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Ultrafast quasi-particle dynamics of charge/orbital ordered and ferromagnetic clusters in $La_{0.7}Ca_{0.3}MnO_3$

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Abstract. We report on the quasi-particle dynamics of the charge/orbital ordered (COO) and ferromagnetic clusters in the optimally doped manganite, $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) single crystal by time-resolved two-color pump–probe spectroscopy. Pump photons with energies of $\sim$1.55 and $\sim$0.21 eV were employed in our transient optical spectroscopy to investigate the percolative phase separation including the COO and ferromagnetic clusters from 4 to 480 K. At 1.55 eV, the transient reflectivity change, $\Delta R/R$, at $\Delta t = 0$ shows a similar temperature dependence as that in resistivity and in neutron scattering intensity. We attribute the reflectivity signal to the characteristic optical response of the COO domains. We identify a new temperature scale $T^* \sim 400$ K for the clean limit to the formation of COO clusters in LCMO. In contrast, the temperature-dependent amplitude of the transient reflectivity change in the mid-infrared(IR) absorption band ($\sim 5\ \mu$m) scales with the volume fraction of the ferromagnetic metallic (FM) phases. Our results suggest ultrafast optical spectroscopy to be a powerful probe to reveal the correlated polarons and charge disorders in phase-separated manganites.

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The 'colossal magnetoresistive' (CMR) manganites are highly correlated systems with strong coupling between spin, charge, orbital, and lattice degrees of freedom, which leads to complex phase diagrams [1]–[3]. As a result of the coexistence of a variety of electronic and lattice interactions that take place in overlapping temperature ranges, the materials tend to show inhomogeneous ground states, including ferromagnetic metallic (FM), paramagnetic insulating (PI), and antiferromagnetic charge/orbital ordered (COO) phases [4]–[6]. Phase transitions between different states can be easily introduced by external disturbances such as temperature and applied fields [5, 6]. The PI phase plays a distinct role in inducing the phase changes and the colossal responses of resistivity with magnetic field. The key feature of the state appears to be the COO clusters. At the optimally doped level of $La_{1-x}Ca_xMnO_3$ (LCMO) (i.e. $x \sim 0.3$), the so-called CE-type COO clusters have been identified by recent optical spectroscopy, x-ray diffraction, and neutron scattering experiments in a wide temperature range well above and below the Curie temperature, T_C [7]–[12]. The 'strength' of these clusters correlates with the resistivity, both as a function of temperature at zero magnetic field and as a function of magnetic field at constant temperature. The coupled dynamics of fluctuating COO phases and Jahn–Teller (JT) distortions of the MnO_6 octahedra are found to be crucial for the metal–insulator (MI) phase transition and the CMR effect. Therefore, it is fundamentally important to elucidate the COO correlation and the resulting polaron ordering and transition from polaronic transport to metallic transport.

Determining the complex interactions between COO phases and their dynamical processes in such a strongly correlated system from frequency-domain spectroscopy means extracting excitation information by deconvolution of all the different spectral components. This inevitably leads to ambiguity in the interpretation of the data, as highlighted by the numerous controversies regarding the interpretation of infrared (IR), Raman, and photoemission spectra among others [11]–[13]. As an experimental alternative, time-domain spectroscopy can distinguish between different excitations by their different relaxation dynamics, potentially giving new and complementary information on the underlaying mechanisms governing the colossal responses of the material.

Most recently, ultrafast optical/infrared spectroscopy has been used to unravel the excitation and relaxation dynamics of charge, spin, and lattice degrees of freedom in doped manganites [14]–[23]. We used two-color pump–probe spectroscopy in this work to investigate the quasi-particle dynamics of the COO and ferromagnetic clusters in the optimally doped manganite, LCMO single crystal. We employ pump pulses with photon energies of $\sim$1.55 and $\sim$0.21 eV to reveal the percolative nature of COO and FM clusters from 4 to 480 K. At 1.55 eV, we observe a similar behavior of temperature dependence in the transient reflectivity change, $\Delta R/R$, at $\Delta t = 0$ (at zero time delay between pump and probe pulses) as that in resistivity and in neutron scattering intensity. The transient reflectivity signal is attributed to the characteristic optical response of the COO domains. We identify a new temperature scale $T^* \sim 400$ K for the clean limit to the formation of COO clusters in LCMO. In contrast, the temperature-dependent amplitude of the transient reflectivity change in the mid-IR absorption band ($\sim 5\,\mu$m) scales with the volume fraction of the FM phases. Our results indicate that ultrafast spectroscopy provides a sensitive probe to study the correlated polarons and charge disorders in phase-separated manganites.

