Quasiparticle Relaxation Dynamics in Two Distinct Gap Structures: La$_{0.67}$Ca$_{0.33}$MnO$_3$ and LaMnO$_3$

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Abstract

The spin and quasiparticle relaxation dynamics in La$_{0.67}$Ca$_{0.33}$MnO$_3$ and LaMnO$_3$ single crystals and thin films is investigated as a function of temperature and magnetic field by pump-probe spectroscopy. The unusually slow spin-lattice relaxation dynamics is governed by the temperature- and magnetic field-dependent pseudogap in La$_{0.67}$Ca$_{0.33}$MnO$_3$, and by the temperature-independent Jahn-Teller gap in LaMnO$_3$. Our results show that the coupled dynamics of charge, spin and lattice is strongly correlated with the distinct gap structures in these manganites.
Perovskite manganites, $R_{1-x}A_x\text{MnO}_3$ (R and A are rare- and alkaline-earth ions, respectively) have attracted much attention because of the large negative magnetoresistance and the magnetic-field-induced phenomena. The strong correlation between spin, charge, orbital, and lattice degrees of freedom leads to complex phase diagrams and to the coexistence of various forms of ordering. Of particular interest in this context has been the observation of a temperature-dependent pseudogap in a variety of colossal magnetoresistance (CMR) oxides and its relationship to the ferromagnetic (FM) metal-to-insulator (MI) transition [1–4]. Key to the pseudogap and many other properties of the manganites appear to be the existence of nanoscale charge/orbital fluctuations, which cooperate with Jahn-Teller distortions and compete with the electron itineracy favored by double exchange [1]. A profound knowledge of these ordering processes and their mutual interactions is essential for a better understanding of CMR. Dynamical information on the electronic states of the pseudogap can be obtained, if charge or spin excitations are introduced via pulsed photoexcitation, and the relaxation dynamics of the quasiparticles (QP’s) is studied on a picosecond time scale. Ultrafast optical pump-probe spectroscopy has provided significant insight in the dynamics of spin, electron and lattice in metals [5,6], and recently in transition metal oxides [7–12].

Here, we report the time-resolved pump-probe reflectivity measurements of photoexcited spin and QP relaxation dynamics in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) and $\text{LaMnO}_3$ (LMO) single crystals and thin films as a function of temperature and magnetic field. Our results are fourfold: First, both manganites reveal an unusually slow ($\sim 10 \mu\text{s}$) carrier relaxation process which disappears as the transition temperature is approached from below. This slow decay process is attributed to spin-lattice relaxation of carriers in localized (intraga) states. Second, the quasiparticle relaxation rate is governed by the temperature-dependent pseudogap in LCMO and by the temperature-independent Jahn-Teller distortion gap in LMO. Third, the magnetic-field-induced increase of spectral weight in the pseudogap is evident in both the quasiparticle and spin relaxation dynamics in LCMO. Fourth, the polaron relaxation time, $\tau_B$, is temperature-independent in LMO, whereas $\tau_B$ follows a $(T_C - T)^{-\beta}$ dependence in LCMO, indicating that the quasiparticle relaxation dynamics involves fully spin-aligned
pseudogap states near the Fermi energy $E_F$. Our results show for the first time that the coupled dynamics of charge, spin and lattice is strongly correlated with the distinct gap structures in these manganites.

LCMO and LMO single crystals and thin films were grown by the floating zone method and pulsed laser deposition, the details of which are reported elsewhere [11,13,14]. The samples were characterized by electrical resistivity and magnetization measurements. The LCMO single crystal and 400-nm thin film have a Curie temperature $T_C = 225$ K and 260 K, respectively. The LMO single crystal shows a Neel temperature $T_N = 145$ K. For the transient reflectivity measurements the samples were mounted in an optical cryostat. The laser system consists 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 600 nm to 10 µm. A two-color pump-probe setup is employed with the pump beam power $< 6$ mW and the probe beam power $< 1$ mW. The unfocused pump beam, spot-diameter $\sim 3$ mm$^2$, and the time-delayed probe beam are overlapped on the sample with their polarization perpendicular to each other. The reflected probe beam is detected with a photodiode detector. A SR250 gated integrator & boxcar averager, and a lock-in amplifier are used to measure the transient reflectivity change $\Delta R$ of the probe beam. For the magnetic-field dependent measurement we used a 9-Tesla superconducting magnetic cryostat from Oxford Instruments, Inc.

Figures 1 (a) and 1 (b) show the time evolution of $\Delta R$ from LCMO and LMO single crystals at different temperatures. The pump and probe wavelength is 800 nm. At low temperature ($T << T_C, T_N$), $\Delta R$ shows initially a fast biexponential decay with relaxation times $\tau_A = 0.5 \sim 4$ ps and $\tau_B = 50 \sim 100$ ps. The fast process reveals the thermalization of photoexcited quasiparticles which occurs on a time scale $\tau_{QP} = 0.3 \sim 3$ ps [15]. The second process is characteristic for polaron relaxation [11,16].

