Effects of interaction and disorder on polarons in colossal resistance manganite $Pr_{0.68}Ca_{0.32}MnO_3$ thin films

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Abstract

The colossal magnetoresistance effect (CMR), the drop of the electric resistance by orders of magnitude in a strong magnetic field, is a fascinating property of strongly correlated electrons in doped manganites. Here, we present a detailed analysis of the magnetotransport properties of small polarons in thin films of the low bandwidth manganite $Pr_{0.68}Ca_{0.32}MnO_3$ with different degrees of preparation-induced octahedral disorder. The crystal and defect structure is investigated by means of high-resolution transmission electron microscopy. We apply the small polaron theory developed by Firsov and Lang in order to study the hopping mobility in the paramagnetic phase and its changes due to the formation of the antiferromagnetic charge ordered (CO) and the ferromagnetic metallic phases. Although it represents a single particle theory, reasonable estimates of small polaron properties such as formation energy, activation energy and transfer integral are possible, if the effects of interactions and disorder are taken into account. Beyond the well-known effect of the magnetic double exchange on the transfer integral, we show that the emergence of band transport of small polarons in the CMR transition sensibly depends on the degree of octahedral disorder, the polaron–polaron interactions and the resulting long range order leading to a structural phase transition in the CO phase.

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1. Introduction

Almost 20 years ago, a seminal publication of Millis et al [1] stated that magnetic double exchange alone cannot explain the magnetoelectric transport behavior of manganites and thus the interplay of double exchange and polaronic effects had to be addressed. Since then, it has been well accepted that the semiconductor-like mobility of manganites is caused by the hopping of small polarons (see oxygen isotope effect in Nd$_{1-x}$Sr$_x$MnO$_3$ and La$_{1-x}$Ca$_x$MnO$_3$ [2], IR study of La$_{1-x}$Ca$_x$MnO$_3$ [3] and electric transport in Pr$_{1-x}$Ca$_x$MnO$_3$ [4, 5]). Furthermore, even in the ferromagnetic metallic (FMM) phase of manganites, where the magnetic double exchange interaction induces an enhanced mobility of quasiparticles, evidence for the presence of small polaron band like transport is found (for La$_{1-x}$Ca$_x$MnO$_3$ see [6, 7]).

Small polarons represent self-trapped charge carriers in a ‘cage-like’ lattice distortion with a size comparable to the lattice constant [8]. Small polaron theory [9, 10] predicts that such quasiparticles show fundamentally different transport regimes, i.e., incoherent thermally activated hopping (TAH) transport at high temperatures and coherent band-like transport at low temperatures. The transition between both transport regimes depends on the electronic bandwidth $D$ [11]. In manganites, $D$ is controlled by the octahedral tilt, which thus determines whether a FMM or an antiferromagnetic charge ordered (CO) ground state is formed at low temperature and intermediate doping [12].

In this contribution, we investigate the polaron magnetotransport in Pr$_{1-x}$Ca$_x$MnO$_3$ manganite thin films at doping $x=0.32/0.34$ (PCMO) and different degrees of octahedral disorder. PCMO belongs to the low bandwidth manganites with an antiferromagnetic CO ground state below $T_{CO}=240$ K. The electronic overlap seems to be rather small. DFT studies [13], see also supplemental (S1), available at stacks.iop.org/MRX/1/046403/mmedia, imply that the unrenormalized bandwidth $D$ is in the range of 760–1300 meV. This corresponds to transfer integrals $J=D/(2*Z)$ between 60 and 110 meV, where $Z=6$ is the coordination number of the Mn site. Because of the magnetic double exchange interaction, magnetically induced spin alignment can increase the transfer integral by about 0.4 J [1]. In the FMM phase of PCMO, the increase of $J$ may enable the colossal magnetoresistance effect (CMR) transition via an increase of the small polaron band-like mobility or due to the formation of new quasiparticles [14, 15].

Figure 1(a) shows the typical hopping conductivity for a well annealed PCMO film at zero magnetic field which persists over a large temperature range down to low temperatures. Applying a sufficiently strong magnetic field $B$ induces an insulator to metal transition (CMR) from hopping conductivity to ‘metal like’ conductivity below a transition temperature $T_{CMR}$. The transition temperature increases and the residual low-temperature resistivity $\rho_B$ decreases with increasing magnetic field. Lattice distortions locally change the Mn-O bond distances as well as bond angles and can thus alter the transfer integral. Indeed, the CMR transition is sensitively affected by preparation-caused lattice disorder. Remarkably, the CMR transition measured at constant magnetic field and increasing post-annealing time of the sample behaves
quite similar to the CMR transition measured at increasing field in a well annealed sample (compare figures 1(a) and (b)).

Analyzing polaron quasiparticles in the paramagnetic charge disordered Pbnm, the antiferromagnetic CO P21mn and the ferromagnetic FMM phases of PCMO by the single particle polaron theory must be done with care. The magnetic field dependent electronic overlap, the strong influence of crystallographic defects, and inter-site Coulomb interactions due to the high polaron carrier density have to be taken into account. The latter are expected to increase significantly the activation energy for hopping transport [16] and are involved in the formation of polaron long-range order, which induces a structural phase transition between the charge disordered and the CO phases [17]. In addition, the first-order phase transition undergoes via phase separation and gives rise to two phase regions over large temperature ranges down to 85 K.

In order to present the effect of disorder on the phase formation and the small polaron properties in the different phases, the manuscript is organized as follows: after presenting some details on thin film preparation (section 2), we give a brief summary of the studies of the crystallographic structure and defects and show that nano-twins and octahedral disorder are the
most common defects in as-prepared PCMO thin films. They result in an inhomogeneous stress-strain state of the films (section 3).

The results on polaron magnetotransport behavior are presented in two main sections: the hopping transport of small polarons at high temperatures (150–300 K) at variable magnetic fields (section 4) and the band-like transport at low temperatures (10–50 K) in large magnetic fields (section 5). Both sections start with a summary of the small polaron theory by Firsov and Lang [11, 18]. In section 6, we show that this theory can be well applied to the three phases of PCMO, if corrections due to magnetic double exchange, Coulomb interaction between carriers and lattice disorder have been taken into account. The influence of defects on individual polaron properties seems to be rather weak in the Pbnm phase, but the charge ordering transition to the P2_1/mn phases strongly depends on octahedral disorder. Due to the small polaronic bandwidth, the band-like mobility in the FMM phase sensitively depends on spin misalignment and structural disorder. In samples with a high degree of octahedral disorder, we find a suppression of the polaron long-range ordering, which coincides with the suppression of the CMR. We thus suggest a common crystallographic origin.