The LCMO single crystal was grown by the floating zone method. The sample was characterized by electrical resistivity and magnetization measurements and had a Curie temperature $T_C = 255$ K. For the transient reflectivity measurements, the sample was mounted in

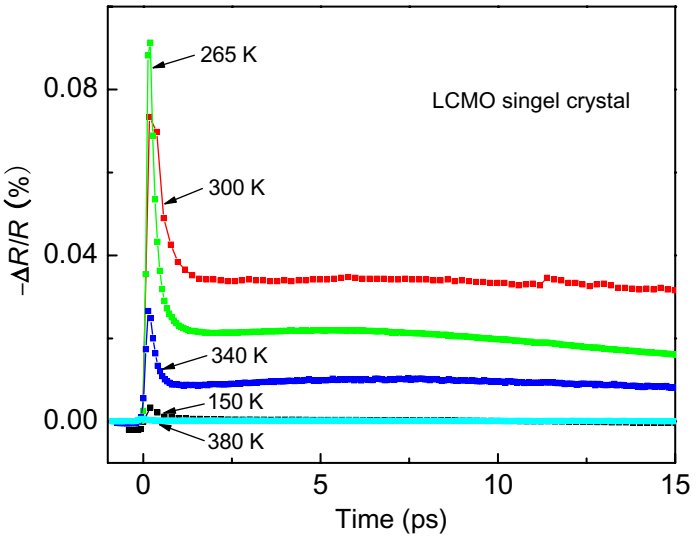

Figure 1. Time evolution of reflectivity change, $\Delta R/R$, for LCMO single crystal at different temperatures by using 1.55 eV pump pulses at short timescale.

an optical cryostat. The laser system consisted of a Ti:sapphire regenerative amplifier (Spitfire, Spectra-Physics) and an optical parametric amplifier (OPA-800C, Spectra-Physics) delivering 100 fs short pulses at a 1 kHz repetition rate tunable from 400 nm to 10 μm. A two-color pump–probe setup was employed with the pump beam power $\leqslant$6 mW and the probe beam power $\leqslant$ 1 mW. The unfocused pump beam, spot-diameter 2 mm, and the time-delayed probe beam were overlapped on the sample with their polarization perpendicular to each other[5]. The energy density of the pump beam was $\sim$0.1 mJ cm^{-2} and that of the probe beam was $\sim$0.02 mJ cm^{-2}. Considering the absorption coefficient of the LCMO of $\sim 9 \times 10^4$ cm^{-1}, we estimated an excited carrier density of $\sim 10^{17}$–10^{18} cm^{-3} according to the photon number that the pump beam applied per unit volume. The reflected probe beam was detected with a photodiode detector. A SR250 gated integrator and boxcar averager and a lock-in amplifier were used to measure the transient reflectivity change, $\Delta R/R$, of the probe beam. In our measurements, the $\Delta R/R$ induced by different wavelengths of the pump beam ($\sim$800 nm and $\sim$5.1 μm) was measured as a function of time delay for the probe beam ($\sim$800 nm).

