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Transport and ordering of polarons in CER manganites PrCaMnO

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Abstract

The temperature-dependent resistivity and the colossal resistance effect induced by strong electric fields of the small-band $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO) manganites are analysed with respect to the influence of the Ca doping, post-annealing, the prehistory of the electric stimulation, and the physical dimensions of the sample. Despite the phase separation between charge and orbital ordered and disordered phases, PCMO reveals the properties of a homogeneous medium with a conductivity governed by the hopping of small polarons if the electric field is not too strong. In contrast, high electric fields induce a structural transition which gives rise to a glassy behaviour in the transient regime. In the low resistance state the small activation energy of charge carrier hopping implies a transition to large polaron hopping.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Charge transport in the low bandwidth manganite $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO) is affected by several external stimulations giving rise to colossal resistance effects. Beyond the influence of hydrostatic pressure [1, 2], photon [3] or electron exposure [4] and magnetic fields [5], high currents are even able to induce a sharp drop of the resistivity [6], the colossal electroresistance (CER).

In doped manganites with a small tolerance factor, Mn^{3+} ions are accompanied by a Jahn–Teller distortion of the lattice, which constrains the charge carrier mobility [7]. Strong electron–phonon-coupling gives rise to the formation of small polarons, and the resistivity is governed by the thermally activated hopping (TAP) of these charge carriers [8, 9]. However, the electrically insulating behaviour of the manganites is controversially discussed in the literature. Several authors interpret the experimental findings in terms of the TAP model [10], but magnetic polarons [11] as well as variable-range-hopping models (VRH) [12, 13] are also considered.

In the adiabatic limit the relation between conductivity and electric field of hopping polarons is given by [14]

$$\frac{\sigma(E, T)}{\sigma_0(T)} = \frac{E_c(T)}{E} \sinh\left(\frac{E}{E_c(T)}\right) \quad (1a)$$

with the ohmic conductivity for small electric fields E

$$\sigma_0(T) = \frac{ne^2 a^2 \omega_0}{2\pi kT} e^{-\frac{\Delta E}{kT}} = C_0/T e^{\frac{\Delta E}{kT}} \quad (1b)$$

and the crossover field E_c from ohmic to non-ohmic behaviour

$$E_c(T) = \frac{2kT}{ea}. \quad (1c)$$

Here, e is the electron charge, k the Boltzmann constant, a the polaron hopping length and n the polaron density, which can be identified with the density of e_g electrons. ω_0 is the vibrational frequency of the involved Jahn–Teller mode. The hopping energy ΔE corresponds to half of the polaron formation energy. The applicability of equation (1) is limited to temperatures greater than half of the Debye temperature $1/2\theta_D \approx 162\text{--}172\text{ K}$ [15, 16].

However, in order to test the validity of this model, the influence of polaron scattering and trapping by crystallographic defects has to be taken into account. Since the contribution of polaron–phonon scattering is small for Holstein polarons [17], equation (1b) may be written as

$$\rho(T) = \rho_0 + C_0 T e^{\frac{\Delta E'}{kT}} \quad (2)$$

in which the first term corresponds to defect scattering and $\Delta E'$ includes the contribution of polaron trapping at defects. In strongly disordered materials hopping of small polarons leads to a VHR-like temperature dependence [18].

$$\rho(T) = \rho_0 e^{\left(\frac{T_0}{T}\right)^{1/4}}. \quad (3)$$

A straightforward confirmation of the small polaron model is complicated by the intrinsic inhomogeneity of the manganites.

PCMO reveals a pronounced phase separation up to room temperature between a charge and orbital ordered $P2_1nm$ and the disordered $Pnma$ phase [19].

Due to their high density, charge carriers form a liquid of interacting mobile polarons in the disordered phase, whereas the polaronic mobility is significantly reduced by charge, polaron and orbital ordering. In the ordered state a sufficiently high current induces an order–disorder transition, which is accompanied by a strong reduction of the resistivity [19]. Moreover, quenched disorder almost present in as-prepared thin film samples suppresses the formation of the ordered phase [20]. The resistivity, therefore, reflects a complex interplay of current transport in a heterogeneous microstructure, depending on extrinsic factors like the temperature and the applied current as well as intrinsic mechanisms like the electron–phonon coupling and the interaction with defects.

