Supporting Information


Evolution of Hot Polaron States with a Nanosecond Lifetime in a Manganite Perovskite

*Dirk Raiser, Stephanie Mildner, Benedikt Ifland, Mohsen Sotoudeh, Peter Blöchl, Simone Techert, and Christian Jooss*
Supporting Information

Evolution of Hot Polaron States with a Nanosecond Lifetime in a Manganite Perovskite

Dirk Raiser1, Stephanie Mildner2, Benedikt Ifland2, Mohsen Sotoudeh3, Peter Blöchl2,3, Simone Teichert1,4,5, Christian Jooss2

1Max-Planck-Institute for Biophysical Chemistry, Am Fassberg 11, D-37077 Goettingen, Germany
2Institute for Material Physics, University of Goettingen, Friedrich-Hund-Platz 1, D-37077 Goettingen, Germany
3Institute for Theoretical Physics, University of Clausthal, Leibnizstrasse 10, D-38678 Clausthal-Zellerfeld, Germany
4FS-SCS Deutsches Elektronensynchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany
5Institute for X-ray Physics, University of Goettingen, Friedrich-Hund-Platz 1, D-37077 Goettingen, Germany

Table of contents

1. Setup of the Transient Absorption Spectrometer
2. Sample Preparation of the PCMO Thin Film
3. Power Dependent Transmission and Optical Density
4. Transient Absorption Measurements
5. Optical Transitions in PCMO
6. Analysis of the Change in Optical Density
7. Analysis of the Long-Term Picosecond Coherent Oscillations
8. Analysis of the Short-Term Picosecond Coherent Oscillations
9. Analysis of the Femtosecond Coherent Oscillations
10. Power Dependence of the Picosecond Dynamics
11. Power Dependence of the Slow Relaxation Process
12. Resolution Limits of the Deconvolution
13. Orbital scheme of the Zener Polaron
14. The Relaxation Process in the Jahn-Teller Dimer
15. Temperature Dependence of Open Circuit Voltage
16. The contribution of heat decay to the slow relaxation process
1. Setup of the Transient Absorption Spectrometer

All presented time-resolved measurements were carried out using a home-build transient-absorption spectrometer, schematically shown in Figure S1.

![Figure S1. The drawing shows the schematic setup of the time-resolved transient-absorption spectrometer, which was used for the presented measurements in this work.](image)

The apparatus is based on the pump-probe technique, where both pulses are generated in the same laser system. The laser system consists of two successive commercial titanium-doped sapphire laser systems (Coherent Inc. Mira-900F and Spectra Physics Hurricane), where the tuneable wavelength of the former one (Mira) is set to 800 nm (1.55 eV) and the repetition rate of the rear one (Hurricane) is set to 880 Hz achieving an amplified output energy of approximately 540 mW with 100 fs horizontally polarized laser pulses (0.61 mJ pulse energy).

Each pulse is split (BS1) into a pump pulse, which is chopped (C) down to 440 Hz and its power is reduced to below 2 mW (4.5 μJ pulse energy), and a probe pulse, which is converted into a white light continuum by focussing it into a thin sapphire window (S) and then delayed in time by a translation stage (TS). While the orientation of the polarization of the pump pulse is adjusted using a waveplate (λ), the probe pulse is further split (BS2) half-half into a reference signal (SM1) and a sample signal (SM2). Both pulses are focussed at the sample position (X) down to a diameter of about 200 μm. The sample which was implemented was a Pr$_{1-x}$Ca$_x$MnO$_3$ thin film with a doping level of $x = 0.35$ (PCMO). The resulting achievable temporal resolution at the sample position is about 200 fs.

In order to enable temperature-dependent measurements the sample was mounted into an Oxford Instruments Microstat He Cryo Cell, which allows usage of liquid nitrogen as well as liquid helium for cooling, while the sample is kept in a moderate vacuum of about $10^{-5}$ to $10^{-4}$ mbar. In the present work liquid nitrogen was used and thus the temperature could be set between 80 K and 400 K.
Figure S2. The white light continuum, which is generated in the sapphire window reaches down to a wavelength of approximately 450 nm (2.76 eV) and has a relatively constant intensity distribution throughout the whole visible spectrum area. A short pass edge filter is used to cut off the spectrum above 750 nm (1.65 eV), due to the sharp intensity rise towards the fundamental of 800 nm (1.55 eV).

2. Sample Preparation of the PCMO Thin Film

The Pr$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.35$) thin film which was used for the time-resolved and power dependent measurements was prepared by reactive ion beam in an oxygen atmosphere with a partial pressure of 1.4·$10^{-4}$ mbar. It was grown at a deposition temperature of $T_{\text{dep}} = 1020$ K on a [001]-oriented MgO single crystal. Xenon with a partial pressure of 1.4·$10^{-4}$ mbar has been used as sputter gas. Details on the preparation of the sputter target can be found elsewhere. [Mildner, S. et al. Phys. Rev. B 92, 035145 (2015)]

The PCMO film has a thickness of $d_{\text{film}} \approx 100$ nm. The applied preparation conditions ensure smooth PCMO films with a high degree of crystallinity as revealed by the X-ray diffractogram shown in Figure S3 (red curve). It reveals epitaxial growth of PCMO with [001]/[110] twinning and a small amount of [112]-misorientations on the MgO substrate. The unlabeled peaks in the diffractogram of PCMO can be attributed to the MgO substrate and the glue, which is used for fixing the sample (cf. black curve in Figure S3). Polished MgO is used as substrate because of its large optical band gap ($E_G > 7$ eV) which allows for unhindered transmission in the investigated spectral range.

For the photovoltaic study, pn-junctions have been prepared by sputter deposition of the p-doped Pr$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.34$) on n-doped SrTi$_{1-y}$Nb$_y$O$_3$ (STNO) with $y = 0.002$ using the same sputter parameters. As before epitaxial growth with [001]/[110] twins was evaluated by X-ray diffraction. Further details of the junction interfaces can be found elsewhere. [Saucke, G. et al. Phys. Rev. B 85, 165315 (2012)]
3. Power Dependent Transmission and Optical Density

An additional static measurement was carried out to gain insight into the intensity-dependent transmission and thus the intensity-dependent optical density of the sample. In order to determine the transmission of the sample, the incoming pump intensities were measured twice. Retracting the sample enables one to measure the reference intensity $I_0$, while inserting the sample in the focal position leads to the transmitted sample intensity $I_T$. Thus the transmission can be determined as their quotient.

$$T = \frac{I_T}{I_0} \quad (3.1)$$

The optical density is then defined as the decadal logarithm of the reciprocal transmission.

$$OD = \log(1/T) = \log(I_0 / I_T) \quad (3.2)$$

The different intensity values below 2 mW were achieved using a variable linear-density filter, which allowed for a precise gradually rise of the intensity. According to the pump condition of the time-resolved measurements, the fundamental wavelength of the ultrafast laser pulses was set to 800 nm and the beam was focused on the 100 nm thick sample resulting in a spot size of a diameter of approximately 200 μm.
Figure S4. Intensity dependences of (a) the transmission and (b) the optical density of the PCMO thin film at three different temperatures 100 K (blue), 200 K (red) and 300 K (black), representing the antiferromagnetic insulating, the orbital/charge ordering and the paramagnetic insulating phases of \( \text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3 \).

For all three temperatures, the transmission as well as the optical density reaches an almost constant plateau-like saturation level for higher intensities \( I_0 \), resulting in a higher transmission and thus a lower optical densities for higher temperatures. While the slope of the saturation plateau of the charge-ordering phase at 200 K is negligible, that of the antiferromagnetic insulating phase at 100 K is greater than that of the paramagnetic insulating phase at 300 K.

The intersection of the linear response and the saturation plateau for the paramagnetic insulating phase lies at about 350 \( \mu \text{W} \) and is thereby higher than that of the charge-ordering phase at about 200 \( \mu \text{W} \). For the antiferromagnetic insulating phase no such intersection is visible due to the absence of a linear response, which might be caused by the limited resolution of the thermal detector for low powers.

The time-resolved measurements were performed at a pump energy of 350 \( \mu \text{W} \), which is 800 nJ per pulse at a repetition rate of 440 Hz or an averaged surface power density of about \( 2.5 \times 10^{10} \text{ W/cm}^2 \) at the focal spot of a diameter of 200 \( \mu \text{m} \). This was on the one hand in order to sufficiently pump the sample throughout the whole depth of it and on the other hand to avoid nonlinear optical effects like two-photon absorption.