Figure 1 shows the photoinduced change in reflectivity, $\Delta R/R$ (normalized), as a function of temperature at 800 nm ($\sim$1.55 eV). $\Delta R/R$ initially shows a fast biexponential decay with relaxation times $\tau_A \sim 1$ ps and $\tau_B \sim 100$ ps along with weak acoustic phonon oscillations [16]. Also, for temperatures below T_C, a very long-lived negative $\Delta R/R$ signal remains for a sufficiently long decay time that the negative signal is clearly observable even after 1 ms (negative time-delay between pump and probe pulses). These relaxation processes have been previously investigated in detail by time-resolved optical measurements and therefore we will only briefly discuss them here. In the FM state, the 1 ps component of the photoinduced absorption in LCMO was attributed to electron–lattice thermalization and a slower change in absorption 20–200 ps was attributed to the photoinduced demagnetization driven by the spin–lattice thermalization [18]. The long-lived negative signal was assigned to

[5] We measured the power dependence of the reflectivity change, which shows linear dependence on the pump intensity. The pump intensity only weakly perturbs the material.

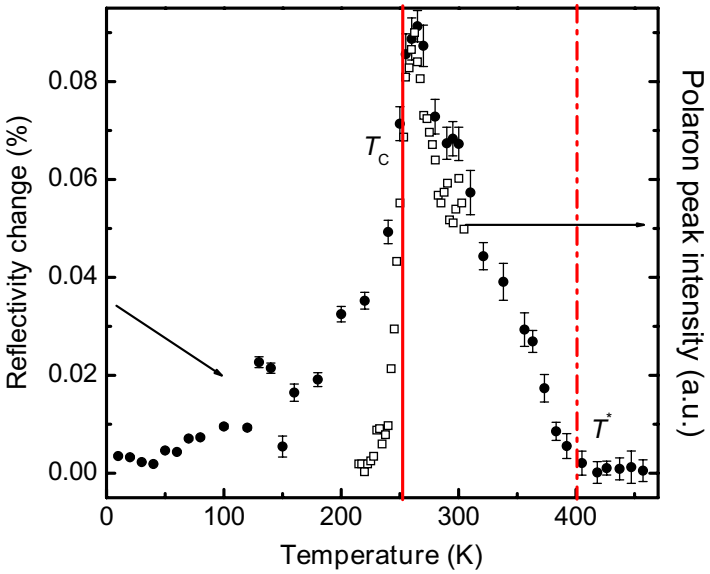

Figure 2. Temperature dependence of the photoinduced change in reflectivity, ΔR_0, at 1.55 eV (circles) compared to the temperature dependence of the intensity of the polaron peak (squares, reprinted from [8] and scaled for comparison) in LCMO. The solid and dashed lines represent the Curie temperature, T_C, and the clean limit temperature to the formation of COO clusters, T^*, respectively.

the photoinduced spin ordering and the anomalously small heat exchange between electrons and spins [21, 22]. Upon increasing the temperature up to the PI phase, the measured dynamics on long timescales were explained by the localized JT polarons.

The 1.55 eV photon energy lies in a broad absorption band in LCMO centered at 1.4 eV [11, 12]. The absorption band is identified with the intersite transition of an electron from the lower JT split e_g level of a Mn^{3+} ion to the e_g level of an adjacent Mn^{4+} ion. After the pump photons bring electrons from the lower JT state to the upper level, the hot electrons will very rapidly release their energy via electron–electron and electron–phonon collisions. Since the nanoscale COO clusters result from the correlation between JT polarons, the broadband around 1.4 eV is attributed to the characteristic optical response of the COO domains.

Figure 2 depicts the temperature dependence of the photoinduced change in reflectivity, $\Delta R/R$, at $\Delta t = 0$ (defined as ΔR_0) at 1.55 eV and the temperature dependence of the intensity of polaron scattering peaks in the PI and FM phases as measured by neutron scattering in LCMO. We see that the $\Delta R/R$ begins to develop well below T_C, rapidly increases its amplitude as $T \to T_C$, and peaks just above the transition temperature from FM to PI. For $T > T_C$, ΔR_0 shows a very similar behavior for the temperature dependence of the resistivity and the neutron scattering intensity, shown as the polaron scattering intensity (proportional to the COO phase fraction) in figure 2 [8]. The agreement between ΔR_0 and the previously reported scattering intensity of COO clusters shows that the transient reflectivity signal at $\Delta t = 0$ reflects the quasi-particle excitations in the correlated COO domains. With further increases in temperature, $\Delta R/R$ gradually loses its intensity, down to almost zero at a new scale of temperature, T^* of $\sim$400 K. We attribute the temperature to the clean limit of the formation