In this contribution we summarize our results concerning the temperature-dependent resistivity of PCMO, taking into account the influence of the stoichiometry, post-annealing steps and the geometrical arrangement of contacts. These results give strong evidence that the charge transport in PCMO is actually governed by the hopping of small polarons. However, equation (1) does not quantitatively describe the conductivity of PCMO due to the high density of charge carriers and interaction effects. In addition, the charge carriers undergo a transition to larger polarons, if a sufficiently high current is applied, which gives rise to a glassy behaviour in the transient regime.

2. Experimental details

$\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ targets with $x = 0.32$ and 0.5 were prepared by a repeated grinding and sintering process of the stoichiometric oxides leading to a pure-phase orthorhombic PCMO. From these targets 330 nm thick films were fabricated by pulsed-laser deposition (PLD) at a deposition temperature of 1020 K and an oxygen pressure of 0.2 mbar. Using (100) oriented SrTiO_3 as a substrate material, the films reveal a c -axis orientation with a small volume fraction of the (110) misorientation due to twinning. Some of the samples were post-annealed at 1170 K in an oxygen atmosphere. This treatment leads to a pure c -axis orientation of the films [20].

For the electrical characterization gold contacts were deposited on top of the films by sputtering. The samples were mounted in a cryo-system and the resistance was monitored during a cooling–heating cycle at a fixed sweep rate of about 3.5 K min^{-1} . Voltage–current curves of a polycrystalline sample cut from the target were measured at various temperatures. Due to the high preparation temperatures the bulk sample reveals a low density of defects, unlike the as-prepared thin film samples. Most of the measurements were performed in a two-point mode, i.e. the voltage was measured at the current-leading contacts. These results will be compared with those in a four-point configuration.

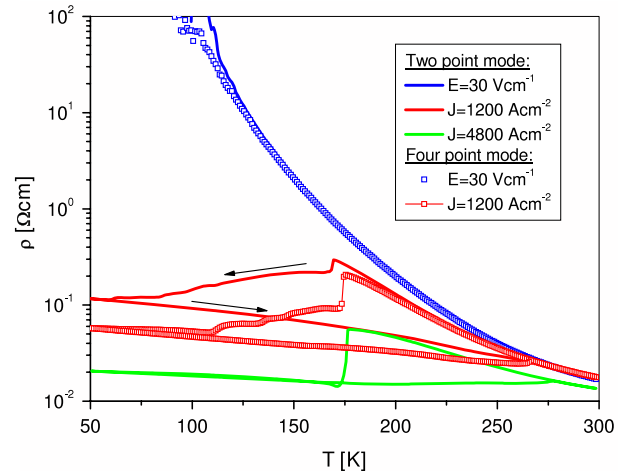


Figure 1. Comparison of two- and four-point measurements. Resistivity versus temperature at fixed electric fields E or fixed current densities J for a thin film sample with $x = 0.5$ in the as-prepared state.

3. Results

Figure 1 reveals the comparison of two- (lines) and four-point (symbols) measurements with respect to the temperature-dependent resistivity. Two different regimes have to be taken into account. Applying a small electric field, the resistivity of PCMO reveals insulating behaviour and the difference between the two measurement modes is negligible. This is in contrast to the resistivity behaviour at electric fields or currents above the critical fields for CER. The most conspicuous feature of the high-current resistivity is the sharp drop at a temperature of about 170 K. Below this step the resistivity is orders of magnitude smaller than in the insulating state. Heating up the sample, this CER state is kept up to the closing point of the hysteresis, typically between 260 and 270 K. Comparing again two- and four-point measurements the principal features are the same, but the difference is only negligible above the closing point of the hysteretic resistivity. In addition, we should clearly state here that Joule heating is not the reason for the step-like change in resistivity because, e.g., the dropping temperature is almost unchanged by increasing the current density from 1200 to 4800 A cm^{-2} .