2. Experimental

In order to investigate the influence of preparation-caused defects, the deposition of the Pr_{1-x}Ca_xMnO_3 thin film samples (d=100/300 nm) was performed by two different methods: pulsed-laser-deposition (samples PLD-X: x = 0.32, T_{dep} = 1023 K, PO_2 = 0.2 mbar) and ion-beam-sputtering (samples IBS-X: x = 0.34, T_{dep} = 973–1073 K, PO_2 = 10^{-4} mbar). Single-crystalline (100) SrTiO_3 (STO) and MgO were used as substrates. They were fixed on the heaters with silver paste to ensure well-reproducible thermal coupling. The parameters of the samples are summarized in table 1.

As-prepared films do not reveal a fully developed CMR. A further increase of T_{dep} is not possible, because too high deposition temperatures (≥1100 K) give rise to growth distortion, e.g., visible in a pronounced surface roughness. Therefore, films were post-annealed in a furnace at 1173 K for annealing times t_a between 3 h and 80 h under air. The sample which was annealed for 80 h shows interdiffusion of Sr and Ca in region of maximum 20 nm thickness near the interface between film and substrate as revealed by secondary ion mass spectroscopy.

Two and four terminal transport properties were measured in a physical property measurement system in the temperature range from 10 K to 300 K and in magnetic fields up to 9 T. Au contacts on the PCMO films are prepared by room temperature sputter deposition. Optical absorption spectroscopy with unpolarized light in the NIR–VIS spectral range was performed using a Varian Cary 5e at different temperatures between 300 K and 80 K.

Transmission electron microscopy (TEM) results presented in this paper were obtained using the JEOL3000F TEM/STEM, equipped with an ultra-high resolution objective-lens pole-piece and an off-axis 1024×1024 Gatan slow-scan camera. The instrument can be operated in either TEM or STEM mode and is equipped with a liquid-N_2 cooling sample holder. The single-domain electron diffraction was obtained either by selected-area electron diffraction (SAED), that can select a small area with a diameter of about 120 nm, or by nano-diffraction with a beam diameter of a few nanometers.
3. Crystallographic structure and defects

All films under consideration reveal epitaxial growth with a predominant (001) orientation. Due to the structural phase transition in a temperature range of 1100–1200 K [19], six orientation variants of the orthorhombic Pbnm unit cell are inevitably present, which all stem from the same pseudocubic R̅3c parent structure at high temperatures. Such a type of twin formation gives rise to the presence of (110) domains with a volume ratio of 10%–50%, which has been confirmed by x-ray inspections and TEM.

The lattice mismatch between PCMO and both types of substrates implies tensile in-plane strain, i.e., a contraction of the unit cell perpendicular to the substrate is expected [20]. Commonly, films on STO reveal such a contraction whereas the c-axis of films on MgO is elongated. However, depending on the exact deposition conditions, compressive in-plane strain of PCMO on STO can be also observed [21] or can evolve during post-annealing. Consequently, preparation induced lattice disorder seems to dominate over substrate induced misfit strain. Defect annihilation with increasing deposition temperature or post-annealing time gives rise to higher CMR transition temperatures. However, we observe no simple relation between the global lattice strain and the appearance of CMR [see also 22]. The CMR transition temperatures of the samples are given in table 1.

| Sample | Substrate | T_{dep} (K) | t_a [h] | T_{CMR} at 9 T (K) |
|--------|-----------|-------------|---------|-------------------|
| PLD-1  | STO       | 1023        | a.p.    | No CMR            |
|        |           |             | 2       | 69                |
|        |           |             | 5       | 83                |
|        |           |             | 10      | 102               |
|        |           |             | 20      | 126               |
|        |           |             | 40      | 170               |
|        |           |             | 80      | 190               |
| PLD-2  | STO       | 1023        | a.p.    | No CMR            |
|        |           |             | 2       | No CMR            |
|        |           |             | 5       | No CMR            |
|        |           |             | 10      | 45                |
|        |           |             | 20      | 65                |
|        |           |             | 40      | 81                |
|        |           |             | 80      | 94                |
| IBS-1  | STO       | 973         | a.p.    | No CMR            |
| IBS-2  | STO       | 973         | 20      | No CMR            |
| IBS-3* | STO       | 1023        | a.p.    | No CMR            |
| IBS-4* | MgO       | 1023        | a.p.    | 63                |
| IBS-5  | MgO       | 1023        | 10 (1073 K) | 90 |
| IBS-6  | STO       | 1073        | a.p.    | 75                |

PLD and IBS correspond to the method of preparation, i.e., to pulsed-laser-deposition and ion-beam-sputtering. Post-annealing was performed at 1173 K for t_a h. The samples marked by (*) were prepared in the same run. With exception of sample IBS-5 (d=100 nm) the sample thickness was fixed to 300 nm.
We have performed a detailed analysis of the crystallographic structure (for schematic visualization, see figure 11) and crystallographic defects in PCMO films by means of high resolution transmission electron microscopy (HRTEM) and SAED. Figure 2 shows results of a temperature dependent TEM study of an annealed PLD film ($t_a = 20$ h). At room temperature, i.e., above the charge ordering temperature, the film only exhibits the orthorhombic Pbnm structure. This space group only allows a uniform Mn-O-Mn bonding angle. Its value can be calculated from the lattice parameters of this phase to $153^\circ$.

Cooling down to $T = 85$ K, large sample areas show up a superstructure (figure 2(c)), where the crystallographic $b$-axis is doubled (figure 2(d)). Careful analysis of this type of superstructure in bulk samples of the same composition has revealed that the doubling of the $b$-lattice parameter is uniquely related to the P2$_1$mn phase [23]. The phase transition is of first

Figure 2. Analysis of the charge disordered (Pbnm) and charge ordered (P2$_1$mn) phases with HRTEM and SAED in a planar view TEM sample prepared of sample PLD-1 ($t_a = 20$ h). (a) [001]-grown twin of a size of several $\mu$m imaged at [001] zone axis. The two dark contrasts mark crystallographic defects, most probably anti-phase boundaries. (b) Electron diffraction, no superstructure is visible. (c), (d) Same area as in (a) after cooling down to $T = 85$. The evolution of the charge ordered superstructure along the crystallographic $b$-direction can be visualized in the HRTEM image (area marked with CO) and (d) is seen by SAED.
order, where the $b$-lattice parameter shrinks by about 1% from $b = 5.48 \text{ Å}$ in Pbnm to $b/2 = 5.39 \text{ Å}$ in the P2$_{1}$mn structure. Since method and results for structure determination of the CO insulating phase for $x=0.5$ is presented in detail in [23], our refinement for $x=0.32$ is only briefly summarized in the supplemental material (S2) and is visualized in figure 11(b).

