] With the appearance of the FM phase by further decrease of the temperature, the gap is gradually filled due to the increase of the spectral weight below 0.6 eV. This behavior is typical of the narrowband manganites with low Curie temperature (T_C).[26] Our sample shows, therefore, qualitatively similar behavior to the other CO-OO manganites in the insulating state and to the FM state of low-T_C manganites when the FM phase appears.

As for the photoexcitation effect in the absorption spectrum [Fig. 8(c)], the spectral weight lower than 0.8 eV is barely modified. This suggests little change of the metallicity, which is consistent with the result that there is little photoinduced magnetism. The absorption spectrum higher than 0.8 eV increases a little by the photoexcitation; this might suggest some electronic-structure change around 1.4 eV. Optical conductivity measurements of manganites by several authors show the existence of the 1.5 eV peak.[27] The peak is not assigned definitely yet and its relationship to the observed conductance increase is unclear.

Before we end this section, we should mention the applicability of the simple analysis as presented above because we are certain that the sample is highly inhomogeneous. The dielectric constant and hence the optical properties of the phase-separated manganites are not well investigated. Therefore, as a first step, let us employ the simple but widely used effective-medium theory here. The theory treats a random inhomogeneous mixture of more than two kinds of materials as a homogeneous medium of an effective dielectric constant $\varepsilon_{\mathrm{eff}}$. The microstructure of each material is modeled by rotational ellipsoids. When the material is composed of two components A and B whose dielectric constants are ε_A and ε_B with probabilities f and $1-f$, respectively, $\varepsilon_{\mathrm{eff}}$ is derived from a quadratic equation of $\varepsilon_{\mathrm{eff}}$,

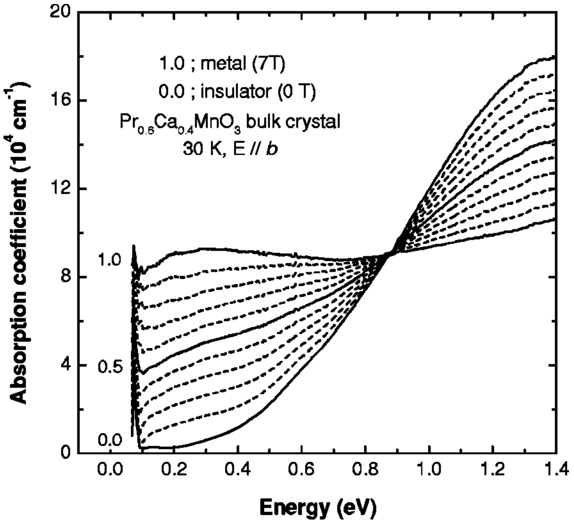

FIG. 10. Calculated absorption coefficient spectra by the effective medium theory. Experimental data of a $Pr_{0.6}Ca_{0.4}MnO_3$ single crystal at 30 K in 0 T and 7 T are used as the insulator and the metal, respectively (Ref. 26). Metallic fraction p is varied in increments of 0.1, and the results for $p=0.0$, 0.5, and 1.0 are denoted with solid lines.

$$\varepsilon_{\mathrm{eff}}^2+\left(\frac{f-L}{L-1}\varepsilon_A+\frac{1-f-L}{L-1}\varepsilon_B\right)\varepsilon_{\mathrm{eff}}+\frac{L}{L-1}\varepsilon_A\varepsilon_B=0, \qquad (3)$$

where L is a depolarization factor that depends only on the shape of the ellipsoid.[28] When the calculated values are compared to the experimental results, L is treated as a fitting parameter that depends on the microstructures, surface roughness, inhomogeneity, and so on. This equation comes from the self-consistent requirement that the total polarization of the ellipsoids must be equal to that of the effective medium.