Figure 2 reveals the current–voltage dependence of PCMO. The conductivity σ/σ_0 is plotted versus the electric field E/E^* , for a polycrystalline bulk sample ($x = 0.3$) at various temperatures. At the respective temperature, σ_0 is the ohmic conductivity and E^* is the field required to double the conductivity, i.e. the crossover field from ohmic to non-ohmic behaviour. Over a broad temperature range from room temperature down to 170 K the curves coincide, indicating that the basic transport mechanism is the same.

Fitting the ohmic conductivity σ_0 with respect to equation (1b), we find a good concurrence (inset figure 2) with reasonable activation energy of 132 meV. According to [9], the formation energy of Jahn–Teller polarons, which is twice the hopping energy, amounts to 250 meV. In addition, the crossover field increases linearly with the temperature

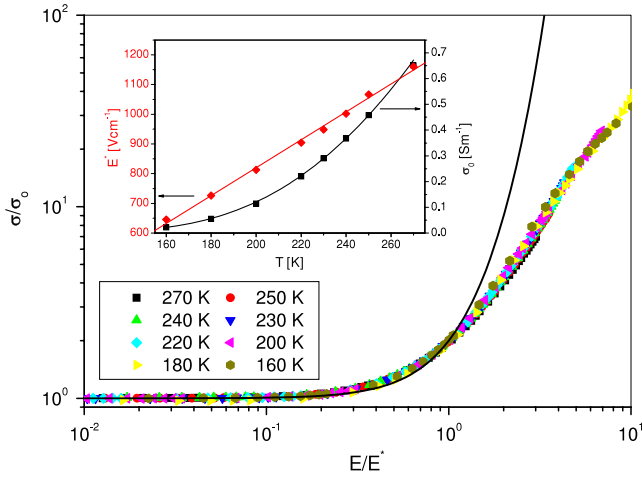


Figure 2. Current–voltage dependence. Conductivity versus electric field of a polycrystalline bulk sample ($x = 0.32$) at various temperatures. The conductivity is normalized to its ohmic value σ_0 , the electric field to the field which doubles the conductivity with respect to σ_0 . The measurement was performed in a two-point mode. The solid line is a fit with respect to equation (1a). Inset: left axis, crossover field versus temperature; right axis, ohmic conductivity versus temperature. The solid lines are fits with respect to equations (1b) and (1c); the corresponding activation energy ΔE amounts to 132 meV.

(equation (1c)). Nevertheless, at high electric fields the conductivity follows almost a power-law dependence rather than an exponential behaviour, which is expected from equation (1a). The latter is indicated by the solid line in figure 2.

A similar temperature dependence is also observed for thin films with the same Ca content. In figure 3(a) the apparent activation energy $Q(T)$ deduced from the logarithmic derivative of the resistivity is plotted versus the temperature.

$$Q(T) = k \frac{d \ln(\rho/T)}{d(1/T)}.$$

In the case of small polaron hopping Q should equal the temperature-independent hopping energy ΔE if the electric current is small. This is indeed observed down to temperatures of about 175 K, i.e. in the whole applicability range of the hopping model. With increasing current, deviations from $Q = \text{const}$ develop at consecutively higher temperatures due to the temperature dependence of the crossover from ohmic to non-ohmic behaviour.

In contrast, samples with a Ca content of $x = 0.5$ (figure 3(b)) reveal a different temperature dependence, indicated by a current-dependent maximum of the apparent activation energy. Basically, this temperature characteristic is not changed if the sample is post-annealed at high temperature; however, Q is shifted by $\approx 20\text{--}40$ meV to higher apparent activation energies. In order to reveal whether the apparent shift is due to a defect annealing induced change of the residual resistivity ρ_0 , we analyse its influence on $Q(T)$. Indeed, the temperature treatment reduces the room temperature resistivity by a factor of four (by a factor of two for $x = 0.32$), indicating a change in the residual resistivity ρ_0 due to defect

