Spectroscopic study of photoinduced charge-gap collapse in the correlated insulators Pr$_{1-x}$Ca$_x$MnO$_3$

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We observed an instantaneous reflectance change triggered by pulse laser irradiation. The laser heating cannot account for the action spectra, which are indicative of the charge-gap collapse. It is found in Pr$_{1-x}$Ca$_x$MnO$_3$ for a wide range of Ca doping, $x=0$, 0.1, 0.2, 0.31, 0.4, and 0.5, which suggests that the photoinduced charge gap collapse is not characteristic of charge-ordered insulators. We propose that the photoinduced charge gap collapse can be a general behavior in strongly correlated insulators.

The phase control in strongly correlated transition metal oxides has been an attractive subject for many years. The perovskite-type manganites $R_{1-x}A_x$MnO$_3$, where R is a trivalent rare-earth ion and A is a divalent alkaline-earth ion, have been extensively investigated since the rediscovery of colossal magnetoresistance (CMR).[1] The mother material, RMnO$_3$, is a typical Mott insulator, while the system tends to be metallic with hole doping as A^{2+} substitutes for R^{3+}. The metallic state is accompanied by ferromagnetic spin ordering through a double-exchange mechanism, which is a dominant driving force of CMR phenomena.[2,3] However, Pr$_{1-x}$Ca$_x$MnO$_3$, which has a smaller one-electron bandwidth W, shows no ferromagnetic metallic phase and undergoes a charge-ordering phase transition.[4,5] In the charge-ordered (CO) insulating state, Mn^{3+} and Mn^{4+} sites are alternately aligned accompanied by spin and orbital ordering because of strong intersite Coulomb interactions and cooperative Jahn-Teller lattice distortion. In previous works, a metallic state has been obtained by magnetic fields,[6] pressure,[7] electric fields,[8] x-ray irradiation,[9,10] and electron beam irradiation.[11] These external fields act on the charge, spin, and/or lattice which are strongly coupled. In a certain temperature region, the system is metastable between CO insulating and metallic phases, resulting in an irreversible field-induced insulator-metal transition.

We have recently reported that the visible-IR pulse laser irradiation also induces an insulator-conductor transition in the CO phase of Pr$_{1-x}$Ca$_x$MnO$_3$.[12,13] By illuminating the sample with a pulse laser in the presence of a static electric field, a stable current path is formed across electrodes, which can be clearly visualized through a change of reflectivity.[14] The current path formation is supposed to consist of two stages.[15] First, metallic clusters are induced by laser emission, which can be detected as instantaneous photocurrent and reflectance change. When the applied electric fields across the electrodes are small, the photocurrent and reflectance changes decay to zero in a few μs. In the second stage, when a large electric field is applied across the electrodes, the metallic clusters are stabilized by electron injection from the electrodes, to form a static current path. In contrast to the magnetic field and x-ray-induced cases, the photoinduced conducting state is unstable when the electric field is removed. This may signal a fundamentally different nature of the photoinduced phase change, which warrants further investigation.

In order to study the role of photoexcitation, we will concentrate on the first stage without electric field in this paper. We measured the action spectra of the reflectance change in Pr$_{1-x}$Ca$_x$MnO$_3$ for a wide range of Ca doping ($x=0$, 0.1, 0.2, 0.31, 0.4, and 0.5) by a pump and probe experiment. As shown in Fig. 1, this doping level covers entirely different phases: antiferromagnetic insulators for all temperature ranges ($x=0$ and 0.1), paramagnetic and ferromagnetic insulators ($x=0.2$), and paramagnetic and CO insulators ($x=0.31$, 0.4, and 0.5). Single-crystal samples of Pr$_{1-x}$Ca$_x$MnO$_3$ were synthesized by the floating-zone technique, which has been reported in detail elsewhere.[6] The polarization dependences are not discussed in this paper because all the samples are multidomain crystals. An optical parametric oscillator (OPO), pumped with a third-harmonic of a Nd:YAG laser with 7 ns light pulse, was used for the pumping laser pulse of a wide energy range (0.5–1.5 eV). The reflectance change of a cw Nd:YAG laser light ($\lambda = 1.06~\mu$m) was monitored with an electrically cooled In-GaAs photodiode. In order to avoid thermal heating, the probe laser beam was mechanically chopped to a width of 1.8 ms at a frequency of 10 Hz, synchronized with the pump-
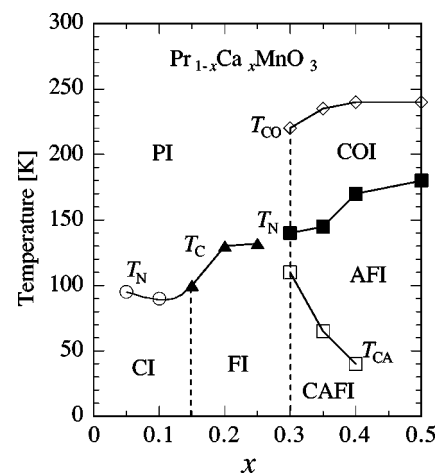