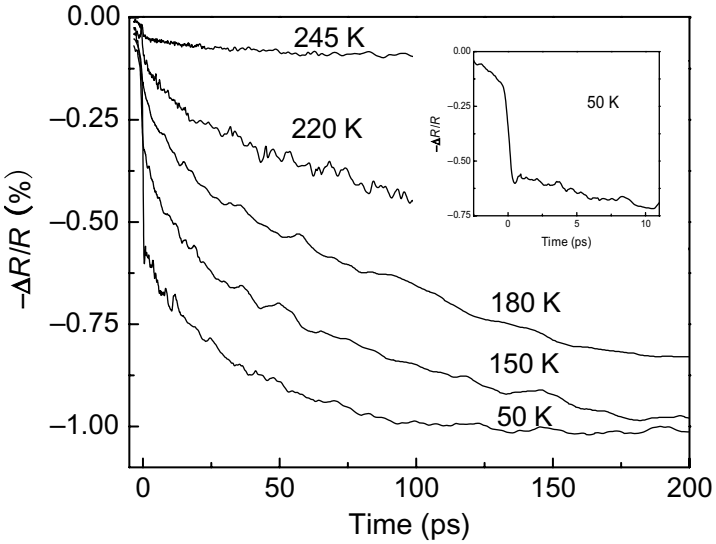

Figure 3. Time evolution of reflectivity change, $\Delta R/R$, for LCMO single crystal at various temperatures below and near T_C by using the 0.21 eV pump photons. The inset shows the 15 K spectrum at the short timescale.

of COO clusters in LCMO. The change of ΔR_0 with temperature could be therefore associated with the percolative nature of the COO clusters in LCMO. Recent theory predicted that the coexisting metallic and insulating clusters appear above the Curie temperature, T_C, resulting from a first-order phase transition and a source of disorder [24, 25]. This temperature window could extend up to T^*, where these clusters dissociate to form uncorrelated JT polarons. So far, tremendous efforts have been devoted to find experimental evidence of such a temperature, T^*. The clear observation of phase transition at the new temperature scale of T^* indicates that the photoinduced change in reflectivity, ΔR_0, at 1.55 eV can be used as a sensitive probe to monitor the formation and percolative behaviors of COO clusters in LCMO. Moreover, we refer the subnanosecond component to the recovery of the COO states. Indeed, these attributions have been discussed thoroughly by Prasankumar *et al* [23] in their pump–probe measurements of the COO manganite: $Nd_{0.5}Sr_{0.5}MnO_3$. We also note a discrepancy between the optical data and the neutron data below T_C. The discrepancy can be attributed to the spectral weight transfer from the JT polaron state (1.55 eV) to an incoherent absorption of a large polaron state (mid-IR absorption peak below 0.5 eV) [11].

For comparison, we also took temperature-dependent measurements of the transient reflectivity change, $\Delta R/R$, by using 0.21 eV pump photons in LCMO. The results are shown in figure 3 and its inset. After a sharp decrease, $\Delta R/R$ is followed by a slow delay relaxation in a timescale of 10–200 ps from 10 to 265 K and that is closely related to heat diffusion from the pump volume into a larger probe volume in the FM states. Similarly, we observe a long-lived negative reflectivity signal for the temperature range of $T < T_C$ in our transient spectra. The extremely slow relaxation shows no dependence of the excitation and detection photon energies and points to a clearly spin-related origin as we discussed in our previous work [21].

