Ultrafast Laser Induced Conductive and Resistive Transients in $La_{0.7}Ca_{0.3}MnO_3$: Charge Transfer and Relaxation Dynamics

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Pulsed laser excitation induced conductance changes in colossal magnetoresistance material $La_{0.7}Ca_{0.3}MnO_3$ were studied on the picosecond time scale. A two-component signal was seen consisting of a fast positive transient associated with the paramagnetic insulating state and a slower negative signal associated with the ferromagnetic metallic state. The fast component corresponds to the photoionization of the Jahn-Teller small polaron. The slow component is explained in terms of the reduced carrier mobility due to photogenerated magnetic excitations. [S0031-9007(98)06798-2]

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The observation of colossal magnetoresistance (CMR) in the doped rare earth manganites has stimulated research on these strongly coupled metallic oxide materials [1–3]. It is now accepted that both double exchange [5] and Jahn-Teller lattice distortions [6] play an important role in the magnetic and transport properties of the manganites. However, the phase diagram of the manganites has a number of intriguing features [4]. The ferromagnetic order in the manganites does not have a simple dependence on the Mn^{3+}/Mn^{4+} ratio. The ferromagnetic Curie temperature (T_C) in $La_{1-x}Ca_xMnO_3$, for example, peaks close to 30% Ca^{2+} (corresponding to 30% Mn^{4+}) concentration rather than 50% Ca^{2+} concentration. Further, as one enhances the Ca^{2+} concentration in the system, disruption of the ferromagnetic order is observed. In fact, for $>50\%$ of the Ca^{2+} concentration no ferromagnetic phase is seen. Also the propensity of the system to form charge ordered insulator also increases with x. These features show that spin, charge, and lattice are strongly coupled in the CMR materials [5–8].

In this paper, we describe the transient transport response of $La_{0.7}Ca_{0.3}MnO_3$ upon excitation with a 100 fs laser pulse. If charge or spin excitations are introduced via pulsed photoexcitation, and the change in conductance of the material is monitored, important information about the interactions among spin, charge, and lattice, and also the relaxation processes of the nonequilibrium state may be obtained on these CMR materials. There have been some studies in the past on the picosecond spin dynamics in magnetic systems [9–12]. For example, the study by Awschalom and Halbout [9] on magnetic polaron dynamics in a dilute magnetic semiconductor $Cd_{1-x}Mn_xTe$ showed that the spin organization and relaxation times are hundreds of picoseconds. To our knowledge, no picosecond dynamical study on CMR materials has yet been reported in the literature.

The epitaxial $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) films used in the study were prepared by the pulsed laser deposition process on $LaAlO_3$ substrates. The details of the deposition and annealing process are described elsewhere [13] and the temperature dependence of the electrical resistance of the films shows a peak at 263 K. The fast optical response experimental system is described in detail elsewhere [14]. Briefly, the film (100 nm thick) to be examined was patterned into a transmission line of minimum width of 30 μm and a length of 5 mm and is biased with a dc current source. 1.5 eV pulses of 100 fs duration with repetition frequency of 9 kHz are obtained from Ti-sapphire laser system. The conductance change (ΔG) of LCMO under the femtosecond laser pulse irradiation was measured in real time by a fast oscilloscope with 20 ps time resolution. Before the laser pulse arrives, a flat dc base line appears which serves as a reference. The laser induced signal, whose amplitude is proportional to the conductance change (ΔG) of LCMO [15] superimposed on this reference base line. If the conductance of LCMO increases due to the laser pulse, a positive signal (conductive transient) will be obtained; i.e., the value of the signal is larger than that of the base line. Conversely, a negative signal (resistive transient) will be obtained if the conductance of LCMO decreases due to the laser pulse.

The pulsed optical response (OR) of the LCMO transmission line is shown in Fig. 1. Figure 1(a) shows the data taken at 280 K where only a positive photoconductance signal is seen (i.e., increasing conductance due to laser pulse, referred to from now on as the conductive transient); Fig. 1(b) shows the response at 7.76 K where only a negative photoconductance signal (referred to as the resistance transient) is seen; and Fig. 1(c) gives the data taken at an intermediate temperature of 158 K, where both the conductive and resistive transients are seen. The conductive transient precedes the resistive transient and has a rise