The damage threshold of the sample under the given conditions was above 5 mW. Taking into account the fundamental wavelength of 800 nm (1.55 eV) and thus a photon energy of \( E_{\text{ph}} = 2.48 \times 10^{19} \) J, the sample gets illuminated with about \( 3.2 \times 10^{12} \) photons per pulse, whereas according to Figure S4 about 90% are absorbed.

The volume per Mn ion of \( \text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3 \) is about \( V_{\text{ion}} = 56.92 \text{ Å}^3 \). Thus, the pumped volume of \( V_{\text{pump}} = 3141 \text{ μm}^3 \) contains about \( 5.52 \times 10^{13} \) Mn ions. Given the photon density of the beam, this implies that in average about 0.06 photons per Mn ion are absorbed for each pulse.
4. Transient Absorption Measurements

The transient absorption spectra were measured for different temperatures between 80 K and 360 K with a minimum step size of 10 K. This permits a precise analysis of the change of the transient absorption spectrum due to the three phases visited in this temperature range. The phases are the paramagnetic insulating (PI), the orbital ordering / charge ordering (OO/CO) and the antiferromagnetic insulating (AFI) phase as shown in Figure S5.

![Figure S5](image)

**Figure S5.** Phase diagram of Pr$_{1-x}$Ca$_x$MnO$_3$ according to [Jirák, Z. et al. J. Magn. Magn. Mater., 53, 153 – 166 (1985)]. The yellow line indicates the doping level of the used film. PI: paramagnetic insulating, OO/OC: orbital ordering / charge ordering, AFI: antiferromagnetic insulating.

The difference in optical density $\Delta OD$ is determined through two successive probe pulses, where the sample gets only excited for the first pulse.

$$\Delta OD = OD_{on} - OD_{off} = \log(I_{0, on} / I_{T, on}) - \log(I_{0, off} / I_{T, off})$$ \hspace{1cm} (4.1)

Assuming a time-independent intensity distribution of the white-light continuum allows for simplification.

$$\Delta OD \approx \log(I_{T, off} / I_{T, on})$$ \hspace{1cm} (4.2)

**Figure S6** shows an example of the transient absorption spectrum of the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ thin film at the lowest temperature of 80 K for a spectral range of 600 nm (2.07 eV) to 700 nm (1.77 eV). In this range, the spectrum shows a completely negative signal due to the ground-state bleaching, which results in a higher transmission of the excited sample within this range.
5. Optical Transitions in PCMO

The spectrum in Figure S7 c) shows the time-integrated difference $\Delta OD$ in optical density of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ for delay times up to a maximum delay of 1 ns.

$$f(E,T) = \int_{0}^{1\text{ ns}} \Delta OD(t,T,E) \, dt$$  \hspace{1cm} (5.1)

Within the accessible spectral range there is only a small range, where a positive difference in the optical density and thus a lower transmission of the sample film is detected. As shown in Figure S7, this excited state absorption is present only for higher temperatures and above probe energies of 2.4 eV. For lower temperatures, the difference in optical density for this probe energy range changes sign. As described in Figure 1 of the paper, charge transfer (CT) transitions may be involved in this energy range. The further analysis of the data therefore is only focussed on the temporal evolution of the Jahn-Teller (JT) peak dynamics, which are assigned to peak (B) in Figure S7 b).

The ground-state bleaching signal below 2.2 eV shows a strong dip in the optical density of down to about -100 mOD within the temporal resolution of this apparatus, which is decaying on a short timescale of below 3 ps. For higher temperatures of the sample, this fast decay time gets shorter. This first fast decay ($\tau_{\text{fast}}$) is followed by a much slower decay ($\tau_{\text{slow}}$) on a short nanosecond timescale, whereby the decay time $\tau_{\text{slow}}$ increases for higher temperatures.

The absolute value of the change in optical density $\Delta OD$ due to the photon excitation increases towards the fundamental wavelength of 800 nm (1.55 eV), which is in good agreement with previously performed measurements of the static absorption of PCMO thin films in this spectral range.
Figure S7. Identification of the involved transitions in PCMO. (a) Spin-dependent density of states (DOS) from DFT calculations for Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. The Mn 3d $e_g$-states are shown in yellow, the Mn 3d $t_{2g}$-states in green and the red area is assigned to the O 2p-states. The $t_{2g}$ and $e_g$ density of states is shown only for a subset on Mn ions, that has a total spin in the up direction. The partial density of states are stacked on top of each other so, that the area rather than the ordinate value is relevant. The total DOS, which also includes the Pr- and Ca-states, is illustrated in black. (b) Measured optical transitions in transmission spectroscopy at 300 K (bold line) and 80 K (dashed line) for Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ [Mildner, S. et al. Phys. Rev. B 92, 035145 (2015)]. The grey line is the result of peak fitting at 300 K. The pump energy at 1.55 eV is indicated by an arrow. Peaks (A) and (B) are assigned to a small polaron hopping transition and a Jahn-Teller type transition (involving hybridization to O 2p-states), respectively. Peak (C) is assigned to charge transfer transitions from O 2p-states into minority $t_{2g}$ and $e_g$ states. (c) Temperature and energy dependence of $\int \Delta OD \, dt$ after photoexcitation at 1.55 eV (800 nm). The dashed line indicates the sign reversal of $\int \Delta OD \, dt$. 
6. Analysis of the Change in Optical Density

The change in optical density $\Delta OD$ contains three distinct coherent oscillations on different timescales. As can be seen in Figure S8 a) there is a short-term and a long-term picosecond oscillation with periods of about 50 ps and 400 ps ($\leftrightarrow \tau_{GHz}$) respectively, while Figure S8 b) shows the fast femtosecond oscillation ($\leftrightarrow \tau_{THz}$). In both cases the change in optical density $\Delta OD$ is shown as an example for a probe wavelength of about 650 nm (1.91 eV) at a temperature of $T = 80$ K.

For all temperatures, both decays (\(\tau_{fast}\) and \(\tau_{slow}\)) were fitted separately to an exponential decay function indicated by the red lines. The absorption of the pump pulse, which initiates the change in optical density at $t_0 = 0$, occurs on a short femtosecond timescale within the temporal resolution of the apparatus and is thus described as an instantaneous rise of the change in optical density, while the subsequent decays are usually represented by exponential functions of the form

$$f(t) = A \cdot e^{-\frac{t}{\tau}} \quad (6.1)$$

In this case, the amplitude A is negative.

![Figure S8](image)

**Figure S8.** Time dependent slice of the difference in optical density amplified by a factor of \(10^3\) ($\Delta mOD$) of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ measured at $T = 80$ K using an 800 nm pump wavelength, showing the temporal development of the signal at 650 nm. a) Slow decay process on a linear time scale up to one nanosecond. b) Close-up of the initial fast decaying dip within four picoseconds.

The resulting decay function describing the change in optical density is convoluted with a Gaussian curve \(g(t)\), which represents the temporal resolution limit due to the chirp and the dispersion of the ultrafast pulses. This basically results in a blurring of the instantaneous rise at $t_0$ and thus forming an S-shaped course, which is mathematically described by a Gaussian error function

$$g(t) = G \cdot e^{-\frac{t^2}{2\sigma^2}} \quad (6.2)$$

$$\Delta OD(t) = f(t) * g(t) = \int_0^\infty dt' A e^{-\frac{t'}{\tau}} \cdot Ge^{-\frac{(t-t')^2}{2\sigma^2}} \quad (6.3)$$
In order to satisfy the different obtained courses of the decays for all measured temperatures, the assumed exponential decay function \( f(t) \), which did not sufficiently satisfy the obtained courses of the data for all temperatures, was further generalized to a stretched exponential decay function \( f_b(t) \). A stretched exponential can be further motivated within a well-established model for the spatio-temporal kinetics of a phase transition given by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model [Weinberg, M. C. et al. J. Non-Cryst. Sol. 219:89-99 (1997); Avrami, M. J. Chem. Phys. 8:212 (1940)]. Since an analytical expression of the convolution of \( f_b(t) \) with a Gaussian curve \( g(t) \) is not in general possible, the resulting decay function containing a stretched exponential decay function is semi-empirical.