FIG. 1. The electronic phase diagram of Pr$_{1-x}$Ca$_x$MnO$_3$. Abbreviations represent paramagnetic insulating (PI), spin-canted insulating (CI), ferromagnetic insulating (FI), and charge-ordered insulating (COI) states, respectively. T_N, T_C, T_{CO}, and T_{CA} stand for antiferromagnetic, ferromagnetic, charge-ordering, and spin-canting transition temperatures, respectively.
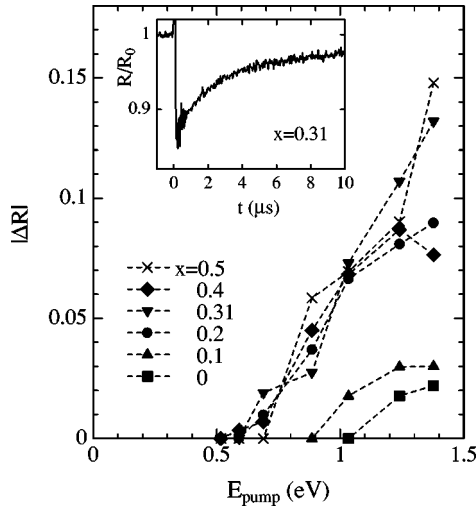
FIG. 2. Pumping energy dependencies of reflectance change, detected at $\hbar\omega = 1.16$ eV ($\lambda = 1.06$ μm). The irradiated photon number was kept constant to be 1.6×10^{17} photons per cm^2. The inset shows the time dependence of reflectance in $x = 0.31$ sample, pumped by a 1.4 eV laser pulse of 7 ns.

FIG. 3. Optical conductivity spectra of $Pr_{1-x}Ca_xMnO_3$ ($x = 0$, 0.1, 0.2, 0.31, 0.4, and 0.5) at 10 K. The peak structures at about 1 eV are assigned to the excitation energy of an electron from O^{2-} to Mn^{4+} as shown in the left inset, while the broad peaks above 2 eV are ascribed to the CT excitation, O^{2-} to Mn^{3+}, as shown in the right inset.

ing pulse laser. All the photoexcitation measurements were performed at 30 K in a He-flow-type cryostat. The optical conductivity spectrum of each sample was obtained via a Kramers-Kronig transform of respective reflectivity data, measured with a combination of a Fourier transform spectrometer and a grating monochromator from 0.05 eV to 6 eV at 10 K.

