Ultrafast photoinduced reflectivity transients in (Nd\textsubscript{0.5}Sr\textsubscript{0.5})MnO\textsubscript{3}

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The temperature dependence of ultrafast photoinduced reflectivity transients is reported in Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} thin film. The photoinduced reflectivity shows a complex response with very different temperature dependences on different timescales. The response on the subpicosecond time scale appears to be only weakly sensitive to the 270 K metal-insulator phase transition. Below \( \sim \)160 K the subpicosecond response displays a two component behavior indicating inhomogeneity of the film resulting from the substrate-induced strain. On the other hand, the slower response on the 10–100 ps timescale is sensitive only to the metal-insulator phase transition and is in agreement with some previously published results. The difference in the temperature dependences of the responses on nanosecond and microsecond time scales indicates that thermal equilibrium between the different degrees of freedom is established relatively slowly, on a nanosecond time scale.

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I. INTRODUCTION

The magnetoresistive (MR) manganites\textsuperscript{1–3} of the type (Re,A)MnO\textsubscript{3} (Re and A are trivalent rare-earth and divalent ions, respectively) have been studied with a broad spectrum of experimental techniques including the ultrafast pump-probe time-resolved spectroscopy.\textsuperscript{4–12} Most of the time-resolved studies were focused on the metallic/magnetoresistive part of the phase diagram.\textsuperscript{4–6,8–10} The subpicosecond response displays a two component behavior at lower temperatures which we attribute to the layered inhomogeneity of the film due to the substrate-induced strain in the film.

II. EXPERIMENT

A sample of Nd\textsubscript{1–x}Sr\textsubscript{x}MnO\textsubscript{3} thin film with nominal composition \( x = 0.5 \) was deposited on an 110-oriented SrTiO\textsubscript{3} substrate by the aerosol metal-organic chemical-vapor deposition.\textsuperscript{17} The pseudocubic 110 direction of the thin film was found to be parallel to the 110 direction of the substrate. The temperature dependence of the magnetic moment parallel to the film and the film resistance \( R \), shown in Fig. 1, indicate a metal-insulator transition (MIT) with an onset at \( T_{MIT} \approx \)265 K and a peak of \( dR/dT \) at 253 K. Despite the nominal Sr concentration \( x = 0.5 \) the transition to the charge ordered (CO) state which is observed below \( \sim \)150 K in bulk to the response observed in the metallic/magnetoresistive part of the phase diagram.\textsuperscript{5} The subpicosecond response displays a two component behavior at lower temperatures which we attribute to the layered inhomogeneity of the film due to the substrate-induced strain in the film.

FIG. 1. The film magnetic moment and resistance as functions of the temperature. The magnetic moment was measured in the external magnetic field of 10 Oe parallel to the film.
samples was not observed in the resistivity measurements. The absence of the CO transition could be either due to a minor discrepancy of the real cation composition from the nominal one or more likely due to the strain resulting from the film-substrate lattice constant mismatch. In magnetic moment temperature dependence we observe a kink at 103 K. The kink is absent in high magnetic field (45,000 Oe) indicating that it is not due to the background susceptibility of the SrTiO3 substrate which has a structural phase transition in the range 80–105 K depending on impurities.

We used a mode locked Ti:sapphire laser operating at \( \lambda = 800 \, \text{nm} \) (1.5 eV) as the source of pump and probe pulses. The train of \( \sim 60 \text{-fs-long} \) pump laser pulses was focused on a 60-\( \mu \)m-diameter spot giving an optical fluence of \( \sim 5 \, \mu \text{J/cm}^2 \) per pulse. The train of appropriately delayed probe pulses, which had the fluence 50–100 times weaker than the pump pulses, was reflected from the same spot and detected by a photodiode. The probe pulses were polarized orthogonally to the pump polarization and a polarization analyzer which was oriented perpendicularly to the pump polarization was mounted in front of the photodiode to eliminate the signal due to pump scattering. High-frequency modulation (200 kHz) of the pump beam intensity enabled low-noise lock-in detection of the photoinduced reflectivity \( \Delta R/\Delta t \) (PIR). The thickness of the film was approximately one optical penetration depth estimated from its optical density. Other details of the experimental pump-probe setup were published elsewhere.18