\[
f_b(t) = A \cdot e^{-\left(\frac{t}{\tau}\right)^b} \quad (6.4)
\]

\[
\Delta OD(t) \equiv \frac{A}{2} \left[ 1 + \text{erf}\left(\frac{t-t_0}{s}\right) \right] \cdot \exp\left\{ \Re\{e^{-\left(\frac{t-t_0}{\tau}\right)^b}\} \right\} \quad (6.5)
\]

The real part hereby accounts for the absolute value of the stretched exponential function \( f_b(t) \), which is complex for certain pairs of \( t \) and \( b \).

\[
|e^x| = |e^{ixy}| = |e^x| \cdot |e^{iy}| = e^x \cdot e^{iy} = e^{ix} = e^{\Re\{z\}} \quad (6.6)
\]

The response function \( K(t) \) of all processes described, is expressed by the following equation.

\[
K(t) = A_{\text{fast}} e^{-t/\tau_{\text{fast}}} + \sum_{j \in \text{THz}} A_{\text{THz},j} e^{-t/\tau_{\text{THz},j}} + \sum_{j \in \text{GHz}} A_{\text{GHz},j} e^{-t/\tau_{\text{GHz},j}} + A_{\text{slow}} e^{-t/\tau_{\text{slow}}} \quad (6.7)
\]

Thus, the complete description of the measured change in optical density \( \Delta OD \) results as

\[
\Delta OD(t) = K(t) \ast g(t) \quad (6.8)
\]

Analytical separation of both processes was possible due to the linearity of the Fourier transformation and the given distinction of the timescales of the two decays. For the fitting of the fast decay, an additional constant end offset is included. This constant offset accounts for the slow decay (\( \tau_{\text{slow}} \)), which can be considered constant on the timescale of the fast decay (\( \tau_{\text{fast}} \)). Subtraction of the final fitting curve (red) from the measured data (black) then leads to the residuals (blue) shown in Figure S8, which are the pure coherent oscillations. In order to gain deeper insight into the underlying coherent processes, these coherent oscillations are analyzed further in the frequency domain, whereas the Fourier transform \( |F| \), as an example for the long-term picosecond oscillations, thus results as

\[
|F| = \left| \int dt \ e^{i\omega t} \Delta OD(t) - \int dt' A_{\text{slow}} e^{-t'/\tau_{\text{slow}}} \cdot g(t-t') \right| \quad (6.9)
\]

With \( \Delta OD(t) \) being the measured change in optical density.
7. Analysis of the Long-Term Picosecond Coherent Oscillations

Figure S9. Normalized three dimensional color-coded wavelength dependency of the spectral weight $|\mathcal{F}|$ of the long-term picosecond oscillations of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ at $T = 80$ K.

Figure S9 shows an example for the result for the normalized absolute values of the complex Fourier transform $|\mathcal{F}|$ for data intervals of 10 ps over a range of 1 ns of the measurement at 80 K. The Fourier spectrum $|\mathcal{F}|(f)$ represents the spectral weight of the coherent $\Delta\text{OD}(t)$ oscillations. It was calculated for a spectral range of the probe pulse of 620 nm to 740 nm. Outside of this range the measurement is limited by the short pass filter towards longer wavelengths or does not show any considerable contribution due to the weak change in optical density towards shorter wavelengths. $|\mathcal{F}|(f)$ can be interpreted as somehow reflecting the spectral weight of the coherent phonon modes induced by the optical stimulation.

The spectrum obtained is dominated by a sharp peak at around 2.5 GHz with a full width at half maximum of about 2 GHz along the wavelength with a rising peak maximum towards longer wavelengths were the change in optical density of the spectrum is larger. Besides this peak, there is hardly any contribution to the overall spectrum by other frequencies resulting in a relatively flat and low plain.

8. Analysis of the Short-Term Picosecond Coherent Oscillations

The short-term picosecond oscillation was analyzed and transformed analogous to the long-term picosecond oscillation as described above. Whereas the selected temporal step size for this transformation is 2 ps over a range of 100 ps. As for the long-term picosecond oscillation, this spectrum also shows one dominating peak, which is comparably flatter along the wavelengths, but again has its maximum at the longest measured wavelength. Apart from that, this peak is located at around 40 GHz with a full width at half maximum of about 50 GHz.

In contrast to the Figure S9 the Fourier transform $|\mathcal{F}|$ in Figure S10 shows a plateau-like behavior for higher phonon frequencies with a minimum in spectral weight at a probe wavelength of about 680 nm.
Figure S10. Normalized three dimensional color-coded wavelength dependency of the absolute values of the Fourier transform $|F|$ of the short-term picosecond oscillations of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ at $T = 80$ K.

The short-term picosecond oscillation is assumed to be a longitudinal elastic strain wave induced by the ultrafast photon excitation, which is propagating to the interface between the film and the substrate, where it is reflected and thus forms a vibration of the entire film until the coherence of the involved phonons is lost [Ogasawara, T. et al. Phys. Rev. B 68:180407(R) (2003), Wu, K. H. et al. J. Supercond. Nov. Magn. 24:721 (2011)].

The velocity of longitudinal elastic waves $v_L$ in PCMO is about 4 nm/ps as obtained from the elastic modulus of PCMO of about $E = 100$ GPa and a density of about $\rho = 6$ g/cm$^3$. Thus, this velocity of an elastic wave results in a period of $\Delta t = 50$ ps for the given thickness of the sample film of about $d_{\text{film}} \approx 100$ nm.

$$\Delta t = 2d_{\text{film}}/v_L \quad \text{with} \quad v_L = \sqrt{E/\rho} \quad (8.1)$$

Therefore the period of an elastic wave travelling through the film in the direction of the propagation of the ultrafast pulses matches very well the low cut-off frequency of the plateau of short-term coherent oscillations of 40 GHz.

For the further temperature dependency analysis only the mean values along the wavelength of the absolute value of the Fourier transform $<|F|>$ for each temperature are examined, due to the relatively weak variation along the wavelengths.

This temperature dependency of these mean values is shown in Figure S11. Regarding this graph, two main trends are obvious. Firstly the central position of the maximum peak for all temperatures is slightly shifted from about 40 GHz at low temperatures towards lower frequencies of about 25 GHz at high temperatures. Secondly the peak value as well as the level of the background signal is decreasing towards higher temperatures. In order to further investigate these trends, for each temperature the resulting frequency dependent slice is then fitted onto a Gaussian curve function of the form

$$y(f) = A_0 + A_1 \cdot e^{-\frac{4\ln 2(f-f_0)^2}{s^2}} \quad \text{with} \quad A_k = \frac{A'_k}{s \cdot \sqrt{\pi/4\ln 2}} \quad (8.2)$$
Figure S11. Color-coded three dimensional mean values along the wavelength of the Fourier transform $|\mathcal{F}|$ of the short-term picosecond oscillations of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ shown for different temperatures between 80 K and 360 K.

This function consists of the sum of a constant background $A_0$ and a scaled Gaussian curve with the amplitude $A_1$, a center position $f_0$ and a full width at half maximum $s$.

The results of these fitting parameters are shown in Figure S12. The amplitude $A_1$ of the Gaussian curve is relatively constant and does not change significantly with the temperature compared to the margin of the error bars.

Figure S12. Temperature dependencies of the Gaussian curve fitting parameters of the spectral weight of the short-term picosecond oscillations shown in Fig. S11. The resulting parameters shown are the center frequency $f_0$ and the amplitude $A_1$ of the maximum spectral weight together with the constant background $A_0$.

The central position $f_0$ and the constant background $A_0$ both show a strong monotonic decrease for rising temperatures. An exponential fit for each parameter is included as a red dashed line as an eye guide. For both curves a slight deviation at around 200 K is present.
9. Analysis of the Femtosecond Coherent Oscillations

The fast femtosecond oscillations are extracted from the data by subtraction of the resulting stretched exponential fits and are exemplarily shown in Figure S13 a,b for two temperatures well below and above the charge ordering transition temperature, respectively.

Figure S13. Probe-energy and time-dependent color-coded fast femtosecond oscillations as obtained from the subtraction of the stretched exponential fit from the measured optical density $\Delta OD$ of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ at a) $T = 80$ K and b) $T = 290$ K and the resulting average along the probe-energy for c) 80 K and d) 290 K. The included dashed purple lines show an envelope with an exponential decay time of 3.4 ps as an eye guide.