In addition to the initial fast relaxation processes, a very long-lived negative $\Delta R$ signal remains sufficiently long, decay time $\tau_{SL} \sim 10$ µs, that a negative $\Delta R$ is clearly observable even after 1 ms (Figs. 1(a) and 1(b)). This component is present in both the metallic
and insulating phase as observed in the transient optical reflectivity and transmission measurements from charge-ordered Pr$_{0.67}$Ca$_{0.33}$MnO$_3$ (PCMO), La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO), and Nd$_{0.67}$Sr$_{0.33}$MnO$_3$ (NSMO). However, there is no evidence of this component in the transient reflectivity change of the paramagnetic phase of LSMO, which shows a phase transition from ferromagnetic metal to paramagnetic metal at 325 K. Therefore, the long-lived negative component of $\Delta R$ is ascribed to a slow spin relaxation process of the magnetically ordered phase.

Figure 2 illustrates the temperature dependence of $\Delta R$ measured at a time-delay $\Delta t = 500$ ps, referred to as $\Delta R'$ in LCMO and LMO. The temperature dependence of $\Delta R'$, for LCMO single crystal ($\lambda_{\text{pump}} = 800 \text{ nm} / \lambda_{\text{probe}} = 800 \text{ nm}$) and thin film ($\lambda_{\text{pump}} = 800 \text{ nm} / \lambda_{\text{probe}} = 5.2 \mu\text{m}$) are qualitatively the same and independent of wavelength (Fig. 2a). $\Delta R'$ increases with increasing temperature followed by an abrupt drop to zero around $T_C$. In contrast, for LMO ($\lambda_{\text{pump}} = 800 \text{ nm} / \lambda_{\text{probe}} = 800 \text{ nm}$) $\Delta R'$ decreases slowly at low temperature and drops toward zero abruptly around $T_N$ (Fig. 2(b)).

The fact, that in both manganites $\Delta R'$ vanishes above the transition temperature, is a strong indication that $\Delta R'$ arises: a) from quasiparticle excitation involving localized (intragap) states, and b) that the decay of these metastable states involves a spin-flip process. The lifetime $\tau_{SL} \sim 10 \mu\text{s}$ of these metastable states is comparable with the spin-lattice relaxation time measured by the $\mu$SR technique [17].

The solid line in Fig. 2(b) shows that $\Delta R'$ in LMO follows approximately a $(T_N - T)^\alpha$ dependence ($\alpha \approx 0.5$), which is similar to the temperature dependence of the magnetization [17]. As the temperature approaches $T_N$ and the magnetic order decreases in LMO the lifetime of the metastable state decreases due to enhanced spin scattering and $\Delta R'$ starts to decrease. The non-zero $\Delta R'$ above $T_N$ indicates that a residual anti-ferromagnetic (AFM) order exists in LMO above the Neel temperature [17]. In contrast to LMO, the $T$-dependence of $\Delta R'$ is more complex in LCMO. The transient reflectivity first increases with increasing temperature and then for $T > 0.9T_C$ follows a $(T_C - T)^\beta$ dependence with $\beta \approx 0.7 - 0.9$ (solid line in Fig. 2(a)). A similar power-law dependence of $\Delta R'$ has been observed in other
A simple physical model accounts qualitatively for these observations. The various processes giving rise to the photoinduced reflectivity change in LCMO are depicted in Fig. 3 (inset). An ultrashort laser pulse first excites electrons via interband transitions. In our experiments, the films absorbed $10^{18} - 10^{20}$ photons/cm$^3$ per pulse; comparable to the charge-carrier density ($\sim 10^{20}$-10$^{21}$ holes/cm$^3$) in LCMO; hence, one expects significant electron excitation during ultrashort pump pulse illumination. These hot electrons very rapidly release their energy via electron-electron and electron-phonon collisions reaching QP states near the Fermi energy (step 1). This generates spin waves (magnons) [7,12]. Spin waves lead to the excitation of metastable states with $\mu$s time scale [7,12]. The QPs can recombine by interaction with states in the pseudogap (step 2) or relax to metastable states via spin-flip processes (magnons are released) caused by strong electron-lattice coupling (step 3). The carriers in the metastable states will relax with a recombination rate $\gamma = 1/\tau_{SL}$, while magnons are absorbed (step 4). As the pseudogap opens up with increasing temperature and the spectral weight of states at the Fermi level decreases the decay rate of excited QPs decreases (step 2) and more quasiparticles will be scattered into metastable states (step 3). This effect leads to the initial rise of $\Delta R'$ which is inverse proportional to the density of states in the pseudogap, i.e., for $T \leq 0.9T_C$, $\Delta R' \propto (T_C - T)^{-b}$ with $b \approx 0.3 - 0.5$ (solid line in Fig. 2(a)). With further increasing temperature ($T > 0.9T_C$), $\Delta R'$ drops significantly toward zero due to the increase of the density of states and occupation of the down-spin conduction electrons, which introduces magnetic disorder.