The sample was mounted on a cold finger of an optical liquid-He flow cryostat. Due to laser heating, the temperature of the illuminated sample volume was estimated to be less than 15 K above the cryostat temperature,19 which was directly measured using a RhFe resistor.

We observed no change of PIR transients when the pump polarization is rotated relative to the thin-film crystal axes. A typical measured PIR transient is shown in Fig. 2. The transient is characterized by three delay regions annotated by capital letters A, B, and C in Fig. 2. At negative delay times (region A) we observe a delay-independent PIR background, which represents the PIR buildup due to relaxation/diffusion processes significantly longer than the interpulse separation of 12.5 ns. The PIR-background amplitude is temperature dependent as shown in Fig. 3. The lock-in out-of-phase signal, which is delay independent within the full delay range, is also shown in the same plot for comparison. The lock-in out-of-phase signal actually corresponds to the PIR which persists during the “dark” part of the 200 kHz pump modulation period. It has virtually the same temperature dependence as the PIR background, with the only difference being a different sign, implying a temperature independent \(-\pi/4 \) phase shift of the induced reflectivity at 200 kHz with respect to the pump modulation. The time scale associated with the PIR background is therefore of the order of \( \mu \)s. The magnitudes of both signals exhibit a peak at \( \sim 240 \, \text{K} \) and the signals change sign at \( \sim 260 \, \text{K} \). Taking into account the \( \sim 10\)-K temperature difference of the illuminated sample volume relative to the cryostat temperature the background-peak temperature roughly coincides with the \( dR/dT \) peak while the sign change coincides with \( T_{\text{MIT}} \).

To aid the analysis of the PIR transients on the subnanosecond time scale we subtract the corresponding delay-independent background offsets discussed above. We refer to the modified transients as ultrafast-PIR (UPIR) transients. In Fig. 4 we show UPIR transients at different temperatures. We observe two well separated time scales (region B and region C in Figs. 2 and 4) in which the transients show different temperature dependences. The regions are separated by a break in Fig. 4. Region B includes dynamics up to \( \sim 1 \, \text{ps} \) while region C includes slower dynamics up to \( \sim 250 \, \text{ps} \).

Let us first look closer at the temperature dependence of the slower transients (region C). At room temperature, the UPIR transient is negative and virtually flat for delays larger than \( \sim 1 \, \text{ps} \). When the temperature is decreased below 260 K a new exponential relaxation component appears, leading to a change of sign of the UPIR transient at longer delay times. The temperature dependences of the relaxation time and the amplitude of the component are plotted in Fig. 5.

At maximum delay (250 ps) the UPIR transient magnitude is finite in the whole temperature range except around \( \sim 260 \, \text{K} \) indicating the presence of a longer, nanosecond-time-scale relaxation process. Similar to the PIR background, it exhibits a change of sign at \( \sim 260 \, \text{K} \) but is virtually temperature independent below 240 K as shown in Fig. 6.

Let us now discuss the ultrafast response above 160 K for

FIG. 2. A typical measured PIR transient (a). The transient is characterized by three delay regions annotated by capital letters A, B, and C (b). Note the logarithmic scale after the break.