In order to further quantify the presence of these oscillations, their damping is investigated. Therefore the average along the probe-energy was calculated and is shown in Figure S13 c,d.

The signals show a beating instead of a clear sinusoidal oscillation, due to the involved number of different phonon modes, and exhibit a damping. Therefore an exponential damping with a decay time of 3.4 ps was implemented as an eye guide, which suits very well for both temperatures. In contrast to the damping coefficient, which is rather equal for both temperatures, the amplitude of the damping envelope decreases for increasing temperatures.

Thus the damping coefficient of the coherent THz phonon modes is on the order of but slightly longer than the decay time $\tau_{\text{fast}}$ of the fast relaxation process (ii).

The temperature dependence of the fast femtosecond oscillations is further analyzed in the frequency domain.
The Fourier transform of the fast femtosecond oscillations is calculated for a temporal step size of 20 fs over a range of 6 ps of the measurements at all temperatures. As for the other coherent oscillations, the Fourier spectrum was calculated for a spectral range of 640 nm to 740 nm. For each temperature there are dominant lines along the wavelengths, which mainly contribute to the oscillations.

As has been done for the fast picosecond oscillations in Figure S11, the absolute values of the Fourier transform of the femtosecond oscillations are therefore averaged along the wavelengths for all datasets and plotted against the temperature for a frequency range of 0 THz to 8 THz (Figure S14). Higher frequencies do not contribute to this spectrum or could not be measured due to the resolution limits of the apparatus.

Figure S14. The color-coded mean values along the wavelength shown for different temperatures between 80 K and 360 K of the three-dimensional color-coded wavelength dependence of the absolute values of the Fourier transform $|\mathcal{F}|$ of the femtosecond oscillations of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$.

The peak maxima here are at approximately 2 THz, but do not take shape of a single peak, then rather assemble in multiple peaks, which vary in their exact frequency values along the temperature. Besides this there is a common trend of decreasing peak values for higher temperatures. Furthermore the contributions to the oscillations of frequencies beyond 4 THz drop rapidly. The further analysis of these oscillations and the underlying frequencies is therefore performed for certain frequency segments within the main work, as well as for the full frequency range up to 4 THz in the following (Figure S15).
Temperature dependent change of the spectrally averaged spectral weight $|F|$ of the femtosecond oscillations of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ for the full frequency range up to 4 THz. Two different fits are applied and shown as dashed blue lines: a) A phase step fit with a linear background and b) a double phase step.

The following table shows the applied functions and the resulting relevant temperature parameters, as well as the resulting adjusted R-square values.

$$
|F| = A_0 + mT + A_1 \cdot \left(1 - \text{erf}\left(\frac{T - T_j}{\sqrt{2} \cdot s_j}\right)\right)
$$

<table>
<thead>
<tr>
<th>$T_j$ [K]</th>
<th>165.26</th>
<th>158.15</th>
<th>221.77</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_j$ [K]</td>
<td>61.26</td>
<td>5</td>
<td>83.38</td>
</tr>
<tr>
<td>Adj. $R^2$</td>
<td>0.8967</td>
<td></td>
<td>0.9296</td>
</tr>
</tbody>
</table>

### 10. Power Dependence of the Picosecond Dynamics

Further power dependent measurements were carried out in order to analyze the nature of the short-term picosecond oscillations and the slow relaxation process in more detail. Therefore the excitation energy was successively raised for values between 0.1 mW and 2.0 mW. Figure S16 exemplarily shows the resulting data for a probe energy of 1.8 eV and excitation powers of 0.1 mW, 0.2 mW, 0.4 mW, 0.8 mW and 1.5 mW.

Figure S16 focusses on the temporal development of the transient signal up to a delay time $t$ of 150 ps allowing for a detailed view of the short-term picosecond oscillations. As can clearly be seen, this oscillation is rather absent for the lowest excitation energies and gets more and more prominent for higher powers.

For further investigation of the strength of the short-term picosecond oscillations the residuals from a monoexponential fit were Fourier transformed as described before. For this Fourier transform a temporal segment of the whole dataset with delay times up to 50 ps with a minimal step size of 2 ps was used, covering the complete short-term picosecond oscillations.
Figure S16. Time dependent slices of the difference in optical density $\Delta$OD of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ measured at room temperature for a probe energy of 1.8 eV and for five different excitation powers (0.1 mW, 0.2 mW, 0.4 mW, 0.8 mW and 1.5 mW).

Figure S17 shows the resulting excitation power dependency of the Fourier transform for probe energies of $E = 1.8$ eV and $E = 2.0$ eV, whereas for both energies the mean values were calculated for a bandwidth of about $\pm 20$ meV.

Figure S17. Three dimensional color-coded excitation power dependency of the spectral weight $|\mathcal{F}|$ of the short-term picosecond oscillations of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ at $T = 300$ K for a probe energy of a) $E = 1.8$ eV and b) $E = 2.0$ eV. c) Excitation power dependent cut through at the peak frequency of 25 GHz.
The resulting spectra for both probe energies closely resemble each other except for the peak intensities, which are more than twice as high for the probe energy of 1.8 eV compared to those for a probe energy of 2.0 eV. The main contribution to the overall spectrum in both cases result from a sharp peak feature at a frequency of around 25 GHz, while there are hardly any modes at other frequencies. This reproduces very well the findings of the temperature dependent measurements. The peak amplitude at 25 GHz monotonically increases for higher excitation powers $P$. As can be seen in the excitation power dependent cut through at $f = 25$ GHz in Figure S17 c) the peak amplitude for the probe energy of $E = 1.8$ eV reveals a linear dependence of the pump power, whereas the smaller peak amplitude for the probe energy of $E = 2.0$ eV seems to be slightly flattening for higher excitation powers but all in all reveals a rather linear power dependence, too. The difference in amplitude between the two probe energies corresponds very well to the static absorption behavior and the general tendency of the amplitude $A_{\text{slow}}$ of the change in optical density.

This once again strengthens an interpretation of an elastic strain wave traveling back and forth through the thin film of PCMO, as the amplitude gets larger the more power is optically deposited in the film.

11. Power Dependence of the Slow Relaxation Process

The datasets from the power dependent measurements at room temperature were also fitted to a convolution of a stretched exponential decay and a Gaussian pulse function, as described before, for the whole available temporal delay up to about one nanosecond and for a probing energy range between 1.7 eV and 2.1 eV.

The resulting values for the amplitude were then normalized for each probe energy separately due to its strong probe energy dependence. For the parameters $A_{\text{slow}}$ (amplitude), $b_{\text{slow}}$ (stretching factor) and $\tau_{\text{slow}}$ (decay time) the mean values along the probe energy range were then calculated, in order to stress any power dependent deviation. Figure S18 shows the resulting probe energy and pump power dependence of the three parameters and their resulting mean values along the probe energy.

The relatively strong fluctuations of the mean values of the decay time $\tau_{\text{slow}}$ result from the limited accessible temporal frame up to one nanosecond, which is on the order of but shorter than the measured decay times. Furthermore the change of the optical density due to the slow relaxation process is comparably small for the lower excitation powers, which additionally increases the uncertainty for the determination of the stretching factors, which was limited to $b = 4$. The stretching factor is rather monotonously decreasing towards higher excitation powers $P$, while the decay time is continuously increasing with the pump power.

The general increase of the amplitude for higher excitation powers is due to the increased number of absorbed photons or, respectively, the larger number of photo-excited electrons within the PCMO film.
Figure S18. Probe energy and power dependence of the fitting parameter of the slow relaxation process of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ measured at room temperature. a) The amplitude $A_{\text{slow}}$ and b) its normalized correlation function. c) The stretching factor $b_{\text{slow}}$ and d) its mean values along the probe energy. e) The decay time $\tau_{\text{slow}}$ and f) its mean values along the probe energy. The error bars represent the standard deviation along the probe energy.
12. Resolution Limits of the Deconvolution

![Figure S19](image)

Figure S19. Time dependence of the change in optical density as a function of the decay time \( \tau \) for a constant amplitude \( A = 1 \), a resolution parameter \( s = 0.2 \) (200 fs) and a temporal step size of 50 fs and decay times \( \tau \) between 10 fs to 1 ps with a step size of 1 fs.