The appearance of the P2$_{1}$mn phase is an indication for charge-ordering of the Zener polaron type, where hole states order at oxygen sites with locally flattened bond angles of about $160.6^\circ$, separated by bonds with much lower angle of about $157.7^\circ$ and $155.5^\circ$ as revealed by the refinement in (S2) (see [17, 23] for $x=0.5$). At 85 K, the volume ratio of the CO phase is estimated to be about 80%. Warming up to 200 K, the CO phase has been almost entirely disappeared. Therefore, the region of phase separation extends on a temperature range between 85 and 200 K. This shows that the charge ordering temperature $T_{CO}$ is somewhat reduced in moderately annealed films compared to single crystals.

In contrast to annealed films, as-prepared epitaxial PCMO films do not show CO phases at temperatures between 300 and 85 K. Such as-prepared films typically show two types of nano-scale defects: nano-twins (figure 3(a)) and disorder in the $c$-lattice parameter (figures 3(b)–(d)). The size of the individual twins extends from 100 nm down to a few unit cells (figure 3(a)). Annealing leads to a complete annihilation of such nano-twins and depending on the annealing time, the size of the twin domains increases up to several $\mu$m.

The presence of disorder in the $c$-lattice parameter can be deduced from the SAED image in figure 3(c) by the streak-like diffusive contrast in the vicinity of the [001] Bragg reflections. Figure 3(d) shows such a line profile of the [002] Bragg peak along the [001] direction. The continuous diffuse intensity is superimposed by two small maxima at incommensurate lattice modulations of $1/\Delta q_{1} = 36.0 \text{ Å} (4.7c)$ and $1/\Delta q_{2} = 19.7 \text{ Å} (2.6c)$ with $c = 7.68 \text{ Å}$ the lattice parameter of the undistorted crystal. No pronounced diffusive scattering contrast is found in other crystallographic directions. This rules out that the main origin of the variation of the $c$-axis lattice parameter is due to isotropic point defects. This type of octahedral disorder was not found in HRTEM studies of annealed films.

Twin boundaries represent coherent interfaces between the six twin domains. The lattice misfit between the domains is accommodated by long range lattice strain of the order of 1% at the twin boundaries. Both, twinning related strain as well as distortions in the long-range order of the $c$-lattice parameter, represent an inhomogeneous stress-strain state of the films. In contrast to homogeneous strain, inhomogeneous strain causes local variations in the octahedral tilt system and therefore local changes of the polaron properties such as e.g., the transfer integral.

4. Hopping mobility at high temperatures

4.1. Model of small polaron hopping and polaron formation energy

According to Firsov et al [18], the temperature dependent resistivity due to TAH of small polarons is given by

$$\rho(T) = \frac{\hbar \cdot a_{0}}{Z \cdot e^{2} \cdot c^{2} \cdot x \cdot (1-x) \cdot k_{B} T}{E_{Ph} f^{-1} \left( \frac{E_{A}}{k_{B} T} \right) e^{\frac{E_{A}}{k_{B} T}}} \equiv \rho_{0} T^{q} e^{\frac{E_{A}}{k_{B} T}}. \quad (1)$$

Here, $E_{A}$ is the activation barrier, $E_{Ph} = \hbar \omega_{Ph}$ is the phonon energy and $a_{0}$ is the hopping distance. Constants have their usual meaning. The pre-factor $\rho_{0}$ depends on the parameter $\eta_{2}$, being defined as
Figure 3. Characterization of structural disorder in a PCMO film without annealing (sample type PLD-1). (a) Nano-twinning in a grain visualized by bright field HRTEM in the [001] zone axis. In the nano-scale [011]-grown twin domain shown in the inset, the $c$-axis is directed normal to the twin boundary. (b) HRTEM bright field image of the same film in the [010] zone axis. Disorder in the $c$-axis lattice parameter is visible as dark and bright contrast. (c) SAED image, showing disorder via extensive diffuse scattering along the [001] direction, which is also visible in the Fourier transformation of the disordered area in (b) (not shown). (d) Line profile of the [002] Bragg peak taken along the [001] direction. The diffracted intensities belong to a lattice spacing of $d_{002} = 3.84 \text{ Å}$ (maximum intensity 14 000) and incommensurable lattice modulations of $1/\Delta q_1 = 36.0 \text{ Å (4.7c)}$ and $1/\Delta q_2 = 19.7 \text{ Å (2.6c)}$.

The polaron formation energy $E_p$ can be extracted from optical spectroscopy data (for manganites, e.g., see [3]). Optically induced intra-band transitions which correspond to hopping between adjacent sites give rise to a skewed Gaussian absorption peak approximately centered on a shifted peak maximum. The functional form for the polaron formation energy is given by

$$
\eta_2 = \frac{J^2}{E_{ph} \sqrt{E_a k_B T}} f(\eta_2) = \begin{cases} 
\pi^{3/2} \eta_2, & (\eta_2 \ll 1) \\
1, & (\eta_2 > 1)
\end{cases},
$$

where $\eta_2 > 1$ ($q = 1$) corresponds to the adiabatic and $\eta_2 \ll 1$ ($q = 1.5$) to non-adiabatic hopping. The extra term $x(1-x)$ has been included to take into account on-site Coulomb repulsion [24].
at photon frequencies $\hbar \omega = 2E_p$. The real part of the optical conductivity is [25, 26]

$$\text{Re} \left( \sigma (\omega, T) \right) = \sigma_{dc} (T) \frac{\sinh \left( \frac{\hbar \omega}{2E_{\text{vib}}} \right)}{\hbar \omega} \frac{E_{\text{vib}}}{2E_p} \left( \frac{\hbar \omega}{2E_{\text{vib}}} \right)^2 e^{-\left( \frac{\hbar \omega}{2E_{\text{vib}}} \right)^2 E_{\text{vib}}/2E_p}. \quad (2)$$