FIG. 3. The photoinduced-reflectivity magnitude at negative delay with the lock-in out-of-phase signal shown for comparison.
delays up to $\sim 1$ ps. In this range the UPIR transient is negative ($\Delta R/R < 0$) with a 130-fs-long leading edge which is followed by a $\sim 300$-fs exponential decay continuing into the slow relaxation component described above. The 130-fs rise time is temperature independent in this range. The magnitude of the UPIR transient peak located at $\sim 100$ fs increases with decreasing temperature exhibiting a broad extremum at 240 K and decreasing again when the temperature is further decreased as seen in Fig. 7~b. The $\sim 300$-fs relaxation time is only weakly sensitive to the MIT as seen from Fig. 7~a, showing a slight increase when the temperature is lowered towards $T_{MIT}$ and a slight decrease below $T_{MIT}$. Unfortunately, additional noise due to the large PIR background, which appears in this temperature range, causes scatter in the data and prevents a more precise determination of the fast relaxation-time temperature dependence.

When the temperature is decreased below $\sim 160$ K the subpicosecond component experiences a remarkable change in shape (see Fig. 4). First, between 160 and 100 K the leading edge shifts together with the peak by $\sim 100$ fs towards the positive delay. In addition, the peak broadens and at 80 K disappears. Below 80 K a positive and slightly steeper leading edge centered again at the zero delay is observed followed by a positive peak at $\sim 50$ fs delay and a minimum around $\sim 200$ fs. After the minimum the UPIR transients still increase slightly on a time scale of $\sim 300$ fs followed by the slow relaxation component already described. The major changes of the shape of the subpicosecond UPIR transients appear at similar temperature as the kink in the magnetic-moment temperature dependence when the $\sim 10$-K laser heating of the illuminated volume is taken into account.

III. DISCUSSION

The 1.5-eV photon energy used in the present experiment lies in the region of optical transitions between split Mn $e_g$
derived bands.\textsuperscript{22} The time-resolved optical reflectivity at 1.5-eV photon energy is therefore directly related to the dynamics of charge carriers, which are the most relevant for the physics of MR manganites. In addition, in Nd\textsubscript{1−}\textit{x}Sr\textsubscript{\textit{x}}MnO\textsubscript{3} the reflectivity edge due to the coherent response at low temperatures is below the probe photon energy. A contribution to the photoinduced reflectivity from the collective charge response due to the free carriers at low temperatures is therefore expected not to be significant in comparison to the interband contribution.

Let us now discuss the different delay regions separately, proceeding from the fastest to the slowest time scale. Above \(\sim 160\) K the 300-fs relaxation time in our sample is just slightly longer than the 200-fs relaxation time measured by us in La\textsubscript{0.82}Pb\textsubscript{0.18}MnO\textsubscript{3} (Ref. 6) and La\textsubscript{1−}\textit{x}Sr\textsubscript{\textit{x}}MnO\textsubscript{3}.\textsuperscript{33} In La\textsubscript{1−}\textit{x}Ca\textsubscript{\textit{x}}MnO\textsubscript{3} Lobad \textit{et al.}\textsuperscript{5} report a sub-100-fs absorption transient, but do not discuss the transient shape in detail. Since our time resolution is \(\sim 80\) fs the 200–300-fs relaxation times measured in Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} and La\textsubscript{0.82}Pb\textsubscript{0.18}MnO\textsubscript{3} are intrinsic to the samples. However, any additional sub-80-fs components are not completely excluded by our measurements and it is not clear whether significant differences in the relaxation time exists between different manganites.