In order to investigate the resolution limits, which are achievable by the deconvolution of the measured changes in optical density, a test dataset was calculated using a constant amplitude of \( A = 1 \) and a resolution parameter \( s = 0.2 \), which corresponds to a full width at half maximum of a Gaussian pulse of 200 fs, was applied. The function was calculated for delay times 200 fs between \(-2\) ps and \(+5\) ps with a step size of \( \Delta t = 50\) fs and for decay times \( \tau \) between 10 fs and 1 ps with a step size of \( \Delta \tau = 1\) fs according to the following equation. An additional random noise \( N \) of 5% of the amplitude was added, which actually by far exceeds the experimental noise.

\[
\Delta OD = Z + N \quad (12.1)
\]

\[
Z = \frac{\sqrt{\pi}}{4\sqrt{\ln 2}} As \left(1 - \text{erf}\left(\frac{2\sqrt{\ln 2}}{s} - \frac{s^2}{8\tau \cdot \ln 2} - t\right)\right) \cdot \exp\left(-\frac{s^2}{16\tau^2 \cdot \ln 2} - \frac{t}{\tau}\right) \quad (12.2)
\]

This equation represents the convolution of an exponential decay \((A, \tau)\) and a Gaussian pulse \((s)\). The resulting data set is shown in Figure S19. The resulting curves were then fitted analogous to the measured data. The initial values for fitting were as default \( s = 0.2, A = 0.25 \) and \( \tau = 1 \).

Figure S20 shows the maximal values of the calculated changes in optical density \( \Delta OD \) as well as the resulting \( \tau \)-dependent fitting parameters \( A_{\text{fit}}, \tau_{\text{fit}} \) and \( s_{\text{fit}} \). As can be seen, the maximal values of the difference in optical density for fast decay times \( \tau \) below 1 ps exhibit a strong decrease towards shorter times, which is due to the blurring of the signal caused by the convolution of the exponential decay with the Gaussian pulse with a full width at half maximum of 200 fs.
Figure S20. (a) Maximal values of the time dependent change in optical density as a function of the decay time $\tau$ for a constant amplitude $A = 1$ and a full width at half maximum of the Gaussian curve of $s = 0.2$ (200 fs). (b)-(d) Resulting fitting parameters of a monoexponential decay fit as a function of the decay time $\tau$.

The decrease of the maximal values does not correlate with the resulting values of the fitting parameters $A_{\text{fit}}$, $\tau_{\text{fit}}$, and $s_{\text{fit}}$, which are all reproducing the expected values throughout the whole given range of decay times, except for the region of very short decay times. The given fluctuations are due to the superposition of the data sets with the 5 % random noise.

Strong deviation from the expected values occurs only for the region below the resolution limit of 200 fs and this deviation gets stronger the closer the decay time reaches to zero and is prominent for all three fitting parameters due to multiple appearances within the fitting equation.

Therefore one can conclude that for decay times, which exceed the resolution limit given by the full width at half maximum $s$ of the Gaussian curve, the reproduction of the amplitude $A$ and the decay time $\tau$ is very accurate and does not exhibit any strong deviation due to the convolution. The only parameter that is significantly influenced by the resolution limit is the maximum value of the difference in optical density. This is why a deconvolution by fitting the signal to a convolution of an exponential decay with a Gaussian curve is mandatory.
13. Orbital scheme of the Zener Polaron

The octahedral crystal field splits the d-orbitals of the Mn ions into a lower $t_{2g}$ shell and an upper $e_g$ shell. The $e_g$ orbitals point directly towards the oxygen neighbors, while the $t_{2g}$ orbitals point towards the octahedral edges and contribute only to weaker $\pi$ bonding. The $e_g$ orbitals form antibonds with the oxygen neighbors, which lifts them energetically up relative to the $t_{2g}$ orbitals. The corresponding bonding orbitals are located in the lower part of the oxygen valence band and are formally treated as oxygen orbitals.

As a consequence of Hund's rule, all valence electrons on a single Mn ion are spin aligned. The three $t_{2g}$ orbitals are always occupied and they are energetically located deep in the oxygen valence band. The $e_g$ states are located above the oxygen valence band. They are empty, when Mn is in a 4+ oxidation state, and filled with one electron in the 3+ oxidation state.

In the undoped system, such as PrMnO$_3$, with one electron in the $e_g$-shell, the $e_g$-orbitals are split into a lower, filled and an upper unoccupied Jahn-Teller state. This splitting is caused by the octahedral distortion. An expansion of the octahedron in a certain direction weakens the antibonds of the orbital pointing to those oxygen neighbors, and thus lowers its energy.

As an electron is removed from the undoped manganite, the spin structure and the Jahn-Teller distortion pattern changes. These processes make the rigid band model invalid and they change the density of states such, that usually a band gap occurs between filled and empty states.

If the electron is removed from the band of lower Jahn-Teller states, it is energetically convenient to split the lower Jahn-Teller and into a filled bonding band and an empty antibonding band. This is only possible, if the Mn ions form ferromagnetic pairs. This is the so-called double-exchange mechanism favoring a ferromagnetic alignment of the spins. The ground state of such a half-occupied ferromagnetic dimer of Mn ions is the so-called Zener polaron.

Our minimal model for the Zener polaron consists of two MnO$_6$ octahedra sharing one bridging oxygen ion. To simplify the discussion, we consider the oxygen bridge as straight and we downfold the oxygen orbitals. This down folding is a theoretical procedure that replaces the oxygen orbitals by an effective hopping between the Mn d orbitals. If oxygen orbitals are drawn, it is only to indicate where oxygen orbitals have a major contribution.

The $e_g$ orbitals of the dimer can be classified by their symmetry as $\sigma$- and $\delta$-orbitals. The $\sigma$-type orbitals preserve their sign under a fourfold rotation around the dimer axis, while the $\delta$-orbitals reverse their sign. If the two octahedra are connected along the z-direction, the $\sigma$-orbitals are the $d_{3z^2-r^2}$ orbitals on Mn and the $p_z$ orbital on oxygen. The orbitals with $\delta$ symmetry are the $d_{x^2-y^2}$ orbitals on Mn. Only the $d_{3z^2-r^2}$ can hybridize via the oxygen ion due to symmetry. To avoid confusion, let us mention that in our orbital drawings, the $z$-axis points horizontally to the right.

The splitting between the $\delta$-orbitals in Figure S21 would be completely absent in the symmetric model. A small hybridization between these states has been introduced in Figure S21 for the sake of clarity.
**Figure S21.** Orbital diagram of a Zener polaron. The left orbital diagram is for a prolate octahedron on the left and an oblate octahedron on the right side. The right diagram is for two prolate octahedra along the dimer axis. The two distortion patterns affect the energetic order of the \( e_g \) orbitals in the two octahedra.

In constructing the orbitals as shown in Figure S21, we start out from the Jahn-Teller split \( e_g \) orbitals. Orbitals with the same symmetry, either \( \sigma \) or \( \delta \), form a lower, bonding wave function, to which the orbitals on the two Mn sites contribute with equal sign, and a higher antibonding orbital with opposite sign. The splitting is negligible for the \( \delta \)-orbitals and large for the \( \sigma \)-orbitals. If the original orbitals have different energies as in the left scheme of Figure S21, the resulting hybridized orbitals are dominated by the orbital that is energetically closer.

Irrespective of the type of Jahn-Teller distortions, the lowest wave function is a bonding \( \sigma \)-orbital, which is non-bonding with respect to the oxygen p-orbital. If both octahedra are prolate along the dimer axis as in the right scheme of Figure S21, already the unhybridized \( \sigma \)-orbitals are lower resulting in a lower lying, and thus more stable wave function for the electron. It is this effect that favors this particular cooperative Jahn-Teller distortion with two neighboring prolate octahedra, which otherwise would be unfavorable due to the imposed strain.

Only the antibonding \( \sigma \)-orbital has a symmetry, that allows to accommodate an oxygen orbital. This wave function is therefore denoted as an oxygen-hole state. As the total weight of an orbital, filled and empty, equals unity, the contribution of the oxygen orbital to an empty wave function implies that this amount is missing in the occupied wave functions. This deficiency of the oxygen p-electrons is described as an oxygen hole.