The growth of conducting clusters and the recovery to the insulating state are observed as a change of reflectance. The time dependences of the reflectance at 1.06 μm (1.16 eV) were measured in the range from -5 μs to $+40$ μs of laser pulse. As shown in the inset of Fig. 2, a sharp decrease of the reflectance and a gradual recovery, with a time of as long as about 10 μs, are observed in all compounds. In the following, we refer to the peak change ΔR, defined as ($R - R_0)/R_0$, where R_0 and R is the reflectance before and at the *instance of laser irradiation,* respectively. $|\Delta R|$ increases almost linearly to the pump laser intensity. In our present experiments, the incident photon number was kept constant at 1.6×10^{17} photons per cm^2 at each pulse with a spot size of about 500 μm. We plot $|\Delta R|$ in Fig. 2, detected at 1.06 μm, as a function of pumping photon energy E_{pump}. A monotonical decrease of $|\Delta R|$ toward low energy is observed in all samples. However, we can see a clear x dependence in the intensity. The spectra for $x = 0.2$, 0.31, 0.4, and 0.5 are almost identical. It is striking that the $x = 0.2$ sample (a ferromagnetic insulator) behaves similarly to the $x = 0.31$–0.5 compounds, because, in previous works, external field-induced insulator-metal transitions were considered to be characteristic phenomena of CO insulators. The value of $|\Delta R|$ is about 0.1 at 1.4 eV pumping and decreases to zero at about 0.5 eV, indicating an energy gap $\Delta_{ref} \approx 0.5$ eV. The lightly and undoped samples $x = 0$ and 0.1 show smaller $|\Delta R|$, about 1/3 in $x = 0.1$ and 1/5 in $x = 0$ at $E_{pump} = 1.4$ eV, compared to highly doped compounds. The reflectance change decreases toward the low-energy region, which disappears at 0.9 eV and 1.0 eV in $x = 0.1$ and $x = 0$, respectively.
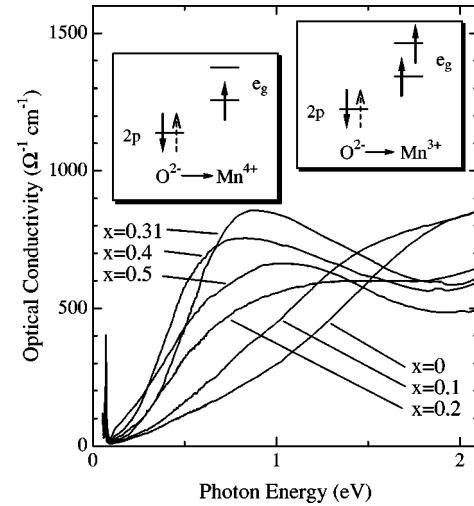
In order to investigate the origin of the x dependences of the reflectance change, the electronic structure of the compounds was studied by optical reflectivity measurements for a wide energy region in each sample. The obtained optical conductivity spectra at 10 K, $\sigma(\omega)$, are shown in Fig. 3. All spectra show insulating behaviors, growing up from $\sigma(\omega) = 0$ at $\hbar\omega = 0$. The spiky structures around 0.06 eV are due to optical phonon modes. One can see broad peaks at 1 eV in the $x = 0.31$, 0.4, and 0.5 samples. As reported previously in temperature- and magnetic-field-dependent optical spectroscopy measurements,[16] the broad peak structure at about 1 eV in the $x = 0.4$ system is assigned to the charge-ordering gap, corresponding to the excitation energy of an electron from the O^{2-} to Mn^{4+} site. It is natural that the observed peaks in the $x = 0.31$ and 0.5 spectra are also ascribed to the same origin. On the other hand, in the $x = 0$ spectrum, a monotonical increase of $\sigma(\omega)$ is observed up to 2 eV. Arima *et al.* have reported an optical spectrum of $LaMnO_3$,[17] in which a peak of $\sigma(\omega)$ is observed around 2 eV, which is assigned to a charge transfer (CT) gap. The $PrMnO_3$ spectrum in our experiments is similar to their results, indicating that the weak peak structure at about 2 eV can be assigned to the CT excitation gap, electron transfer from O^{2-} to Mn^{3+}. Therefore, a gradual spectral weight transfer from 2 eV to 1 eV while increasing x corresponds to an increase of the transfer probability of $O^{2-} \rightarrow Mn^{4+}$, because Ca doping on the Pr site introduces holes on the Mn sites.

The x dependence of the gap Δ_{ref} on the reflectance change measurements can be naturally understood in terms of the spectral weight shift in $\sigma(\omega)$: $\Delta_{ref} \approx 0.5$ eV for the $O^{2-} \rightarrow Mn^{4+}$ transfer for $x \geq 0.2$ and $\Delta_{ref} \approx 1$ eV for $O^{2-} \rightarrow Mn^{3+}$ transfer for $x \leq 0.1$. The x dependence of $|\Delta R|$ represents the stability of the insulating state. The $x = 0$ and 0.1 compounds show small $|\Delta R|$, while large reflectance changes are observed in $x \geq 0.2$. All experimental results indicate that the instability of the insulating phase increases with the hole doping, which saturates at $x = 0.2$.

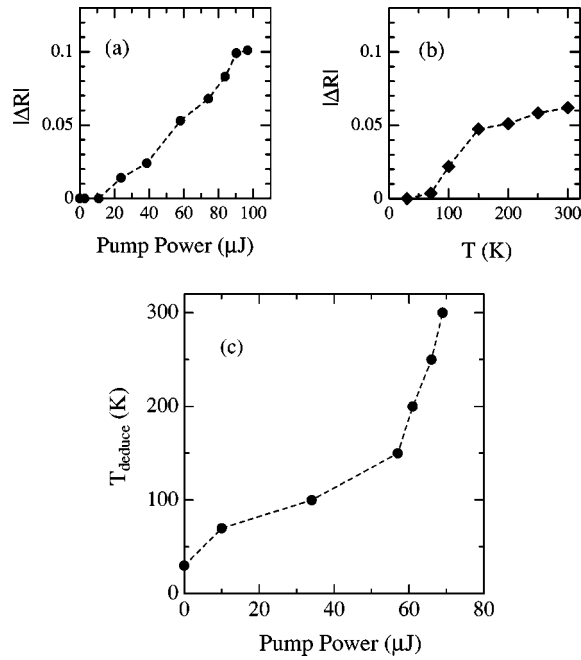In any photoexcitation experiment, one cannot avoid the