Figure 4 shows magnetic-field dependent measurements of $\Delta R$ at 305 K (well above $T_C$) as a function of time for LCMO thin film grown on NdGaO$_3$ (110) substrate. Magnetic fields are applied in the Faraday geometry, generating an isothermal magnetic entropy change. The results of Fig. 4 are consistent with our model. The quasiparticle relaxation dynamics shows strong magnetic field dependence for $B$ ranging from 0.5 to 3 T. The magnetic-field dependence of $\Delta R$ for LCMO is very similar to the temperature dependence of the zero-field $\Delta R$ shown in Fig. 1(a). The increase in the amplitude of $\Delta R'$ is due to the increase of $T_C$. 

CMR manganites, e.g. Nd$_{0.67}$Sr$_{0.33}$MnO$_3$ [10].
with applied magnetic field; this results in an increase of magnetic correlations (spatially and temporally) with enhanced spin alignments. The magnetic correlations are strong enough to overcome thermal fluctuations at the new transition temperature.

The model also correctly explains the temperature dependence of the polaron relaxation time $\tau_B$ for LMO and LCMO single crystals (Fig. 3). In LMO single crystal, $\tau_B$ is found to be completely temperature independent below $T_N$ consistent with a static Jahn-Teller gap. For LCMO single crystal, $\tau_B$ remains nearly constant below 0.45 $T_C$ and starts to increase above 0.7 $T_C$. A similar $T$-dependence has been reported in LCMO thin films [11]. The polaron relaxation time $\tau_B$ follows a $(T_C - T)^{-\beta}$ dependence, i.e., $\tau_B \propto 1/\Delta R'$, shown as a solid line in Fig. 3. This result strongly supports our model that the quasiparticle relaxation dynamics involves fully spin-aligned pseudogap states near $E_F$.

In summary, we investigated the spin and quasiparticle relaxation dynamics in LCMO and LMO single crystals and thin films as a function of temperature and magnetic field by time-resolved pump-probe spectroscopy. The quasiparticle relaxation rate is governed by the temperature- and magnetic field- dependent pseudogap in LCMO and by the temperature-independent Jahn-Teller distortion gap in LMO. Both manganites exhibit metastable (localized) states with lifetime $\tau_{SL} \sim 10 \mu s$, which decay via spin-lattice coupling. Our results show that the coupled dynamics of charge, spin and lattice is strongly correlated with the distinct gap structures in these manganites.

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Figure Captions:

Fig. 1. Transient reflectivity $\Delta R$ of: a). LCMO and b). LMO single crystals around $T_C$ (or $T_N$) at 800 nm. The dotted lines indicate the zero line.

Fig. 2. Temperature dependence of $\Delta R$ (normalized) at $\Delta t = 500$ ps: a) LCMO single crystal ($\lambda_{\text{pump}} = 800$ nm/$\lambda_{\text{probe}} = 800$ nm) and 400-nm thin film ($\lambda_{\text{pump}} = 800$ nm/$\lambda_{\text{probe}} = 5.2$ $\mu$m), and b) LMO single crystal ($\lambda_{\text{pump}} = 800$ nm/$\lambda_{\text{probe}} = 800$ nm). The solid lines indicate the power-law dependence.

Fig. 3. The relaxation time $\tau_B$ as a function of temperature $T$ for LCMO and LMO single crystals. The solid line indicates the power-law dependence. The inset depicts a schematic diagram of carrier excitation/relaxation processes in LCMO. For details see text.
Fig. 4. Transient reflectivity $\Delta R$ from LCMO as a function of time for applied fields ranging from 0.5 to 3 T at 305 K ($\lambda_{\text{pump}}, \lambda_{\text{probe}} = 800 \text{ nm}$). The dotted lines indicate the zero line.
a) LCMO

single crystal

\( T_C = 225 \text{ K} \)

b) LMO

single crystal

\( T_N = 145 \text{ K} \)
Reflectivity Change ($\Delta R'$) vs Temperature ($T/T_C$)

- **LCMO**
  - Single crystal: ▲
  - Thin film: ■

Reflectivity Change ($\Delta R'$) vs Temperature ($T/T_N$)

- **LMO**
  - Single crystal: ●
Reflectivity Change ($\Delta R$) vs. Time (ps) for LCMO/NGO 305K.

Plot shows the reflectivity change at different magnetic fields (0.5 T, 1 T, 1.5 T, 2 T, 3 T) over time. The reflectivity decreases with time at each field level.