The only dipole allowed transition is the one between the two \( \sigma \)-orbitals, the bonding and the antibonding one. The absorption band is strong because the transition is dipole allowed and the matrix element is large: The transition corresponds to a dipole oscillation due to the charge transfer between the two neighboring Mn sites. The transition is present irrespective of the octahedral distortions, but the one with two prolate octahedra is expected to have the larger matrix elements.

In a completely antiferromagnetic structure (G-type antiferromagnetism following Wollan [Wollan, E.O., Koehler, W.C. Phys. Rev. 100, 545 (1955)]) this transition is absent: Hund’s-rule splitting inhibits the delocalization between antiferromagnetic Mn sites. The transition between the d-orbitals on a given site is dipole forbidden.
14. The Relaxation Process in the Jahn-Teller Dimer

In order to understand the relaxation process in an optically excited Zener polaron, we investigated a dimer of two octahedra, each described by Jahn-Teller model.

A Jahn-Teller monomer describes the interaction of two e_g orbitals, d_{3z^2-r^2} and d_{x^2-y^2}, coupled to the two Jahn-Teller active octahedral distortion modes, Q_2 and Q_3. We denote the amplitude of the Q_2 modes by X and that of the Q_3 mode by Z. The mode Q_3 describes a prolate Z > 0 or oblate Z < 0 distortion of the octahedron along the z-direction, while Q_2 describes a distortion, where the octahedron is, for X > 0, expanded along the x-axis and compressed along the y-axis or vice versa for X < 0.

Adding the kinetic-energy operators for the octahedral distortions to the Born-Oppenheimer Hamiltonian yields the complete non-adiabatic Hamiltonian for electrons and nuclei. The Born-Oppenheimer Hamiltonian of each Jahn-Teller monomer is

\[ \hat{H}_{JT}^j(X_j, Z_j) = g \left( \begin{array}{c} d_{x^2-y^2,j} \\ d_{3z^2-r^2,j} \end{array} \right) \left( \begin{array}{c} Z_j \\ X_j \end{array} \right) + \frac{1}{2} g \left( X_j^2 + Z_j^2 \right) \]  \hspace{1cm} (14.1)

where j identifies a particular octahedron in the dimer and g is the electron-phonon coupling constant. The first term is the electron-phonon coupling term, which is an operator acting on the electronic wave functions. The quadratic term is the restoring energy. The prefactor of the restoring force has been chosen such that the equilibrium displacement \( \sqrt{X_j^2 + Z_j^2} \) for one electron per Jahn-Teller monomer equals unity and thus defines the length unit for the octahedral distortions.

The Jahn-Teller dimer is obtained by coupling two Jahn-Teller monomers. A hopping term is introduced between the d_{3z^2-r^2} orbitals of the two monomers. We choose octahedra that are connected along the z-direction.

\[ \hat{H}_{JTD} = \sum_{j=1,2} \hat{H}_{JT}^j(X_j, Z_j) + \begin{pmatrix} d_{3z^2-r^2,1} \\ d_{3z^2-r^2,2} \end{pmatrix} \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix} \begin{pmatrix} d_{3z^2-r^2,1} \\ d_{3z^2-r^2,2} \end{pmatrix} \]  \hspace{1cm} (14.2)

Finally, we add a term that accounts for the cooperative distortions of the environment.

\[ \hat{H}_{CJTD} = \hat{H}_{JTD} + \frac{1}{2} c \cdot \left( X_1^2 + X_2^2 + (Z_1 + Z_2 - 1)^2 \right) \]  \hspace{1cm} (14.3)

This term penalizes deviations from the equilibrium structure. The underlying idea is that the environment has adjusted in an optimal way to the equilibrium structure of the dimer, so that any deviation from it leads to a less favorable structure.
In the ground state, the symmetry-lowering distortions described by $X_1$ and $X_2$ vanish. Therefore, we introduce the simplifying assumption $X_1 = X_2 = 0$, which maps the model on an effective two-dimensional model in the $Z_1, Z_2$-plane.

Expressed in terms of the symmetric distortion coordinate $x = (Z_1 + Z_2) / 2$ and the antisymmetric distortion coordinate $y = (Z_1 - Z_2) / 2$ the Born-Oppenheimer surfaces are

$$E_j^{BO}(x, y) = g \cdot (x^2 + y^2) + 2c \cdot \left(x - \frac{1}{2}\right)^2 + g \begin{cases} -x - \sqrt{y^2 + (t / g)^2} & \text{for } j = 1 \\ +x - |y| & \text{for } j = 2 \\ +x + |y| & \text{for } j = 3 \\ -x + \sqrt{y^2 + (t / g)^2} & \text{for } j = 4 \end{cases}$$

(14.4)

The energy surfaces are not strictly energy ordered as they should be. They are rather divided into those ($j = 1, 4$) with the electron in a $\sigma$-type state and those ($j = 2, 3$) with the electron in a state with $\delta$-symmetry.

Our first-principles calculations of PCMO position the $\sigma$-antibonds, the final states of the optical transition, slightly above the states with $\delta$-symmetry. Therefore, we choose $t = g$, such that all three excited Born-Oppenheimer states are degenerate for the ground-state structure. The parameter for the cooperative effects has been set to $g$, but its effect has been investigated.

An optical excitation consists of an initial Franck-Condon transition and a subsequent relaxation process. During the initial step, which may last a few femtoseconds, the atomic structure cannot yet respond. Therefore, it proceeds in the frozen structure of the ground state, namely $Z_1 = Z_2 = x = 1/2$ and $y = 0$. The transition takes the electron from the first Born-Oppenheimer surface ($j = 1$) to the antibonding $\sigma$-state ($j = 4$).

The electron on the upper Born-Oppenheimer surface can pass through the band crossing onto the Born-Oppenheimer surface ($j = 2$) describing the state with $\delta$-symmetry.

While this process is barrier-less for the model parameters chosen, it is thermally activated in the real system. According to our ab-initio calculations, the energy surface of the $\sigma$-states lies above the one with $\delta$-symmetry. This indicates, that the minimum for the $\sigma$-states is separated from the conical intersection. Hence a thermal fluctuation is required to take the system from the minimum to the conical intersection from where it can relax into the surface of $\delta$-states.

We would stress our model too far, if we would try to extract precise times scales for the activation. However, we obtain guidance from experiment: The first relaxation process occurs on a time scale of 0.98 ps at room temperatures and 1.78 ps at low temperatures. This time scale is substantially larger than an oscillation of a Jahn-Teller mode - a time scale that would be expected if the transition was spontaneous. Furthermore, the temperature dependence in the experiment hints towards a thermally activated process. As the system undergoes a phase transition between the two temperatures considered, the latter conclusion must be taken with a grain of salt.

Once on the surface of a $\delta$-state, the system relaxes adiabatically towards the seam separating the surface of the $\delta$-states from the ground state energy surface. After passing through the conical intersection, the system can relax into the ground state without crossing the conical
intersection again. Rather, as shown in Figure 8c it can circle the conical intersection in the \((X_1, Z_1)\)-plane, that is by an octahedral distortion, which breaks the four-fold symmetry of the model. Thus the "isolated" Zener polaron model, without accounting for the environment would rapidly relax back into the ground state.

Initially, that is before the optical excitation, both octahedra are prolate along the dimer axis. In the absence of cooperative effects, that is for \(c = 0\), one octahedron relaxes into an oblate shape along the dimer axis, while the other becomes undistorted. This is because the electron localizes on one of the two Mn-sites. Such a configuration is analogous to a charge-ordered state.

The role of the cooperative effects, which are tuned by the parameter \(c\), is substantial for the formation of a long-lived hot polaron. The parameter \(c > 0\) shifts the minimum of the second energy surface towards the structure of the ground state. Beyond a critical value, a minimum on the surface of the \(\delta\)-state splits off from the conical intersection. This minimum is reached by the excitation before the system escapes through the conical intersection onto the ground-state energy surface. In that case, the system will be trapped on the second Born-Oppenheimer surface. This state would be long lived because the transition to the ground state surface is symmetry forbidden and cannot proceed by emitting light. An alternate pathway is via thermal fluctuation, that takes the system to the conical intersection, from where it can relax by radiation-less decay. This time scale is controlled by the parameter \(c\) describing the strength of the environment. The shorter one of the two decay times discussed is \(\tau_{\text{fast}}\).