Figure 4 shows the temperature dependence of the photoinduced change in reflectivity, ΔR_0, at the probe energy of 1.55 eV, which is induced by the pump energy of 0.21 eV. In contrast

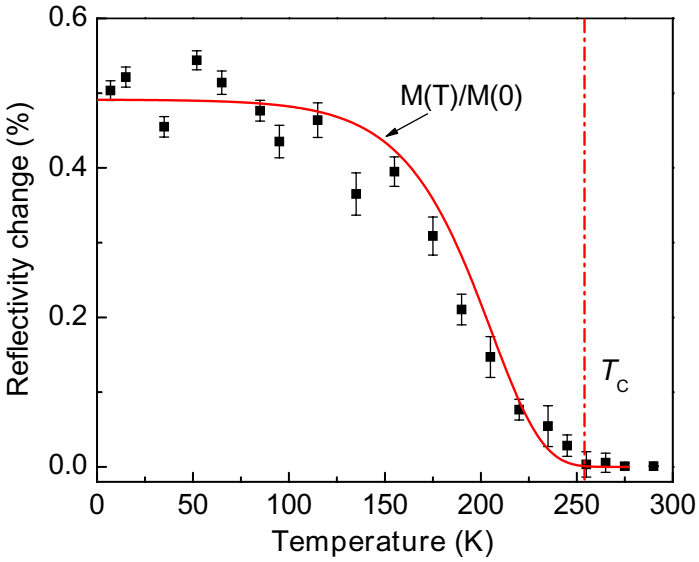

Figure 4. Temperature dependence of the photoinduced change in reflectivity, ΔR_0, at the probe energy of 1.55 eV induced by the pump energy of 0.21 eV. The temperature dependence of magnetization, $M(T)/M(0)$ is scaled for comparison. The dashed line indicates the Curie temperature, T_C.

to the 1.55 eV data, first ΔR_0 slowly decreases its amplitude as we increase the temperature from 10 to 120 K. Then a significant drop in ΔR_0 can be observed as the temperature approaches 120 K up until it reaches T_C (∼255 K). Finally, ΔR_0 loses its intensity near the phase transition temperature as $T > T_C$. Regarding the optical absorption at low energies between 0.2 and 0.5 eV, progress was recently made through the optical conductivity spectra of $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ ($y = 0.35$) [12], a material that clearly presents mixed-phase tendencies. According to their temperature and magnetic field dependent studies, Lee *et al* [12] assigned the absorption band peak at around 0.2 eV at low temperature to the FM phases. Our results are consistent with this attribution. In particular, the change of transient reflectivity, ΔR_0 in temperature at 0.21 eV photon pumping, can be related to percolations of the FM clusters: the total volume of the FM clusters decreases with increasing temperature from 10 K in LCMO. The decrease of ΔR_0 with increasing temperature from 10 K to 300 K is thereby a strong indication of the development of the region associated with delocalized carriers (FM clusters). In this context, the spontaneous MI transition is associated with a high-to-low volume transition of the FM clusters. Also it is important to mention that the smooth change of ΔR_0 across T_C is consistent with the FM transition in an inhomogeneous system. Moreover, as shown in figure 4, the temperature dependence of ΔR_0 below T_C shows great consistency with that of the magnetization and this implies the first-order character of the FM-to-PI phase transition. This is in good agreement with results obtained using other techniques [26, 27].

In summary, we used time-resolved two-color pump–probe spectroscopy to investigate the quasi-particle dynamics of the ferromagnetic and charge/orbital ordering clusters in the optimally doped manganite, LCMO single crystal. The pump pulses with different photon energies of ∼1.55 eV (∼800 nm) and ∼0.21 eV (∼5 μm) were employed in our transient optical spectroscopy to reveal the percolative nature of the COO and the ferromagnetic clusters from 4

to 480 K. At 1.55 eV, the transient reflectivity change, ΔR_0, was attributed to the characteristic optical response of the COO domains. From its temperature dependence, we identified a new temperature scale $T^* \sim 400$ K for the clean limit to the formation of COO clusters in LCMO. In contrast, the temperature dependence of ΔR_0 at the probe energy of 1.55 eV induced by the pump energy of 0.21 eV could be directly related to the volume fraction of the FM clusters. Our result indicates that transient optical spectroscopy can provide a sensitive probe to study the correlated polarons and charge disorders in phase separated manganites.

Acknowledgments

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