$E_{\text{vib}}$ is the phonon zero-point energy $\hbar \omega_{\text{Ph}}/2$ at low temperatures and corresponds to $k_B T$ at high temperatures. Equation (2) requires that the peak width is mainly governed by phonon-induced broadening. In the Firsov–Lang theory this implies that $\sigma_{dc}$ is the non-adiabatic hopping conductivity and that the quantity $\eta_3$ is small [11].

$$\eta_3 = \frac{J^2}{E_a \cdot k_B \cdot T}. \quad (2a)$$

### 4.2. Application to PCMO

Sometimes, the variable range hopping (VRH) model proposed by Mott [27] has been applied to the semiconductor-like resistivity of low bandwidth manganites. However, impurity hopping conductivity is expected at temperatures well below half of the Debye temperature [28], which is of order of $\Theta_{\text{Debye}} \approx 320 \text{ K}$ [29]. By fitting the VRH model to the experimental data we can exclude the applicability of this model to PCMO in the temperature range from about 100 to 300 K even for as-prepared films with strong lattice disorder. Therefore, we have focused our analysis on the model of TAH.

For PCMO, a doping level of 0.32 Ca atoms per pseudo-cubic unit cell with a lattice parameter of $a_0 = 3.86 \text{ Å}$ corresponds to a polaron charge density of about $n = 5.6 \times 10^{21} \text{ cm}^{-3}$. The coordination of the polaron lattice site is $Z = 6$ and the hopping distance between next-neighbored Mn or O sites equals the lattice constant $a_0$. A clear identification of the phonon mode relevant for small polaron formation is still missing. There is strong evidence that both the Jahn–Teller phonon mode at $E_{\text{Ph}} = 71 \text{ meV}$ as well as octahedral bending modes, e.g., at $E_{\text{Ph}} = 42 \text{ meV}$ can couple to the charge dynamics of Pr$_{1-x}$Ca$_x$MnO$_3$ in a wide temperature range [30–32]. Consequently, quantitative estimates of polaron properties are exemplarily done for both phonon modes.

It is hardly possible to distinguish via dc transport measurements whether hopping of polarons evolves adiabatically or non-adiabatically. For an activation energy $E_A$ of about 140 meV and transfer integral $J$ ranging from 60 to 110 meV (supplemental material (S1)), the parameter $\eta_2$ amounts to 0.8–2.8 (1.4–4.8), dependent on whether a Jahn–Teller or a Mn-O-Mn bending mode is selected.

We therefore assume that the hopping in PCMO is close to the adiabatic limit. In this limit, equation (1) gives a room temperature resistivity of $\rho(T = 300 \text{ K}) \approx 0.06 \text{ (0.1) } \Omega \text{ cm}$, which is close to the range of experimental values (figure 1). The essential features described in the next sections are quite similar in both types of assessment (supplemental material (S3)).

In order to study the effect of lattice disorder, magnetic field and charge ordering on polaron hopping we determine the apparent activation energy
Equivalently, using the obtained apparent activation energy in a ‘local’ Arrhenius analysis, the intercept of the extrapolated straight line with the $1/T=0$ axis gives the apparent pre-factor $\rho_0$. $E_A(T) = \text{const}$ and $\rho_0(T) = \text{const}$ implies the validity of the single polaron model without any corrections.

$$E_A(T) \equiv \frac{d}{dT} \ln \left( \frac{\rho(T)}{T^4} \right).$$

4.2.1. Hopping mobility in zero-field. Figure 4(a) shows the temperature dependence of the apparent activation energy deduced from the adiabatic limit for samples with different degree of lattice disorder. For as-prepared films deposited at rather low temperatures (IBS-1, $T_{\text{dep}} \approx 973$ K) $E_A \approx 145$ meV is essentially temperature independent above $T=150$ K, i.e., above half of the Debye temperature. Post-annealing causes a slight overall reduction of $E_A$ to 135 meV (IBS-2). At zero magnetic field, the rapid decrease of $E_A(T)$ at temperatures $T < 120$ K implies enhancement of tunnel-like contributions in the hopping regime [9]. This reduction of the apparent polaron activation barrier, however, cannot give rise to band-like conductivity as observed in the CMR regime at high magnetic fields.
The most noticeable deviation from the model of TAH of small polarons is a pronounced peak in $E_A(T)$ in the temperature range of $T=120$–$250$ K. It is present (IBS-3 and 4) or evolves after post-annealing (PLD-1), if the substrate temperature during deposition is larger than 973 K. With increasing post-annealing time, the $E_A(T)$ peak shifts to higher temperatures and increases in height. The appearance of the peak is not affected by the method of preparation (IBS or PLD) or the choice of substrate. Note that the samples IBS-3 and IBS-4 were simultaneously deposited in the same run but on different substrates (STO and MgO). Their $E_A(T)$ curves are very similar.

Figure 4(b) reveals the temperature dependent apparent activation energy and pre-factor for a well-annealed sample prepared by PLD. $E_A$ and $\rho_0$ are essentially constant at sufficiently high temperatures (typically above 220 K). At lower temperatures, the adiabatic $E_A$ significantly increases up to 210 meV and $\rho_0$ simultaneously decreases by about two orders of magnitude. This peak/dip feature does not depend on whether adiabatic or non-adiabatic hopping is assumed (supplemental material S3).

The optical conductivity $\sigma$ of the PCMO thin film IBS-5 was measured at various photon energies and different temperatures (supplemental material (S4)). Figure 5(a) shows the absorption maximum in the low-energy range at room temperature. This peak was fitted by two skewed Gaussian peaks P1 and P2. (b) Temperature dependence of the fitting parameters $E_p$ and $E_{\text{vib}}$ of the low-energy peak P1, which is related to optical induced small polaron hopping.

**Figure 5.** Small polaron absorption peak in optical absorption spectroscopy with unpolarized light for the sample IBS-5 (supplemental material S4). (a) Real part of the optical conductivity (symbols) deduced from the absorption coefficient in the thin film limit at $T=300$ K. The peak was fitted by two skewed Gaussian peaks P1 and P2. (b) Temperature dependence of the fitting parameters $E_p$ and $E_{\text{vib}}$ of the low-energy peak P1, which is related to optical induced small polaron hopping.
skewed Gaussian peaks P1 and P2 (equation (2)). According to the optical studies on LCMO [33] we expect that the peak P1 centered at $\hbar \omega = 740 \text{ meV} \approx 2 \, E_P$ is related to photon induced small polaron hopping process between occupied and unoccupied polaron sites. The peak P2 centered at $\omega = 1474 \text{ meV} \approx 4 \, E_P$ corresponds to the on-site ‘Jahn–Teller’ transition between the split Mn3$de_g$ orbitals hybridized to the O2$p$ states.