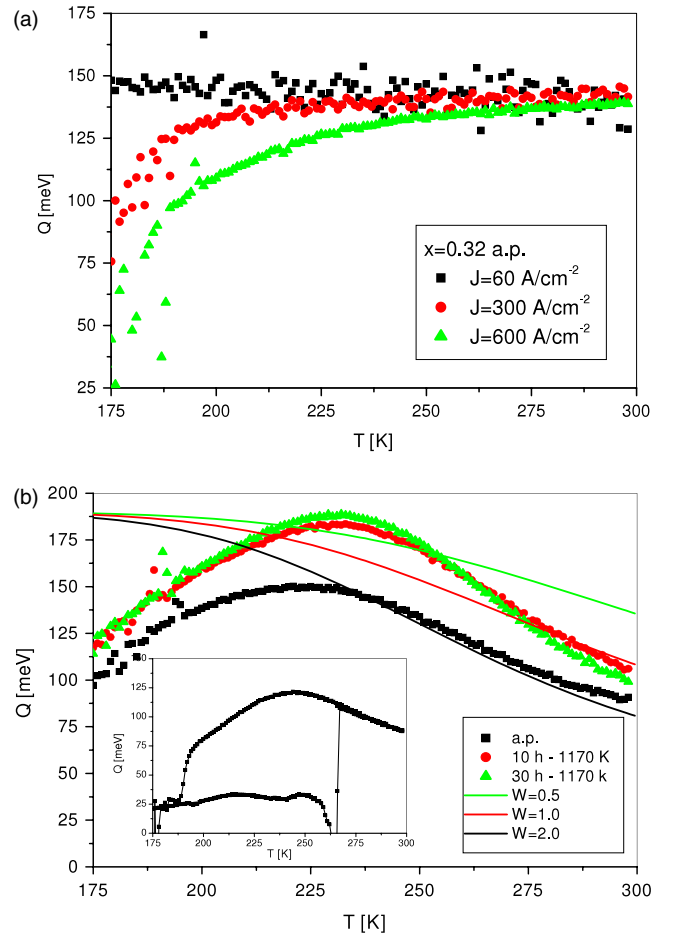


Figure 3. Dependence of the apparent activation energy $Q(T)$ on Ca doping and post-annealing times. $Q(T)$ for thin film samples deduced from cooling curves which are measured at a fixed current density J . (a) Film with $x = 0.32$ in the as-prepared state for three different J . (b) Films with $x = 0.5$ in the as-prepared and post-annealed (1170 K) states for $J = 600 \text{ A cm}^{-2}$. The solid lines are calculated from equation (2) for an activation energy $\Delta E' = 190 \text{ meV}$ and different residual resistivities $W = \rho_0/\rho_{\text{TAP}}(300 \text{ K})$. Inset: cooling and heating curves for the 30 h annealed film (1170 K) at $J = 4800 \text{ A cm}^{-2}$.

annihilation. We have estimated $\rho_0 \approx 4 \text{ m}\Omega \text{ cm}$ by taking the high-temperature limit of $\rho(T)$ at a temperature of 550 K for the annealed samples with high doping ($x = 0.5$). Also after the high-temperature treatment ρ_0 is comparable to the TAP resistivity at room temperature.

It follows directly from equation (2) that a residual resistivity leads to an apparent activation energy Q which increases with decreasing temperature and decreasing ρ_0 . In figure 3(b) Q is calculated by applying equation (2) for three different resistivity ratios $W = \rho_0/\rho_{\text{TAP}}(300 \text{ K}) = 0.5, 1.0$ and 2.0 , assuming a rather high hopping energy of about 190 meV (solid lines). Although there is some rough agreement, the consideration of a temperature-independent residual resistivity due to polaronic scattering cannot explain either the maximum in $Q(T)$ or the slope of this dependence. The slope of $Q(T)$ above the maximum should decrease due to defect annihilation, in contrast to the experimental data. Nevertheless, the temperature dependence of the TAP resistivity clearly fits