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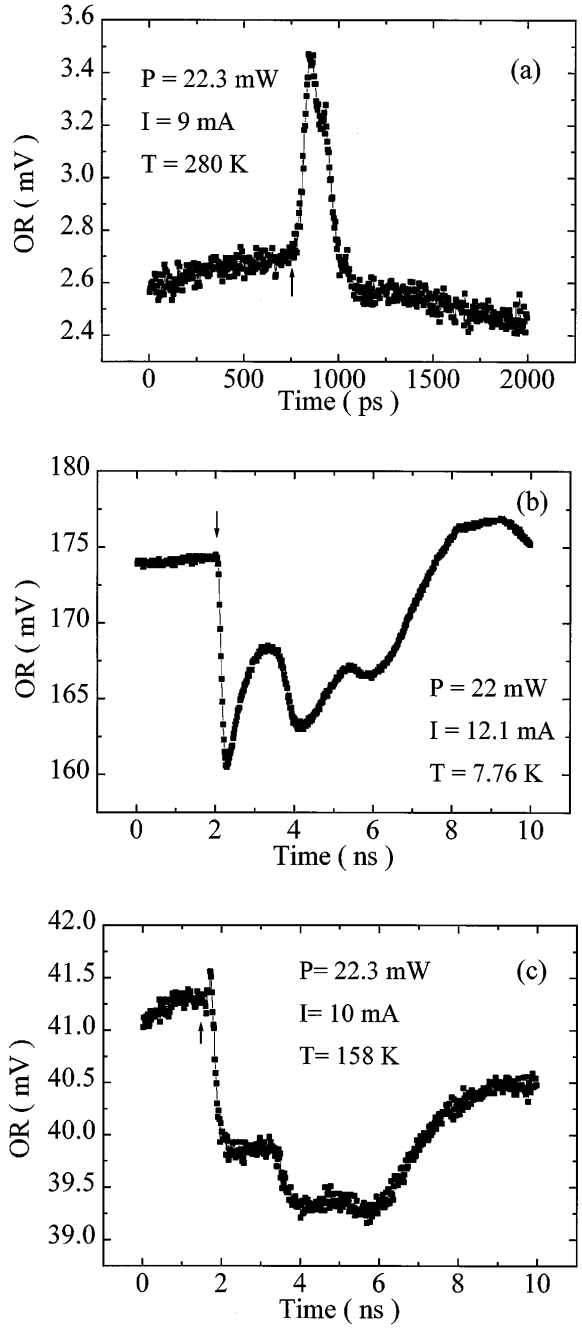

FIG. 1. The OR of the LCMO thin film. An upward signal represents conductance increase while a downward signal indicates conductance decrease. The laser power, bias current, and the temperature are shown in the figures. The arrow indicates the arrival of the laser pulse.

and fall time an order of magnitude faster than the latter. (It must be noted that the resistive transient shows some periodic oscillations which are due to reflections of the signal arising from impedance mismatch in the circuit and this corresponds to the connection between the sample and the terminal leading to the outside of the cryostat.) Figure 2 shows the temperature dependence of the conductance change deduced from the conductive and resistive transients [15]. The temperature dependence of the resistance of the thin film is also shown. The temperature dependence of the resistive transient is opposite to the conductive transient behavior and rises as the temperature is lowered. We first note that these signals cannot be explained by a simple bolometric effect, i.e., resistance change by heating. The sign of the conductive transient is in contradiction with our expectation for the bolometric effect below T_C. For the resistive transient, the temperature dependence of the resistance change due to the laser illumination is just the reverse of that expected for the bolometric effect; i.e., it should increase with increasing temperature if it is bolometric in origin.

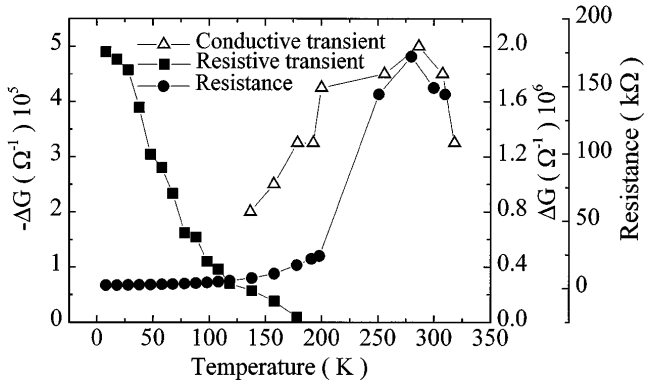

FIG. 2. The temperature dependence of the conductance change deduced from the conductive and resistive transients. Laser power $P = 22.3$ mW and the bias current $I = 10$ mA. The temperature dependence of the electrical resistance is also shown.