Although the dielectric constants of the pure CO-OO phase and the fully FM phase relevant to our sample are not available, we can safely assume that the known dielectric constants of the CO-OO insulating and magnetic-field-induced metallic phases of the $Pr_{0.6}Ca_{0.4}MnO_3$ bulk crystal[25] are suitable for estimating qualitatively the optical spectra of the phase-separated manganite. The absorption spectra thus calculated using Eq. (3) are shown in Fig. 10. The experimental data were taken at 30 K with the incident light polarized along the b axis.[25] The spectra are calculated in increments of 0.1 in the metallic fraction p, and the spectra of $p=0.0$, 0.5, and 1.0 are drawn as solid lines. The growth of the lower-energy weight with an increase of the metallic regions and the pseudo-gap-like feature around $p\sim0.5$ are found in the calculated spectra, which are also observed in the Cr-doped manganite film [Fig. 8(b)]. We assumed here that the metallic domains are nearly spherical ($L=\frac{1}{3}$). The calculated results show a qualitatively similar p dependence, if two-dimensional disklike metallic domains ($L=\frac{1}{2}$) are assumed.

Change of the calculated spectra as a function of p is rather continuous and gradual, and there is no jump or discontinuity. Applied to the Cr-doped manganite, this implies that few FM clusters are created, as little change of the absorption spectra suggests little variation of the metallic fraction.

C. Optical-phonon modes

For a cubic perovskite, three F_{1u} phonon modes are infrared-active. They are called external, bending, and stretching modes, distinguished by the types of collective motions. The phonon peak at 0.073 eV (590 cm^{-1}) in Fig. 7 is the stretching mode. Since the stretching mode corresponds to the vibration of the atoms along the chemical bond connecting Mn and O ions, this mode is strongly affected by the change of Mn-O-Mn bond length.

The 0.088 eV (710 cm^{-1}) phonon mode observed around 130 K is known to appear in the charge-orbital order of manganites.[25,29] It is accounted for by the unit-cell doubling by superlattice forming in the ordered state, which makes new Γ-point modes by folding the phonon-dispersion branches. Thus, the shift of the stretching mode and the appearance of the mode at 0.088 eV strongly suggest that the charge-orbital order develops near 130 K. The disappearance of the peak at lower temperature, on the other hand, is possibly because the order becomes short-ranged and coexists with FM regions. This behavior is similar to the result of other phase-separated manganites $\mathrm{Bi}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ ($x>0.5$),[29] which show the shoulder at the higher-energy side of the peak in the two-phase coexistence of CO-OO and FM phases and the splitting of the stretching mode in the long-range CO-OO state. Thus, the observed phonon mode behavior is consistent with the view that the ferromagnetic clusters begin to appear near 130 K [Fig. 5(b), inset] due to the frustration of the charge-orbital order. In addition, the background screening of the phonons at 0.054 and 0.073 eV at lower temperature than 70 K [Figs. 7(b) and 7(c)] is probably due to the free carriers in the metallic phase.[30]

V. CONCLUSION

Photoexcitation effects in conductance, magnetization, and optical spectra have been investigated in the relaxor ferromagnet $\mathrm{Pr}_{0.5}\mathrm{Ca}_{0.5}\mathrm{Mn}_{0.96}\mathrm{Cr}_{0.04}\mathrm{O}_3$ thin film. The conductance increases gradually by the laser irradiation in the FM state, while little magnetization or metallic phase is produced. The photoinduced conductance is stable after the laser is turned off. A possible mechanism has been proposed that the FM clusters are connected by the photoinduced random change of the surrounding metastable insulator resulting in the increased percolative conduction. The calculated results of the Monte Carlo simulations[21,22] and the effective-medium theory support our explanation. The heating effect and deterioration of the sample were rejected as the cause experimentally. Investigations of the excitation-energy dependence and the dynamics of the effect, and the search for other materials that show similar effect, are future problems. We have also studied optical properties of the sample, and revealed that the behavior of the absorption spectra in the insulating and FM states of the sample is qualitatively similar to those of the other CO-OO and low-T_C manganites, respectively. From the optical-phonon spectra, the appearance of the long-range CO-OO phase is suggested just before the FM phase begins to grow. Synthesizing the results, this system can be regarded as an intrinsic random mixture in terms of the magnetic, dielectric, and transport properties; consequently, it shows intricate but intriguing responses. Also, subtlety of the phases provides us with opportunities for the studies of the inhomogeneity induced by the quenched random fields,[22] as well as the orbital physics,[31] in manganites.

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