15. Temperature Dependence of Open Circuit Voltage

If \(V_{\text{OC}}\) is determined by the diffusion of photo-excited charge carriers, which are separated at an interface barrier, the temperature dependent open circuit voltage is given by

\[
e V_{\text{OC}} = E_b - k_B T \gamma \quad \text{with} \quad \gamma = \ln \left\{ \frac{1}{I_{\text{SC}}} \cdot e N_v N_e \cdot \left( \frac{D_p}{n_D L_p} + \frac{D_n}{n_A L_n} \right) \right\} \quad (15.1)
\]

Here \(E_b\) denotes the barrier for charge separation. \(D_n / D_p\) are the diffusion coefficients and \(L_n / L_p\) are the diffusion lengths for electrons or holes. Far from the junction, the density of charge carriers in the conduction or valence band is given by \(n_0\) and \(n_A\), respectively. This equation is derived from the Shockley theory for quasi free charge carriers. [Shockley, W. Bell Labs Tech. J. 28:435-489 (1949)]

For polaronic charge carriers, a similar equation can be derived, where the diffusion of free carriers is replaced by rate constants, describing the lifetime and dissociation of polarons. [Giebink, N. C. et al. Phys. Rev. B 82, 155305 (2010), Ifland, B. et al. Beilstein J. of Nanotechnology 6:1467-1484 (2015)] Independent of the nature of the excited carriers, the linear temperature dependence of \(V_{\text{OC}}\) is the fingerprint of a photovoltaic effect originating from bulk diffusion of long living photo-carriers. In contrast, the open circuit voltage originating from an interface excitation of electron-hole pairs across a barrier \(E_A\) is given by

\[
V_{\text{OC}} = V_0 \cdot e^{E_A/kT} \quad (15.2)
\]
where $E_A$ is the interface barrier and $V_0$ denotes a prefactor, which depends on the photon intensity. The resulting fits and their parameters are shown in Figure S22 and the following tabular, respectively.

<table>
<thead>
<tr>
<th>For $T &lt; 195$ K</th>
<th>For $T &gt; 195$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma k_B$ [mV/K]</td>
<td>$E_b$ [meV]</td>
</tr>
<tr>
<td>-2.6</td>
<td>520</td>
</tr>
</tbody>
</table>

Figure S22. a) Temperature dependent open circuit voltage of a PCMO / STNO pn-junction under monochromatic illumination with $E = 1.55$ eV. The red lines show the resulting fits of the linear and exponential parts of the open circuit voltage. There is a unique cross over temperature resulting from the two fits as $T_{\text{cross}} = 195$ K. b) Comparison of $V_{OC}$ between monochromatic illumination at $E = 1.55$ eV and broad band illumination with a 150 W Xe-lamp. Direct measurement of $V_{OC}$ with a Keithley 2182A Nano-voltmeter is compared to extraction of $V_{OC}$ from I-V curves measured by a Keithley 2430.

The linear extrapolation of $V_{OC}(T)$ towards $T = 0$ K gives a barrier height of $E_b = 520$ meV, for monochromatic illumination and $E_b = 547$ meV for broad band illumination.

16. The contribution of heat decay to the slow relaxation process

The absorption of the pump energy generates hot electrons within the PCMO film. These electrons rapidly thermalize with the lattice on the short ps time scale ($\rightarrow \tau_{\text{fast}}$) via interactions with the phonon system, potentially forming hot polarons. Consequently, after a ps timescale, the temperature of electrons and lattice can be considered as assimilated, albeit higher than the initial temperature before pump pulse absorption. The initial temperature is then re-established via thermal diffusion of heat generated in the PCMO film into the substrate. If excited electrons form a hot polaron state, then the further thermalization is controlled by recombination processes to the ground state (process (3) and (4) in Figure 8). Since radiative recombination is dipole forbidden, the excess energy is then transformed into heat, which can also diffuse into the substrate. Since both the heat decay via thermal diffusion as well as the hot polaron decay may proceed on a nanosecond timescale, we will estimate the impact of
heat decay on the slow ns-relaxation process in this section. We simulate the absorbance drop $\Delta \text{OD}_{\text{heat}}$ and the heat decay time $\tau_{\text{heat}}$ for the case, that the absorbed pump energy is completely transformed into heat. All calculations in the following sections are based on the assumption, that the whole pump energy $Q_0$ is absorbed by the PCMO film and transformed into heat, which causes an approximately homogeneous temperature increase $\Delta T$ within a cylindrically shaped PCMO plate of volume $V = A \cdot d$ after electron-lattice equilibration. $A = \pi \cdot (100 \, \mu \text{m})^2$ corresponds to the cross section of the pump pulse and $d = 100 \, \text{nm}$ is the PCMO film thickness. Despite the depth $z$ dependence of the pump energy absorption in the PCMO film according to $\sim 1 - e^{-\alpha z}$, the assumption of a homogeneous temperature distribution within the pumped PCMO region is reasonable because the excited electrons move very fast and interact several times with the phonon system during the electron-lattice equilibration.

16.1 Estimate of heat induced $\Delta \text{OD}$

By means of static temperature dependent optical absorbance measurements (Figure S23 a)) we can determine the change of the optical density $\Delta \text{OD}_{\text{heat}}$ related to a pump induced temperature increase and compare it with the amplitude $A_{\text{slow}}$ of the slow relaxation process. If the slow relaxation process is only heat decay, we would expect $\Delta \text{OD}_{\text{heat}} = A_{\text{slow}}$.

First, the maximum temperature increase $\Delta T_0(T_i)$ within the pumped PCMO region is calculated via

$$Q_0 = m \cdot c_p(T_i) \cdot \Delta T_0(T_i) = \rho \cdot A \cdot d \cdot c_p(T_i) \cdot \Delta T_0(T_i)$$  \hspace{1cm} (16.1)

$P = 6.89 \, \text{g/cm}^3$ and $c_p(T)$ are the mass density and the specific heat of PCMO. $Q_0 = 800 \, \text{nJ}$ is the pump energy (see Section 3) and $T_i$ is the initial temperature before pump pulse absorption. Then the absorbance $\text{OD}(T)$ at an arbitrary photon energy within the probe region, e.g. $\hbar \omega = 1.75 \, \text{eV}$, is used to estimate $\Delta \text{OD}_{\text{heat}}(T_i)$ from the temperature increase $\Delta T_0(T_i)$. In Figure S23 b) this is exemplarily shown for $T_i = 300 \, \text{K}$. Here, the measured $\text{OD}(T_i)$ at $\hbar \omega = 1.75 \, \text{eV}$ is linearly extrapolated to higher temperatures.

The temperature dependence of $\Delta \text{OD}_{\text{heat}}(T_i)$ in comparison with the actual $A_{\text{slow}}(T)$ obtained from time resolved $\text{OD}(t)$ measurements as well as the calculated temperature increase $\Delta T_0(T)$ is presented in Figure S23 c). In the temperature range 100 K – 250 K the absolute value of the $A_{\text{slow}}(T)$ is about 30 – 50 % larger than $\Delta \text{OD}_{\text{heat}}(T_i)$. Since we have used the upper limit of $\Delta T_0(T_i)$ for this estimation, we conclude that in this temperature range, a pump pulse induced heating of the PCMO film alone cannot explain the OD drop after pump energy absorption.
Figure S2. a) Optical absorbance spectra of a 100 nm thick PCMO (x = 0.35) film at different temperatures. b) The absorbance at E = 1.75 eV as a function of temperature with linear extrapolation (red line) to high temperatures. The hatched box exemplifies the determination of ΔOD_{heat}(T_i) from the calculated temperature increase ΔT_0(T_i) in PCMO for T_i = 300 K. c) ΔT_0 (black line), ΔOD_{heat} (open symbols) determined with ΔT_0 and A_{slow} (solid symbols) determined via exponential fitting of time-resolved ΔOD(t) measurement as a function of the initial temperature T_i.

16.2 Heat diffusion into the MgO substrate

Because of the rather high thermal conductivity of the MgO substrate and the large aspect ratio of the pumped volume, we consider only heat transfer into the MgO substrate perpendicular to the interface and disregard in-plane heat diffusion within the PCMO film.