Figure 5(b) shows the temperature dependence of the fitting parameters of the hopping-related peak P1, i.e., the polaron formation energy $E_P$ and the vibrational energy $E_{vib}$. $E_P$ amounts to about 370 meV at room temperature and increases to about 395 meV at low temperatures. At temperatures below $\Theta_{\text{Debye}}/2$, $E_{vib} \approx \hbar \omega_{ph}/2 \approx 47 \text{ meV}$ is temperature independent. Above the plateau, $E_{vib}$ increases approximately linear with temperature and the slope corresponds to 1.38 $k_B$. Note that the fitting parameter $\sigma_{dc}$ at room temperature corresponds to a resistivity of about 0.06 $\Omega \text{ cm}$, which is close to 0.085 $\Omega \text{ cm}$ observed in a dc-measurement of the same film. However, since the parameter $\eta_3$ (equation (2a)) amounts to about 1–3, the contribution from electronic dispersion may significantly alter the shape, the maximum peak position as well as the width of the peak [34, 35]. The obtained values for $E_P$ ($E_{vib}$) are thus only estimates in the sense of a lower (upper) limit.

4.2.2. Hopping mobility in magnetic fields. Application of magnetic fields strongly affects the polaron mobility and gives rise to an apparent activation energy $E_A$, which changes with field and temperature. Similar to the zero-field behavior, the obtained features in $E_A$ do not depend on the applied model, i.e., adiabatic or non-adiabatic hopping.

Figure 6(a) compares $E_A(T)$ of samples in different annealing stages at an applied field of $B = 9 \, T$ and figure 6(b) shows exemplarily the temperature and field dependence of the adiabatic $E_A(T)$ and the apparent pre-factor $\rho_0(T)$ for a moderately annealed sample. The main observations are: (i) samples prepared under conditions, which do not result in a pronounced zero-field peak/dip feature, reveal an apparent activation energy, which monotonously decreases with decreasing temperature (IBS-2 and 3). (ii) The zero-field peak/dip feature at low temperatures is less pronounced in magnetic fields, i.e., the apparent activation energy decreases and the pre-factor increases with increasing magnetic field (figure 6(b)). (iii) The degree of reduction depends on the post-annealing time, i.e., the peak/dip feature is completely suppressed in well-annealed samples (PLD-1 in figure 6(a)).

Therefore, post-annealing increases the peak/dip feature in $E_A(T)/\rho_0(T)$ in zero field and decreases it in magnetic fields. With increasing post-annealing time the transition temperature $T_{\text{CMR}}$ shifts to higher temperatures (figure 1(b) and table 1). In the crossover regime from hopping to a band-like transport, $E_A$ drastically drops down towards zero and thus becomes meaningless for well-annealed samples (PLD-1 in figure 6(a)). This indicates a crossover from hopping conductivity to band transport with ‘metal-like’ temperature dependence below $T_{\text{CMR}}$.

5. Band-like mobility at low temperatures

5.1. Model of band conductivity of small polarons

Coherent band-like transport of small polarons evolves, if the energy fluctuations due to scattering at thermal quasiparticles or at lattice disorder are smaller than the renormalized width of the polaron band $D_p$ [11]. Consequently, at sufficiently low temperatures, small polarons behave as heavy particles with effective mass $m^*$ in a small polaronic band, giving rise to a
resistivity

\[ \rho(T) = \frac{m^*}{ne^2} \left( \frac{1}{\tau_R} + \frac{1}{\tau_{QS}} + \frac{1}{\tau_{PS}} \right) = \rho_R + \rho_{QS}(T) + \rho_{PS}(T), \]  

were \( \rho_R \) is the residual (temperature-independent) defect contribution, \( \rho_{PS} \) corresponds to phonon scattering and \( \rho_{QS} \) is due to magnon scattering [6] in a magnetically ordered phase.

In the Lang–Firsov theory, the resistivity of small polarons due to scattering with optical phonons is given by [18]

\[ \rho_{PS}(T) = \frac{a_0 \hbar}{2 Ze^2} \left( \frac{E_{Ph}}{D_p} \right) \left( \frac{\omega}{\Delta \omega} \right) \left( \frac{J}{E_A} \right)^4 F(T) \sinh^{-2} \left( \frac{E_{Ph}}{2k_B T} \right) \]

\[ \equiv \rho_{LT} T^q \sinh^{-2} \left( \frac{E_{Ph}}{2k_B T} \right). \]
\[ F(T) = \begin{cases} 
1 & (D_p > Z k_B T) \\
Z k_B T & (D_p < Z k_B T) 
\end{cases}, \quad (5a) \]

where \( q = 0 \) or \( 1 \), depending whether the polaronic band width \( D_p \) is larger or smaller than \( Z k_B T \). \( \Delta \omega \) is the dispersion of the involved optical phonons and \( E_{\text{ph}} \) denotes a limiting upper frequency of longitudinal polar phonons involved in the scattering process.

5.2. Application to PCMO

In small bandwidth manganites such as PCMO, the FMM like state with coherent polaron transport is not observed at zero magnetic field, i.e., the temperature dependent resistivity increases up to the measurement limit of \( 10^8 \ \Omega \text{cm} \) at \( T = 4.2 \text{ K} \). The transition to the FMM state can be only induced by application of strong magnetic field. The strong drop of the resistivity from above \( 10^5 \ \Omega \text{cm} \) to \( 10^{-3} \ \Omega \text{cm} \) is due to the CMR and appears by the first order metamagnetic transition [36] from an antiferromagnetic insulating ground state to a ferromagnetic and conducting state. At intermediate temperatures, the meta-magnetic phase transition gives rise to nanoscale phase separation, where the appearance of a conductive phase is embedded in an insulating matrix [37]. The volume fraction of this phase increases with decreasing temperature. Over a broad temperature range below the crossover temperature \( T_{\text{CMR}} \), charge transport thus takes place in an inhomogeneous phase-separated system.