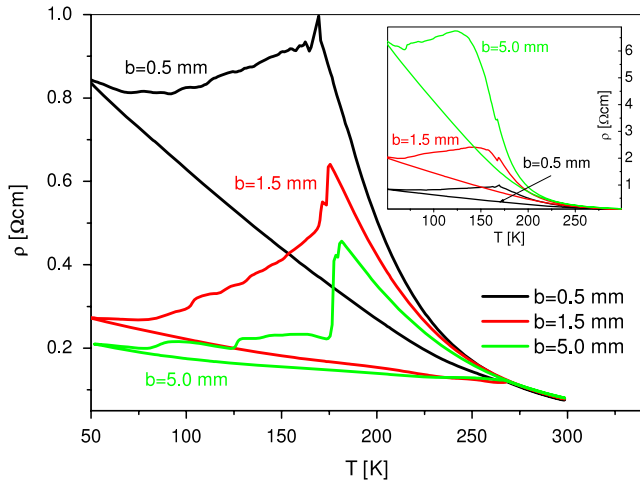


Figure 4. Scaling of the resistance with sample dimensions. Resistivity versus temperature at a fixed current density of $J = 1000 \text{ A cm}^{-2}$ and a fixed current of $I = 1.7 \text{ mA}$ (inset) for a thin film sample with $x = 0.5$ in the as-prepared state. Bridges with width of $b = 0.5, 1.5$ and 5 mm are patterned from the same film.

the experimental results better than the variable range hopping model (equation (3)), which is more appropriate for strongly disordered materials.

If the current is high enough to enable colossal resistance effects, the PCMO cannot be considered as a homogeneous medium. In order to emphasize this, figure 4 reveals the resistivity of bridges with different widths b prepared on the same substrate. For a sample with homogeneous resistivity one may expect that the resistance R is inversely proportional to the cross section, i.e. the width b and the thickness d . This is indeed observed in all experiments above the closing temperature of the hysteresis. In contrast, below the closing temperature, the resistivity decreases with increasing b at fixed current density (figure 4) and increases with b at fixed current (inset figure 4). This anomalous behaviour cannot be explained by a contact resistance in a two-point measurement, because, at a fixed current, the resistivity decreases with decreasing current density (inset figure 4). The same systematic behaviour is observed if the cross section of the film is varied by changing the thickness of the samples. Consequently, in the hysteretic part, the resistivity is not controlled either by the current density or by the current.

In the temperature window below the closing point down to low temperatures, the resistivity behaviour is strongly influenced by the electric and thermal history of the sample. For the cooling branch of the $\rho(T)$ curves, the drop in resistivity appears in a small temperature window at about 170 K. Almost unaffected by the applied current, the maximum resistivity corresponds to an electric field which amounts to 530–650 V cm^{-1} for $x = 0.3$ and 300–350 V cm^{-1} for $x = 0.5$, respectively. However a CER can also be induced by quite different fields and temperatures if the time dependence is taken into account. Impressing an electric field on the sample in an isothermal experiment, the CER can proceed after a holding time of several seconds (figure 5). In this measurement ($x = 0.3, T = 125 \text{ K}$), the CER is induced by applying a field

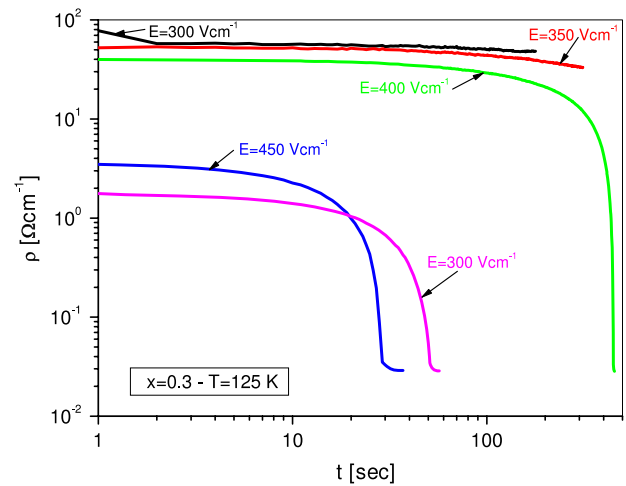


Figure 5. Time dependence of the resistivity at a fixed temperature of 125 K at different electric fields for an as-prepared thin film with $x = 0.32$. Having induced a CER at 400 V cm^{-1} , a much smaller field of 300 V cm^{-1} enables the transition.

of 400 V cm^{-1} . After such an initialization the original state is not recovered by switching off the voltage. The samples remains in a state of enhanced mobility and the CER can be induced by a much smaller field of 300 V cm^{-1} (see also [21]). A reversible behaviour is only observed at temperatures above 200 K.