The heat diffusion into the MgO substrate leads to a decay of heat Q(t) in the pumped PCMO region according to

\[ Q(t) = Q_0 \cdot e^{-\frac{t}{\tau_{heat}}} \Rightarrow \frac{dQ(t)}{dt} = -\frac{Q(t)}{\tau_{heat}} \]  

(16.2)
\( \tau_{\text{heat}} \) is the characteristic decay time. Because of energy conservation, the heat decay in the PCMO film corresponds to the heat flow into the MgO substrate, i.e., \( \frac{dQ(t)}{dt} = -\frac{dQ_{\text{MgO}}(t)}{dt} \). The Fourier law describes the heat flow as

\[
\frac{dQ_{\text{MgO}}(t,T)}{dt} = \kappa_{\text{MgO}}(T) \cdot \frac{A}{s} \cdot \Delta T(t,T) \quad (16.3)
\]

where \( s \) is the penetration depth of the heat flow into MgO, \( \Delta T(t,T) \) is the temperature difference between MgO and PCMO and \( \kappa_{\text{MgO}}(T) \) is the thermal conductivity of MgO at the effective temperature \( T \). Merging both equations for \( t = 0 \) yields:

\[
\frac{Q_0}{\tau_{\text{heat}}(T)} = \kappa_{\text{MgO}}(T) \cdot \frac{A}{s} \cdot \Delta T_0(T) \quad \Rightarrow \quad \tau_{\text{heat}}(T) = \frac{Q_0 \cdot s}{\kappa_{\text{MgO}}(T) \cdot A \cdot \Delta T_0(T)} \quad (16.4)
\]

We get a rough estimate of the penetration depth \( s \) in MgO by assuming that the transfer of half of the pump energy into MgO generates a heated volume \( V = A \cdot s \) that is in thermal equilibrium with the PCMO film

\[
s = Q_0 \cdot \left( \rho_{\text{MgO}} \cdot A \cdot c_p^{\text{MgO}}(T) \cdot \Delta T_0(T) \right)^{-1} \quad (16.5)
\]

For the calculation of \( \tau_{\text{heat}}(T) \) we adopt temperature dependent \( c_p \) and \( \kappa \) data for PCMO and MgO from Refs. [Raychaudhuri, A. K. et al. Phys. Rev. B 64, 165111 (2011)], [Biswas, A. and Das, I. Phys. Rev. B 74, 172405 (2006); Handbook of physical properties of semiconductors, Springer, Volume 3: II–VI Compound Semiconductors, Chapter 1 (2004)]. Notably, the effective temperature of the MgO substrate below the pumped PCMO region is not stationary. It may range from the initial temperature \( T_1 \) to about \( T_1 + \Delta T_0(T) / 2 \) at maximum, where the thermal equilibrium between PCMO and MgO should definitely be achieved. Thus, we cannot use fixed values of \( \kappa_{\text{MgO}}(T) \) for calculating \( \tau_{\text{heat}}(T) \) with equation (16.4). To account for the temperature variation of the thermal conductivity due to heating of the MgO, we determine the maximum and the minimum values of \( \tau_{\text{heat}}(T) \) in the range \( T_1 \leq T \leq T_1 + \Delta T_0(T) / 2 \). In Figure S24 a) the range of \( \tau_{\text{heat}}(T) \) values is shown as blue hatched area in comparison with the experimentally observed relaxation time \( \tau_{\text{slow}}(T) \). The lower curve is obtained using \( \kappa_{\text{MgO}}(T) \). The upper curve corresponds to materials parameters for \( T_1 + \Delta T_0(T) / 2 \) and obviously overestimates \( \tau_{\text{heat}}(T) \). Figure S24 b) presents exponential fitting of the measured \( \Delta OD(t) \) data at 80 K and 300 K using the minimum and maximum values of \( \tau_{\text{heat}} \) as fixed fit parameters.

At room temperature we find a rather good agreement of \( \tau_{\text{slow}}(T) \) and \( \tau_{\text{heat}}(T) \) which suggests that heat decay is the predominant process underlying \( \tau_{\text{slow}}(T) \) at high temperatures. However, at low temperatures \( T_1 < 200 \text{ K} \) heat decay is faster than the experimentally observed decay. This result is in agreement with the presence of a slow relaxation process of electronic origin in addition to heat decay, particularly below the charge ordering transition temperature.
Figure S24. Simulation of the effect of heat decay via the MgO substrate on the slow ΔOD(t) relaxation. a) The experimental time constant $\tau_{\text{slow}}$ (black symbols) and the heat decay time constant $\tau_{\text{heat}}$ calculated according to equation (16.4) for temperature increase in the interval $T = [T_i, T_i + \Delta T_0(T_i) / 2]$ (blue hatched area) as a function of the initial temperature $T_i$. b) Exemplary exponential simulation of ΔOD(t) data measured at $T_i = 80$ K (blue diamonds) and $T_i = 300$ K (red diamonds) using fixed parameters $\tau_{\text{heat}}$ and $\Delta \text{OD}_{\text{heat}}(T_i)$ as amplitude at $T_i = 80$ K (blue lines) and 300 K (red lines). Solid and dotted lines represent the minimum and maximum values of $\tau_{\text{heat}}$, respectively.

16.3 Power dependence of heat decay

Based on the power dependent OD(t) measurements at room temperature shown in Sections 10 & 11, we again determine the heat induced absorbance change $\Delta \text{OD}_{\text{heat}}(P)$ from static OD(T) measurements as explained in Section 16.1 and calculate $\tau_{\text{heat}}(P)$ like in Section 16.2 as a function of the pump power $P$. The results are shown in Figure S25 in comparison with the power dependent amplitude $A_{\text{slow}}(P)$ and time constant $\tau_{\text{slow}}(P)$ of the slow relaxation process. The top axis displays the maximum temperature $T = 300 K + \Delta T_0(P)$ (calculated with the equation in Section 16.1), that can be achieved, when the whole pump power turns into heat. At high pump powers the transformation of the pump energy into heat leads to a pronounced temperature increase with temperatures up to 650 K. The determination of $\Delta \text{OD}_{\text{heat}}(P)$ via linear extrapolation of static OD(T) (see Figure S23 a)) to such high temperatures seems questionable. Since we have performed the time-resolved measurements at a pump power of $P = 0.35$ mW, we restrict the determination of $\Delta \text{OD}_{\text{heat}}(P)$ to the low pump power range where $A_{\text{slow}}(P)$ is proportional to $P$, i.e. $P = 0.8$ mW at maximum.

As presented in Figure S25 a), the heat induced absorbance drop $\Delta \text{OD}_{\text{heat}}(P)$ obtained from static OD(T) measurements matches $A_{\text{slow}}(P)$ very well for $P \leq 0.8$ mW. Again, this suggests that heat decay dominates the observed slow relaxation process at room temperature. The simulated decay time $\tau_{\text{heat}}(P)$ grows non-linearly with $P$ (Figure S25 b)) because of the pronounced decrease of $\kappa_{\text{MgO}}(T)$ with increasing temperature (c.f. equation (16.3)). The experimental time constant $\tau_{\text{slow}}(P)$ follows the same trend but seems to reach a plateau like saturation just below $P = 1$ mW and then increases even fast with increasing pump power.

The disagreement of the trends of $\tau_{\text{slow}}(P)$ and $\tau_{\text{heat}}(P)$ might indicate that even at room temperature there is another slow relaxation channel on the ns-timescale of presumably electronic nature, which evolves along with heat decay. However, at room temperature this process is of minor influence on the slow relaxation process in OD(t).
Figure S25. Pump power dependence of the fitting parameters of the slow decay process. (a) The measured amplitude $A_{\text{slow}}(P)$ (black) and the simulated heat induced absorbance drop $\Delta OD_{\text{heat}}(P)$ (blue). (b) The measured decay time $\tau_{\text{slow}}(P)$ (black) and the simulated time constant $\tau_{\text{heat}}(P)$ (blue).

In summary, the comparison of the experimental parameters obtained from the measurements with related heat decay simulations presented in this section support, that the dominant effect leading to the nanosecond decay time at temperatures above the charge ordering transition is a pump-induced heating of the electronic and polaronic system. However, below the charge ordering transition, heat decay is not capable of explaining the relatively long decay times, indicating that the observed slow relaxation process cannot be simply explained by heat diffusion.