The pronounced hysteresis of the resistivity with respect to field-cooling and field heating in figure 7(a) can be attributed to the nano-scale phase separated state, where the magnetization of the ferromagnetic phase is affected by domain wall pinning at defects. With increasing post-annealing time, i.e., with subsequent defect annihilation, this hysteresis becomes smaller. In addition, \( T_{\text{CMR}} \) shifts to higher temperatures.

In the temperature range, where the volume fraction of the metal-like conducting phase is large and the hysteresis is small, the resistivity is mainly related to the residual contribution and the phonon scattering [6]. In the low-temperature approximation of equation (5) the phonon scattering of small polarons can be written as

\[ \rho_{\text{PS}}(T) \approx \rho(T) - \rho_R \approx 4 \rho_{\text{LT}} T^q e^{E_{\text{ps}}/k_B T}. \quad (5b) \]

5.2.1. Low temperature mobility in magnetic fields. In order to analyze the applicability of equation (5b), we again define the temperature-independent prefactor \( \rho_{\text{LT}} \) and the phonon energy \( E_{\text{ph}} \) as apparent quantities, i.e., \( \rho_{\text{LT}}(T) = \text{const} \) and \( E_{\text{LT}}(T) = \text{const} \) implies the validity of the model. Figures 7(b) and (c) show the temperature dependence of the apparent phonon energy \( E_{\text{ph}}(T) \) deduced from equation (5b) in the small-band limit \( (q = 1) \) for the sample PLD-1 after different post-annealing times \( t_a \) (\( B = 9 \text{ T} \)) and at different magnetic fields \( B (t_a = 20 \text{ h}) \). At 10 K, the obtained phonon energy \( E_{\text{ph}} \approx 5 \text{ meV} \) is not strongly affected by \( t_a \) and \( B \).

For increasing \( t_a \) and increasing \( B \) likewise, the temperature range, where the model can be applied is strongly enhanced. After long-term post-annealing \( (t_a = 80 \text{ h}) \) and at \( B = 9 \text{ T} \) the narrow band model gives an almost constant \( E_{\text{ph}}(T) \) over the largest temperature range up to
Figure 7. Small polaron analysis of the low-temperature resistivity $\rho(T)$ for sample PLD-1. (a) Low-temperature resistivity at 9 T after different post-annealing times $t_a$. Arrows indicate the sweep direction, i.e., field-cooling or field-heating. (b) Apparent phonon energy $E_{Ph}$ versus temperature for $B = 9$ T after different post-annealing times $t_a$. $E_{Ph}$ was calculated from the field-cooled resistivity according to equation (5a) in the small-band limit ($D_P < Z k_B T$). The calculated phonon energy in the large-band limit ($D_P > Z k_B T$) at $t_a = 80$ h is also shown for comparison (open symbols). (c) Apparent small-band phonon energy $E_{Ph}$ versus temperature after post-annealing for 20 h for different magnetic fields $B$. 

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$T = 40$ K. In contrast, the large-band model ($D_p > Z k_BT$) is worse, i.e., the apparent phonon energy significantly changes with temperature (see open symbols in figure 7(b)).

The small-band model can be applied to the low-temperature resistivity and the range of validity is limited by the finite volume fraction of the FMM phase, i.e., the appearance of pronounced phase separation, which is affected by the magnetic field and lattice disorder. However, the low-temperature approximation equation (5b) describes the T-dependence of the resistivity better than the sinh-dependence (equation (5)). This discrepancy cannot be attributed to additional scattering contributions. This observation is supported by recent DMFT calculations for the non-adiabatic case, where it has been concluded that equation (5b) well describes the band-like transport of small polarons over a large temperature range [10].

In contrast to $E_{\text{ph}}$, the pre-factor $\rho_{LT}$ changes by orders of magnitude with respect to post-annealing time and applied magnetic field. In figure 8(a), the temperature averaged value $\rho_{LT}$ ($T = 15–25$ K) is plotted versus post-annealing time and magnetic field. It is important to note that the residual resistivity $\rho_R$ reveals the same strong dependence like the pre-factor (inset). This indicates a strong correlation between phonon and defect related scattering, where the
changes of resistivity due to post-annealing or magnetic field increase are indistinguishable (figure 8(b)).

6. Discussion

Most probably, nano-twins and c-axis disorder have a common origin in a quench of the equilibrium octahedral tilt structure. The deposition of epitaxially grown PCMO films typically takes place at temperatures close to the rombohedral–orthorhombic phase transition at about 1073–1173 K. At this phase transition, the octahedral tilt angles drastically increase to a total tilt of about 11° and further increase to about 15° while cooling down to room temperature [19]. This should have a big impact on the evolution of the stress-strain state of the films.

In principle, disorder in the octahedral tilt system can have three different effects on small polaron transport: (i) small polarons may be trapped at disorder sites, which should give rise to a defect contribution to the activation energy \( W_D \). (ii) Octahedral disorder may create local variations of the transfer integral \( J \) and thus affects bandwidth, magnetic double and superexchange. (iii) Octahedral disorder may counteract long-range charge ordering and thus affect the subtle phase formation in PCMO in addition to the inter-site Coulomb interaction between polarons \( W_C \). In the following, these contributions are discussed in the charge disordered Pbnm phase (\( T > T_{CO} \approx 220 \text{ K} \), 6.1) and in the CO phase (6.2).

6.1. Contributions to the activation barrier in the paramagnetic phase

Since the hopping seems to take place near the adiabatic limit, the contribution of the transfer integral to the activation barrier \( E_A \) is significant.

\[
E_A \approx \frac{E_P}{2} - J. \tag{6}
\]

In order to analyze the additional corrections due to magnetic fields, disorder and high carrier concentrations, we include the magnetization dependence of \( J \) and the additional contributions due to defects and inter-site Coulomb interaction.

\[
E_A \approx \frac{E_P}{2} - J(M) + W_D + W_C. \tag{6a}
\]

6.1.1. The Coulomb contribution \( W_C \). In highly doped manganites at \( x = 0.33 \), the contribution of the inter-site Coulomb interaction between charge carriers is rather large and can be estimated by [16]

\[
W_C \approx \frac{x e^2}{12 \varepsilon_s \varepsilon_0 a_0}. \tag{7}
\]

Here, \( \varepsilon_s \) is the static dielectric constant. For PCMO, \( \varepsilon_s \) is in the range of 30 [38] to 57 [39], i.e., \( W_C \) is of the order of 40–20 meV for next neighbor interactions.