In contrast, the \textit{amplitude} of the subpicosecond relaxation component clearly behaves differently below \(T_{MIT}\) in manganites with different compositions on the La site. In La\textsubscript{0.82}Pb\textsubscript{0.18}MnO\textsubscript{3} (Ref. 6) the amplitude increases with decreasing temperature, in La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3} (Ref. 33) the increase in amplitude is less pronounced while in Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} the amplitude even decreases below \(T_{MIT}\). It remains to be more systematically investigated whether this is correlated with the hole doping, as current data suggest, or it is simply connected with the cation species type and/or the ionic radius on the La site. Below \(\sim 160\) K the subpicosecond behavior in our Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} thin film is much more complex than in manganite thin films with smaller hole doping.\textsuperscript{5,33} Despite anomalies observed in the ultrafast optical response and the magnetic-moment-temperature dependence there is no signature of any anomaly in the resistivity temperature dependence. This can be explained by the layered inhomogeneity of the film due to the substrate-film lattice-mismatch strain. It has been shown that thin films of Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} deposited on LaAlO\textsubscript{3} substrate display a layered structure with a \(\sim 20\)-nm-thick insulating layer near the substrate and a less strained layer on top, which undergoes MIT.\textsuperscript{15} In addition the remaining strain in the top layer of the Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} film is sufficient to almost completely suppress the CO transition.\textsuperscript{15} Similar behavior was observed also in La\textsubscript{0.66}Sr\textsubscript{0.33}MnO\textsubscript{3} thin films.\textsuperscript{20} In our case the substrate lattice parameter is \(\sim 1.5\%\) larger than the average pseudocubic lattice parameter of bulk Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3}. Despite that the strain in our case has different sign than in the case of LaAlO\textsubscript{3} substrate, the absence of any anomaly in the resistance temperature dependence suggests a similar layered inhomogeneity of the film. Since the thickness of the film is of the order of the optical penetration depth, optical (and magnetization) measurements detect contributions from top and bottom layers while in the electrical transport measurement the top high-conductivity metallic layer effectively shortens out the bottom insulating layer below MIT.

We therefore attribute anomalies observed below \(\sim 160\) K in the subpicosecond UPIR transients to the bottom insulating layer(s). We analyze the transients below \(\sim 160\) K in terms of an additional positive subpicosecond exponentially relaxing component originating from the bottom insulating layer. The component partially cancels the leading edge of the negative 300-fs component observed above \(\sim 160\) K reproducing the observed leading edge shift, as can be seen from the solid lines in Fig. 4. Unfortunately it is not possible to extract either amplitudes or relaxation-times temperature dependences of both components reliably since the fits are extremely ill conditioned. We can therefore only estimate the relaxation time of the additional component to be below 100 fs while the relaxation time of the negative one remains in the 200–300 fs range.

Let us now discuss the origin of the anomaly attributed to the bottom insulating layer. The SrTiO\textsubscript{3} substrate undergoes a second-order structural phase transition from cubic to tetragonal symmetry at \(\sim 105\) K. The temperature range at which major anomalies are observed in our Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} thin film are very similar to this temperature. However, the leading edge shift of the UPIR is already evident in the 130-K UPIR transient well above the substrate structural phase transition. In addition the substrate lattice parameters splitting below the structural transition is less than 0.1% (Ref. 21) which is more than ten times less then the substrate-film lattice mismatch. We therefore believe that the observed anomaly is not purely substrate-induced effect but that it is related to the Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} instability towards CO. Unfortunately from our data alone we cannot determine whether the additional sub-100-fs relaxation is indeed related to CO since there is no data yet available on time-resolved PIR at low excitation densities on charge ordered manganites.

Proceeding towards longer time scales we look next at region B. The relaxation on a 100 ps time scale observed in La\textsubscript{1−}\textit{x}Ca\textsubscript{\textit{x}}MnO\textsubscript{3} and La\textsubscript{1−}\textit{x}Sr\textsubscript{\textit{x}}MnO\textsubscript{3} was attributed to the magnetization relaxation dynamics by Lobad \textit{et al.}\textsuperscript{5} while Ren \textit{et al.}\textsuperscript{8} attribute it to polaron relaxation dynamics. It still needs to be confirmed, for example by time resolved Faraday rotation measurements, whether the 100-ps component is indeed related directly to the magnetization relaxation as proposed by Lobad \textit{et al.}\textsuperscript{5} In case of Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} we observe a similar temperature dependence of the relaxation time of the 100-ps component as Lobad \textit{et al.}\textsuperscript{5} (Fig. 5), although the relaxation is somewhat faster in Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3}.