4. Discussion

The model of thermally activated hopping of small polarons condensed in equations (1) reasonably depicts the temperature and field dependence of the resistivity if the currents are not too high. In the ohmic regime the resistivity complies with the properties of a homogeneous system: scaling with the dimensions of the sample and interface effects do not play a significant role. The hopping energy for a Ca content of 0.3 amounts to 130 meV for bulk and to 150 meV for thin film samples. This energy is expected for Jahn–Teller-polarons and the difference might be caused by trapping effects. Surprisingly, this approximate applicability is valid for the charge-orbital-polaron disordered as well for the ordered states above and below the bulk ordering temperature of 230 K. A probable reason seems to be the phase separation in a temperature window between 300 and 80 K [19, 22] which may blur the differences between ordered and disordered polarons in macroscopic measurements.

Analysing the quantitative validity of equations (1), we find that the magnitude of the resistivity is much smaller than predicted by the pre-factor C_0 in equation (1b). Considering typical values for the hole density ($n = 1.3 \times 10^{27} \text{ m}^{-3}$), the Jahn–Teller Q_2 mode ($\omega_0 = 1.4 \times 10^{13} \text{ Hz}$ [23]) and the hopping length as the next neighbour distance in the ab -plane ($a = 0.38 \text{ nm}$), C_0 ($x = 0.3$) should be of the order of 1 $\mu\Omega \text{ m K}^{-1}$. Experimentally, we observe a value of about $10^{-2} \mu\Omega \text{ m K}^{-1}$ for as-prepared samples.

In addition, the agreement between the hopping model and the experimental results is less satisfying, if the hole

doping is increased from $x = 0.32$ to 0.5. Although we cannot completely rule out a higher density of defects in thin film samples with higher Ca content, we expect that both the lack of quantitative agreement and the increasing deviations at higher Ca contents are a consequence of the high charge carrier densities. The TAP model is suitable for individual non-correlated polaron hopping, but the polarons in doped manganites should be regarded as a strongly interacting polaronic liquid. For a Ca content of $x = 0.5$ the maximum of the apparent activation energy is observed at a temperature of about 230 K (figure 3(b)), which is frequently attributed to charge ordering [23]. Since coherent polaron motion has been observed in polaron ordered nanodomains in the phase-separated state of PCMO [19], this gives strong evidence for a collective behaviour of the polaronic system. Coherent hopping might be an effective mechanism to reduce the pre-factor C_0 in comparison to the single polaron hopping which is assumed in equation (1).

Cooling down to low temperatures the carrier mobility vanishes and the polarons pass into a ‘solid state’. Depending on the level of crystallographic disorder this state is amorphous or a long-range ordered ‘polaron crystal’. In the latter case the out-freezing of mobility is accompanied by a structural transition of first order [19]. This process can be inverted by applying a sufficiently high current, inducing the colossal electroresistance effect. However, the current-induced state does not simply reflect the transport properties of the disordered $Pnma$ high-temperature phase. In a persistent current mode the CER state is stable up to rather high temperatures and the resistivity reveals a TAP-like temperature dependence but with an activation energy which amounts only to about 25 meV (inset figure 3). We expect that polaronic ordering is an essential pre-condition which might give rise to an enhanced double exchange or a soft-mode lattice response becoming slow in comparison to the hopping frequency in the highly driven state. We expect that both mechanisms should reduce the pre-factor C_0 at low currents, and, at high currents, strongly diminish the effective activation barrier, leading to a more band-like carrier mobility.