In the optical spectra of $La_{0.7}Ca_{0.3}MnO_3$, there is a broad peak in the conductivity function centered around 1.2 eV at room temperature which shifts to lower energies with decreasing temperature [16]. This peak is identified with the charge transfer excitation of an electron from the lower Jahn-Teller (J-T) split e_g level of a Mn^{3+} ion to the e_g level of an adjacent Mn^{4+} ion. Because of the significant widths of these energy levels, at the 1.5 eV photon energy the excitation lies on the high energy tail of this absorption band. Because this absorption band shifts to lower energies with decreasing temperature, its overlap with the photon energy will decrease. Figure 3 shows schematically the electronic structure of the Mn^{3+} and Mn^{4+} ions and the possible optical transitions. The upper panel shows the energy of Mn e_g and t_{2g} levels around the paramagnetic-ferromagnetic transition region for adjacent Mn^{3+} and Mn^{4+} ions. The spin up e_g levels in the Mn^{3+} ions are split by E_{JT} due to the Jahn-Teller effect. In the Mn^{4+} the spin up e_g states are shifted upwards (relative to the unsplit Mn^{3+} ion spin up e_g levels) by E_B due to the oxygen breathing mode distortions. The spin down e_g level (not shown in the upper panel) of Mn^{4+} is higher by Hund's coupling energy $E_J = J_H S_C$ relative to the spin up e_g level of Mn^{4+}, where J_H is the exchange constant of Hund's coupling, S_C is the Mn ion core spin ($S_C = \frac{3}{2}$).

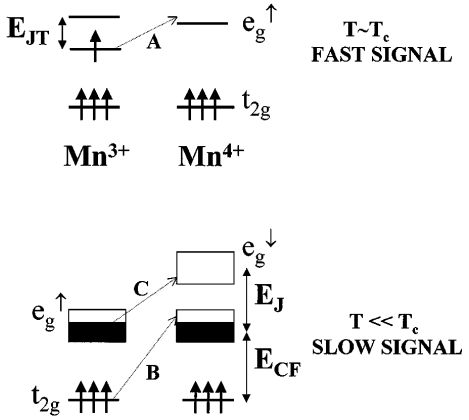

FIG. 3. The schematic electronic structure of the e_g and t_{2g} levels of Mn^{3+} and Mn^{4+} ions and the optical transitions relevant to the experiment.

Transition A is the dipole active photoionization of the Jahn-Teller small polaron. The lower panel shows the energy levels in the metallic ferromagnetic state at low temperatures. The spin up and spin down e_g bands are separated by E_J. The aligned core spins in the t_{2g} levels lie below the spin up e_g levels by the crystal field energy E_{CF}. Process B promotes a t_{2g} core electron of Mn^{3+} to the spin up e_g bands of Mn^{4+} by a dipole allowed charge transfer process. The transition between the spin up e_g bands and spin down e_g bands depicted by C is allowed only by an electric dipole spin flip process. Another possible transition involves electrons from the spin up e_g level of Mn^{3+} to the spin down t_{2g} level of Mn^{4+} with spin flip process. These are the only relevant optical processes for the 1.5 eV photon of this experiment. The temperature dependence of the transients will be determined by two factors: the absorption of photons which depends on the variation with temperature of the relative energy level of the corresponding transitions and the effect of the electron transfer on the conductance.

Process A will result in promoting an electron from a Mn^{3+} to a neighboring Mn^{4+} which will increase the conductivity and account for the conductive transient. It corresponds to the photoionization of the Jahn-Teller small polaron. The temperature dependence of this fast response may be also understood in these terms. This process would be enhanced with increased Jahn-Teller splitting of the Mn^{3+} e_g band, which will increase the overlap of the photon energy with the absorption band (since we are on the higher energy tail of the absorption band). Therefore, the absorption cross section will increase with increasing temperature. Also, the difference in the mobility of the initial (polaron) state and final (band) states should reduce as the samples go deeper in the ferromagnetic state. The localized small polaron in the paramagnetic state gradually transforms into an itinerant large polaron in the ferromagnetic state and its mobility increases. The decrease of the signal beyond the peak resistivity temperature is indicative of the temperature dependence of the mobility. The response time of the conductive transient is understood as the time for the hot electron to thermalize and become localized. The results show that this time is on the order of 150 ps and is nearly temperature independent.