For comparison, in (La,Pb)MnO\textsubscript{3} (Ref. 6) the peaks below \(T_{MIT}\) in the relaxation-time and amplitude temperature dependences of the 100-ps component are not observed. Instead, the relaxation time and the amplitude below \(T_{MIT}\) steadily increase with the decreasing temperature with a trace of a hump more than 100 K below \(T_{MIT}\). In La\textsubscript{1−}\textit{x}Ca\textsubscript{\textit{x}}MnO\textsubscript{3} Ren \textit{et al.}\textsuperscript{8} report a monotonic decrease of the relaxation time below \(T_{MIT}\). While in La\textsubscript{1−}\textit{x}Ca\textsubscript{\textit{x}}MnO\textsubscript{3} the different behavior may be related to the higher fluence used in their experiment, it is not clear at the moment what is the origin of...
the observed difference in (La,Pb)MnO₃. One possible reason for the absence of the peak below $T_{MIT}$ in (La,Pb)MnO₃ is a surplus oxygen content of the film leading to cation vacancies on the Mn and La sites. The disorder could cause faster relaxation due to a broken translation symmetry, but it could also lead to low-lying long-lived localized states. The contribution from such states cannot be excluded on the basis of current data on (La,Pb)MnO₃.

The residual UIR transient amplitude at 250 ps measures the amount of decay between successive laser pulses (12.5 ns). Its temperature dependence is similar to that of the PIR background on the $\mu$s time scale with the sign change at 260 K, but without the peak below $T_{MIT}$. We observe a similar behavior in (La,Pb)MnO₃. The absence of the peak below $T_{MIT}$ indicates that the response on the nanosecond time scale is (at least in part) not bolometric in origin, while the change of sign at 260 K suggests that the optical transition contributing to PIR on both time scales is the same.

Let us finally discuss the $\mu$s time scale corresponding to the large temperature-dependent PIR background. The slowly decaying signal observed at negative delay times (region A) seems to be a general feature present in transient PIR on the GMR manganites observed by us and others. Its temperature dependence exhibits a peak at the temperature which is usually of the order of 10 K below $T_{MIT}$, with the exception of (La,Pb)MnO₃, where the peak is $\sim$100 K below $T_{MIT}$.

A similar background, albeit with a smaller magnitude, was observed in the high-$T_c$ cuprates and the charge-density wave (CDW) semiconductor K₀.₃MoO₃. In these cases the background is peaked at the superconducting/CDW $T_c$ and was attributed to the intragap localized states. No corresponding out-of-phase lock-in signal similar to that in the manganites was observed in either the cuprates or K₀.₃MoO₃. Despite the fact that the behavior of the background in manganites is somewhat different, we have previously tentatively attributed the PIR background to a similar mechanism. A detailed analysis of the data presented in this paper suggests that this assignment for manganites needs to be reconsidered, since in manganites the PIR-background temperature dependence and the constant $-\pi/4$ background phase shift are more consistent with a bolometric response as explained below.

The expected amplitude of the bolometrically induced reflectivity change is given by

$$\frac{\Delta R}{R} = \frac{1}{\alpha R} \frac{\partial R}{\partial T} \Delta T,$$

where $\Delta T$ is the temperature oscillation amplitude. The specific heat and the thermal conductivity of the substrate and the manganite film below MIT are both relatively smooth functions of temperature without any significant anomalies. $\Delta T$ is therefore expected to be a relatively smooth function of temperature, and can contribute neither to the change of the PIR-background sign at 260 K nor to the observed peak below $T_{MIT}$. On the other hand, the reflectivity around 1.5 eV in manganites is virtually constant above $T_{MIT}$, but exhibits a systematic drop when the temperature is lowered below $T_{MIT}$ with further, albeit slower, decrease towards lower temperatures. The shape of the PIR-background temperature dependence in Fig. 3 is therefore consistent with the temperature dependence of the derivative $(1/R)(\partial R/\partial T)$ which has a peak just below $T_{MIT}$ and is very close to zero or may be even negative above $T_{MIT}$.