The CER is also observed in the amorphous state of solidified polarons [20], in which short-range ordering seems to play a similar role. As we have shown in a preceding contribution, the current-induced order–disorder transition in the vicinity of an interface to a metallic contact differs from those in the bulk due to the presence of a Schottky barrier [24]. Therefore, the difference between two-point and four-point measurements (figure 1) reflects the intrinsic properties of the interface with respect to the current-induced transition. It is not surprising that the CER transition regime reveals some kind of ‘glassy’ behaviour. The electric transport takes place in path-like structures [3] and the electric response is not a unique function of the applied external field. Consequently, the resistivity depends on the timescale, the modality and the previous history of the electric stimulation. An electric-current-based characterization of the temperature-dependent CER seems to be more convenient because a mean electric field, defined by the contact distance, does not reflect the local field distribution closely connected with the CER in

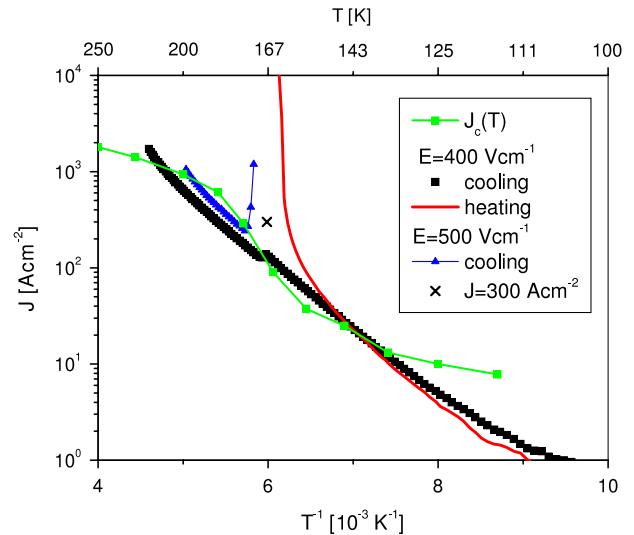


Figure 6. CER due to different electric stimulations and prehistories. The plot shows the current density J versus temperature for an as-prepared thin film with $x = 0.32$. Solid lines represent J at a fixed electric field. The strong increase of the current indicates the onset of the CER in the heating curve with $E = 400 \text{ V cm}^{-1}$ and the cooling curve with $E = 500 \text{ V cm}^{-1}$. Squares: J_c deduced from time-dependent measurements (see figure 5). Cross: CER in a cooling experiment with constant current density (see figure 1).

the inhomogeneous phase-separated medium. However, the current density $J(E, T)$ is also not a unique function of electric field and temperature. Figure 6 shows $J(T)$ as a function of temperature for different electric stimulations and prehistories for films with $x = 0.32$. Cooling down at a fixed ‘subcritical electric field’ of 400 V cm^{-1} , the current density decreases exponentially with decreasing temperature in accordance with the TAP model and a CER is not induced. Applying the same electric field at low temperature, the temperature dependence is altered and a CER takes place at about 160 K. A CER during cooling requires an electric field of 500 V cm^{-1} . For comparison the cross in figure 6 denotes the transition point in a fixed current experiment shown in figure 1.

Comparing these various experiments with different temperature-dependent prehistories of the electric stimulation we have to accent that there exists no true critical current density which induces a CER by all means, illustrating the glassy behaviour of the transient regime. Nevertheless, cooling down the sample to its virgin state at a fixed temperature, J_c can be defined as the current density which enables a CER within a time window of 10 min (see figure 5 and the symbols in figure 6, respectively). It reflects the current density at which CER-related effects have to be taken into account.

In summary, our results indicate that Jahn–Teller polarons govern the conductivity in PCMO, but correlation effects due to the high density of charge carriers and ordering have to be taken into account. Applying strong electric fields leads to the low-resistivity CER state, which is stable up to 270 K and in which the mobility of the polarons is strongly enhanced. The transition between these two states is accompanied by a structural transition, giving rise to a resistivity which does not scale with the sample’s dimensions and sensitively depends

on the timescale, the modality and the previous history of the electric stimulation.

Acknowledgments

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