The slow resistive transient occurs predominately in the metallic-ferromagnetic state. The long decay time of the signal suggests a spin relaxation process. Spin flip processes can occur in this experiment through spin-orbit interaction or the exchange interaction. There are two optical processes that may contribute to this signal. First, the optical transitions between the spin up e_g bands and the spin down e_g bands (process C) are expected to be centered around $J_H S_C = 1.7$ eV at low temperatures [17]. The optical conductivity due to these transitions is expected to be weak in the ferromagnetic state since they require a spin flip which is only weakly allowed by an electric dipole process through the spin-orbit interaction. A second optical process that may contribute to the slow resistive transient is the dipole allowed spin conserving t_{2g} to e_g charge transfer transition depicted in Fig. 3 as process B. The t_{2g} to e_g crystal field splitting of LCMO is close to 2 eV [18]. This process produces a magnetic excitation in the system. If the excited state decays through a rapid spin flip process either through the spin-orbit interaction or the exchange interaction between the excited ion and its neighbors, then magnons will be produced. Once the spin flip process occurs in either optical process, and decays into magnons, the conductivity decreases both because of the disruption of the hopping process and electron scattering by the magnons. The slow relaxation of the photoresponse may then be understood in terms of the long magnon lifetime. The temperature dependence of the resistive transient may be understood in terms of the temperature dependence of the resistivity of the sample since the amplitude of the signal is proportional to $\Delta R/R^2$, where R is the resistance of the sample and it increases with increasing temperature. Nevertheless, the resistance change (ΔR) also decreases somewhat with increasing temperature in our experiment. This indicates that the disturbance of the pulse laser excitation to the transport properties becomes weaker with increasing temperature. This can be explained qualitatively as follows. At lower temperatures, the spins are all aligned, so the effect of the disturbance is expected to be maximum, whereas at higher temperatures, where the spins aligned randomly, the effect of the disturbance to the spin system is reduced. Therefore, the effect of the pulse laser excitation on the conductance is proportional to the spin order or the magnetization of the sample.

The nature of the optical excitations in the manganites change significantly as one goes from the paramagnetic insulator state above T_C to the ferromagnetic metal state below T_C. Thus, although it is appropriate to talk in terms of atomic levels for the ionic sites while discussing the conductive transient, the situation becomes much more bandlike when one is talking about the resistive transients seen

dominantly at the lower temperatures where the system is more metallic. However, even in the band picture some of the arguments presented above using ionic energy level pictures must translate into the nature of the bands under optical excitation. In the ionic picture, for example, the resistive transient would involve a t_{2g} electron excitation from a Mn^{3+} to the e_g level of a Mn^{4+} and the relaxation of the hole in the original Mn^{3+} would be impeded since the e_g electron from the same ion will not be allowed to fill this hole. In addition, the superexchange for this excited state may create local antiferromagnetic disorder which would further perturb the system. In the band picture one would expect the optical excitation to result in the excitation of a t_{2g} electron to the e_g conduction band leaving behind a hole in the t_{2g} bands. If the decay of this t_{2g} hole can occur via a spin orbit or exchange interaction induced spin flip then magnons are created reducing the electron mobility. The system relaxation time will then be determined by the decay time of the magnons. It is noted that this time constant increases from a value of around a nanosecond at 8 K to a value over an order of magnitude larger at a temperature of 170 K. At present, this result is not understood. It may indicate a complex interplay between double exchange and the J-T effect and the magnon excitations as the temperature is raised toward T_C. This issue needs further investigation.

In summary, the femtosecond optical excitation at 1.5 eV photon energy gives rise to dramatically different photoresponses in the paramagnetic and ferromagnetic states of the manganites, resulting in a conductive and a resistive transient, respectively. The former arises from the photoionization of a Jahn-Teller small polaron, while the latter is associated with the reduction of the electron mobility in the metallic state due to long lived spin excitations. The conductive transient measures the thermalization and localization time of an electron made itinerant by a photon, and this is found to be 150 ps and nearly independent of temperature. The resistive transient at the lowest temperatures, where the J-T effects are not manifest, decays slowly with nanosecond response and this decay time is further enhanced over an order of magnitude at higher temperatures where the J-T effects begin to dominate. The pulsed optical response technique clearly enables us to measure the dynamics of the various processes that dictate the transport properties of the manganites.

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