6.1.2. The magnetic contribution \( J(M) \). In the Pbnm phase, the apparent activation energy in magnetic fields decreases with decreasing temperature. This decrease is governed by the effect of the double exchange interaction on the transfer integral. \( J \) is strongly modified by the next
neighbor spin alignment $\theta_{ij}$ \cite{1} with

$$J(M) = J_{FM} \cos \left( \frac{\theta_{ij}}{2} \right) \approx \frac{J_{FM}}{\sqrt{2}} \sqrt{1 + \frac{M^2}{M_s^2}} \equiv J_{PM} \sqrt{1 + \frac{M^2}{M_s^2}}$$  \hspace{1cm} (8)

$M_s$ denotes the saturation magnetization.

For not too large magnetizations $M < M_s$, equations (6a) and (8) imply a linear decrease of $E_A$ with the square of the paramagnetic magnetization. Actually, the temperature dependent apparent activation energy at different magnetic fields can be combined to a single master curve by plotting $E_A(T,B)$ as a function of $B^2/T$ \text{or} $M^2$ (figure 9). The field depending upturns in the $E_A-M^2$ scaling is observed for data points corresponding to temperatures above the peak in $E_A(T)$ (figure 4). Using $J = J_{PM} \approx 60–110$ meV (supplemental (S1)), equation (8) implies that full spin polarization increases the $J$ by about $\Delta J \approx 25–45$ meV. Experimentally, the maximum reduction of the activation energy due to paramagnetic magnetization (at 9 T) amounts to about 27 meV for moderately annealed samples.

6.1.3. The disorder contribution $W_D$. In the Pbnm phase the zero-field activation energy ranges from about 130 to 144 meV (see also figure 10(a)). $E_A$ is not strongly affected by the choice of substrate and the method of preparation but commonly decreases with increasing deposition temperatures and post-annealing time. Therefore, the trapping contribution $W_D$ to the activation barrier is of the order of 10–15 meV.

The spread is larger in strong magnetic fields (113–133 meV at 9 T, see figure 10). In addition, the dependence of the apparent activation energy on the magnetization is more pronounced for samples with a low degree of disorder (compare the moderately annealed samples PLD-1 and PLD-2 in figure 9). This implies that disorder in the octahedral tilt system rather gives rise to local variations in the transfer integral than to trapping.
Summing up all contributions in equation (6) for the charge disordered Pbnm phase of well-annealed samples in zero-field, we have $W_C \approx 30$ meV, $J \approx 60$–110 meV, $W_D = 0$ and $E_A \approx 130$ meV and thus the polaron formation energy should be of the order of 320–420 meV. Since the formation energy determined from optical conductivity (figure 5(b)) amounts to about $E_p \approx 370$ meV, $J \geq 85$ meV seems to be a rather reasonable choice for the transfer integral. According to equation (8), this would imply a reduction of the activation energy in strong fields of about 35 meV, which is very close to the experimentally observed reduction of about 33 meV in long-term annealed samples (sample PLD-1 at $t_a = 80$ h in figures 4 and 6).

### 6.2. The effect of charge order and Meyer–Neldel compensation

It is instructive to review the deviations from single polaron hopping, i.e., the appearance of temperature and field depending apparent activation energies and pre-factors, with respect to the Meyer–Neldel compensation rule. This rule states that in a thermally activated transport process, a decrease of mobility due to an increase of the activation energy is partly compensated by an increase of the pre-factor [40].

$$\rho_0 \propto e^{\frac{-E_A}{k_B T_{MN}}},$$  \hspace{1cm} (9)

where $T_{MN}$ is the Meyer–Neldel temperature.

Generally, the Meyer–Neldel analysis is applied to systems with TAH of charge carriers, where the activation energy and the pre-factor are changed by sample property variations, such as doping or defect concentrations [41]. A publication by Emin [42] on thermally activated polaron hopping states that Meyer–Neldel compensation arises in the adiabatic treatment of small polaron hopping, if the effect of the charge on the barrier at the coincidence positions via a change on the atomic vibrations is taken into account. This can be expressed by an effective contribution to the transfer integral, where $J_{eff} = k_B T_{MN}$.

![Figure 10. Meyer–Neldel analysis of hopping conductivity. $\rho_0(B)$ versus $E_A(B)$ as a function of the magnetic field $B$ for various samples. The data points represent average values in the temperature range from 280 K to 300 K, where the apparent quantities are practically temperature independent. As indicated by the arrow, the lines connect data points of the same sample measured at different magnetic fields from $B=0$–1 T (right data point) to $B=9$ T (left data point).](image-url)
Near room temperature (280 K–300 K), i.e., in the paramagnetic phase, the apparent quantities depend only weakly on temperature and thus can be represented by field dependent mean values. Figure 10 shows the mean apparent $E_A(B)$ and the pre-factor $\rho_0(B)$ for various samples and annealing states for magnetic fields between 0 and 9 T. The linear dependence in the semi-log plot implies that PCMO follows the Meyer–Neldel rule. The Meyer–Neldel temperature $T_{MN}$ is not strongly affected by the details of the preparation and amounts to $370 \pm 30$ K. Since $k_B T_{MN} \approx 33$ meV, the Meyer–Neldel temperature agrees well with the maximum magnetically induced change of the transfer integral of $\Delta J \approx 35$ meV as expected for $J \approx 85$ meV.

Reducing the temperature towards $T_{CO}$, a pronounced peak (up to 80 meV) in the activation energy appears in well-annealed samples and zero field (figure 4). The peak is completely suppressed in the presence of sufficient strong magnetic fields. Such samples commonly show a CMR transition and, as revealed by TEM analysis, the formation of the CO P2$_1$mn phase. This implies that the temperature independent part of $E_A(T)$ corresponds to the Pbnm phase and that the peak in $E_A$ is caused by charge ordering.

In the P2$_1$mn phase, the influence of defects is much stronger. Octahedral disorder reduces the peak in the activation energy and counteracts its reduction in magnetic fields. A high degree of disorder can completely suppress the charge ordering peak. Such samples remain in the Pbnm phase also at low temperatures and only the healing of lattice disorder enables the emergence of the CO phase.