To estimate the maximum magnitude of the bolometrically induced reflectivity change we take the available data for Nd₀.₇Sr₀.₃MnO₃ (Ref. 29) where the reflectivity drop below $T_{MIT}$ is $\sim$0.04 in the temperature range of $\sim$30 K. A similar reflectivity drop is expected in Nd₀.₅Sr₀.₅MnO₃ judging from a similar temperature dependence of the optical conductivity. Taking into account the estimated 0.5-K temperature oscillation amplitude we obtain $\Delta R/R \sim 4 \times 10^{-3}$ for the maximum in-phase bolometrically induced reflectivity change. This is in a fair agreement with the observed maximum amplitude of the PIR background which is $\sim 10^{-3}$. The PIR-background amplitude and its temperature dependence are therefore consistent with a bolometric response.

Further, the temperature independent phase shift of $-\pi/4$ between harmonically modulated average laser intensity and the surface temperature oscillation observed at 200 kHz in our experiment is a characteristic of a one-dimensional diffusion process. In our case the heat diffusion length on a time scale of the lock-in modulation frequency is a few $\mu$m as estimated from typical heat-capacity and thermal-conductivity data for manganites and the substrate. Since the laser beam diameter of 60 $\mu$m is much larger than the heat diffusion length at the modulating frequency the heat diffusion is indeed expected to be effectively one dimensional, further supporting the bolometric origin of the PIR background in the manganites.

A similar $-\pi/4$ temperature-independent phase shift observed in (La,Pb)MnO₃ (Ref. 6) suggests the bolometric origin of the PIR background in that case as well.

IV. CONCLUSION

We measured temperature dependence of ultrafast photoinduced-reflectivity transients in Nd₀.₅Sr₀.₅MnO₃ thin film. On the subpicosecond time scale the transients are only weakly sensitive to the metal-insulator transition at $\sim$270 K, but instead show a remarkable change in shape below $\sim$160 K. Major changes in the shape are correlated with an anomaly observed in the magnetization temperature dependence, but no anomaly is observed in the temperature dependence of the resistivity in this temperature range. The absence of the anomaly in resistivity is attributed to the substrate-film lattice-mismatch induced inhomogeneity of the film. The changes of the transients could be attributed to an additional sub-100-fs relaxation component, which originates from the most strained layer of the film near the substrate. Although the substrate undergoes a structural phase transition in the same temperature range, the small changes of the substrate lattice parameters below the phase transition and the higher onset temperature of the changes in the transients suggest that the observed anomalies are not due to the
substrate but are related to the CO instability of bulk Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. The slower 10–100- ps photoinduced-reflectivity relaxation dynamics is sensitive only to the ~270-K MIT exhibiting peaks in relaxation time and amplitude just below the MIT temperature, similar as in some previously studied manganites with different doping.

On even slower time scales the photoinduced reflectivity is also sensitive to the ~270-K MIT only. While the ultrashow-response temperature dependence on the $\mu$s time scale is consistent with the expected bolometric response, the relaxation on the 1–10 ns time scale shows a different temperature dependence and is most probably not bolometric. This indicates that the thermal equilibrium between different degrees of freedom (charge, spin) is not reached faster than on the nanosecond time scale.

31 Since the thickness of the film is much smaller than the heat diffusion length on the $\mu$s time scale, the heat diffusion out of the experimental volume is governed by the heat diffusivity in the film and in the substrate and the thermal resistance of the boundary between the film and the substrate. For purpose of estimation we neglect the boundary heat resistivity, assume a negligible film thickness, and calculate the surface temperature oscillation amplitude and phase in a simple model assuming a semi-infinite homogenous material using the substrate thermal constants and the thin-film optical constants.