FIG. 4. Pumping power dependence of reflectance change $|\Delta R|$ at 1.16 eV in the $x=0.4$ sample at 30 K (a) and temperature dependence of reflectance (b), detected at $\hbar\omega=1.16$ eV ($\lambda=1.06$ μm). (c) represents pumping power dependence of the expected surface temperature T_{deduce} deduced from (a) and (b).
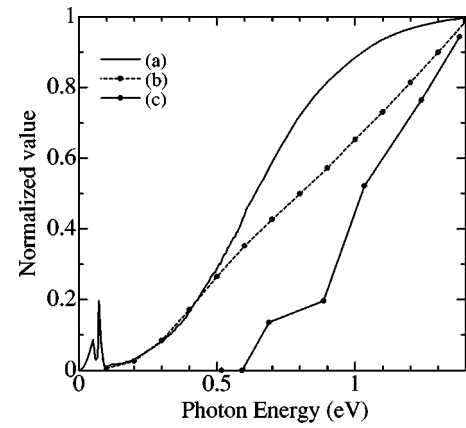

FIG. 5. Absorption coefficient (a), pumping energy dependence of the calculated surface temperature change (b), and action spectrum of the reflectance change detected at $\hbar\omega=1.16$ eV (c), all normalized at 1.4 eV.

bolometric effect completely. The ns pulses used here are more prone to the bolometric effect compared to sub-ps pulses. In order to estimate the temperature swing during the pulse irradiation, we show the reflectance change at 1.06 μm in the $x=0.4$ sample, $|\Delta R|$, as functions of the pumping laser power and temperature, in Figs. 4(a) and 4(b), respectively. $|\Delta R|$ grows up to 0.1 with increasing pumping power, while the temperature dependence of $|\Delta R|$ is dull and tends to saturate around room temperature. If we assume that the temperature increase by laser irradiation causes the reflectance change, the expected surface temperature vs the irradiated laser power would look like Fig. 4(c). The upward concave shape of the temperature T vs the laser power is inconsistent with a local heating picture. It is reported that the specific heat of manganites increases monotonically with temperature.[18] Therefore, the surface temperature T should be an upward convex function of the impute power.

Further evidence excluding the simple heating picture is the action spectra of the reflectivity change. We estimated the local temperature rise by laser irradiation assuming that the absorbed light energy is instantaneously distributed to all degrees of freedom within the absorbing volume. Using a set of measured parameters (heat capacity[18] and optical absorption coefficient), we calculated the surface temperature change, from which the expected reflectance change was

read off from Fig. 4(b). Figures 5(a), 5(b), and 5(c) show the absorption coefficient, pumping energy dependence of calculated surface temperature change, and action spectrum of reflectance change for the $x=0.31$ sample, respectively. All values are arbitrarily normalized at 1.4 eV. The overall trend in the calculated temperature change is not consistent with the experimentally observed action spectrum. In the low-energy region, absorbed photons which are supposed to cause local heating do not contribute to the reflectance change, which implies that action spectra of reflectance change cannot be explained by a simple heating picture. Just as in ordinary solids, we expect that the tail of the absorption gap consists of localized states below the ''band gap (CT excitation).'' As such, photoexcitation in this range of spectrum does not contribute to a drastic alteration of the electronic state. Figure 5 thus signifies that photoexcitation into the proper electronic states is essential for the reflectance change. The large change signals the collapse of the energy gap, be it the charge-ordered gap or the Mott gap. It is to be added, however, that a considerable surface temperature swing is possible as well. In order to obtain a better estimate of the bolometric effect, measurements employing thin films are under way.

In summary, we observed a sudden decrease of the reflectance at 1.16 eV synchronized with pulse laser irradiation in $Pr_{1-x}Ca_xMnO_3$ ($x=0$, 0.1, 0.2, 0.31, 0.4, and 0.5). The optical conductivity spectra show a gradual crossover of the spectral weight from 2 eV to 1 eV with hole doping, which is consistent with x dependences of the photoexcitation gap in reflectance change measurements. The action spectra in the reflectance change cannot be explained by a laser heating effect. We conclude that laser irradiation excites localized electrons to destroy the charge gap, which may be a general behavior not only of CO insulators but also of strongly correlated insulators in general.

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