Since charge ordering gives rise to the freezing out of mobile polarons, the peak-dip feature in $E_A(T)$ and $\rho_0(T)$ (figures 4 and 6) might also suggest a Meyer–Neldel compensation. However, the analysis of the peak-dip feature does not reveal a single valued Meyer–Neldel temperature. The charge ordering transition is of first order and undergoes via a two phase area, where CO and disordered phases coexist. The CO phase may have a larger resistivity than the charge disordered phase. The difference cannot be huge, since $\rho(T)$ in single crystals, where the CO transition is most pronounced is only showing a kink with a slight increase in the slope of $\rho(T)$. In addition, in situ TEM studies of electric stimulation of the mixed phase show, that the electric current leads to a motion of CO domains [17]. This clearly shows that the CO areas contribute to the electric transport in the two phase region.

We thus argue that the peak-dip feature in $E_A(T)$ and $\rho_0(T)$ represents the influence of charge order or at least of charge short range order while decreasing the single polaron mobility and increasing the polaron–polaron next neighbor interactions. For moderately annealed samples, the polaron formation energy $E_p$ increases below the charge ordering temperature to a value which is about 25 meV larger than at room temperature (figure 5(b)). According to equation (6a), the increase of $E_p$ due to structural phase transition would be a natural explanation for the increase of $E_A$, which then also contains contributions from the polaron–polarons Coulomb interactions. An increase of $E_A$ because of structure-induced decrease of the transfer integral seems to be unlikely, because in the P2$_1$mn phase some of the Mn-O-Mn bonding angles are flattened (157.7°–160.6°) compared to the bonding angle in the Pbnm phase (153°, figure 11(a)). The decrease of $\rho_0$ may arise from the transition from individual to cooperative hopping of the polarons during ordering. We can assume that having a number of polarons simultaneously at their coincidence points between two sites may change the activation barrier as well as the transfer rates and thus would result in a Meyer–Neldel like behavior as suggested in [42].
6.3. Coherent transport of polarons in the FMM phase

Our study of the insulator–metal transition in PCMO films with different degree of octahedral disorder shows that coherent band-like transport of polarons only evolves at high fields and low temperatures, if the defect density is not too high. The defect-induced suppression of the CMR effect coincides with the suppression of the long-range CO P21mn phase formation in zero field. This raises the question whether the coincident suppression just accidentally happens due to the defect-induced variation of the transfer integral $J$ or whether the long range order of small polarons is required for the emergence of the CMR via a fully developed double exchange contribution $\Delta J(M)$ and thus a sufficiently large polaron bandwidth $D_p$. 

![Figure 11](image)

**Figure 11.** Structure models of (a) the charge disordered Pbnm, (b) the antiferromagnetic charge ordered P21mn and (c) the ferromagnetic conducting P21mn phases in PCMO ($x=0.3$). The viewgraph shows a [001] projection of the unit cells with lattice parameters $a$ and $b$. The color code and thickness of the $p$–$d$ orbitals indicate the bonding angle and the relative hole occupation, respectively. The magnetization of the Mn 3$d$ spins parallel to the $c$-axis are indicated according the CE-type antiferromagnetic and ferromagnetic states in (b) and (c), respectively.
As far as we know, no unique determination of the space group of the FMM phase has been published for PCMO. Therefore, we have used the determined P21mn structure model for \( x = 0.33 \) and the intensity variation of two neutron diffraction peaks published in [43] to model the field-induced changes of the displacement vectors. The results are shown in the supplemental material (S2) and are visualized in figure 11(c). Since the modeling of the magnetic field induced structural changes is based on two reflections only, the suggested displacements of the atom position \( \Delta_i \) are not unique. However, all explored alternative settings which are in agreement with the intensity variations in the diffraction patterns have in common a smoothening of Mn-O-Mn bond angles. This occurs preferentially at those ferromagnetic zig-zag chains which are preformed in the CE type antiferromagnetic and CO structure (figure 11(b)).

Our structure model thus implies that the meta-magnetic transition to the ferromagnetic state is accompanied by a preferential increase of the transfer integral at the Mn-O-Mn chains with smoother bond angle and that the formation of a CE type CO state is a precursor of the magnetic field induced FMM state. The overall effect of charge order and magnetic field is an increase of the polaron bandwidth with a strong increase in polaron mobility according to equation (5).

With respect to the influence of disorder and magnetic fields on the band-like transport, it is interesting to consider the stability of the small polaron state. The formation of polarons is commonly described by three coupling parameters \( \alpha, \lambda, \) and \( \delta \), which are related to fundamental energy scales: the electron–phonon binding energy \( g \), the energy of the involved phonon mode \( E_{\text{ph}} \), and the bare electronic bandwidth \( D \) [44].

\[
\alpha \equiv \frac{g}{E_{\text{ph}}} = \sqrt{\frac{E_p}{E_{\text{ph}}}}, \quad \lambda \equiv \frac{E_p}{Z J}, \quad \delta \equiv \frac{E_{\text{ph}}}{J}.
\]  

(10)

Because of the dependence on the bare bandwidth \( D \), the coupling constants \( \lambda \) and \( \delta \) decrease with increasing spin polarization [45] (see also equation (8)).

A small polaron state requires that \( \alpha \) and \( \lambda \) exceed critical values of the order of unity. Using \( E_p \approx 370 \, \text{meV}, \ J \approx 85 \, \text{meV} \) and \( E_{\text{ph}} \approx 42 \, \text{meV} \) for the Zener mode (71 meV for the Jahn–Teller mode), we obtain \( \lambda \approx 0.7, \ \alpha \approx 3 \) (2.3) and \( \delta \approx 0.5 \) (0.8) for the paramagnetic high-temperature phase. Therefore, the electron–phonon coupling is rather strong but the small polaron state is close to the stability boundary because of the smallness of \( \lambda \). Charge ordering seems to increase the polaron formation energy and, therefore, stabilize the small polaron state.

A large coupling constant \( \alpha \) gives rise to a very small polaron bandwidth. Since the adiabacity parameter \( \delta \) is of the order of 0.5–1.0, \( D_p \) in the FMM phase can be calculated according to [46]

\[
D_p \approx D_0 e^{-\alpha^2}.
\]  

(11)

For a coarse estimate of \( D_p \) we have applied the mobility model for small polaron bandwidth (equation (5) with \( D_p < k_B T \)) to the well annealed sample PLD-1 (\( t_a = 80 \, \text{h}, \ B = 9 \, \text{T} \)). Using \( E_{\text{ph}} \approx 4.4 \, \text{meV}, \ \rho_{L,T} \approx 1.3 \times 10^{-6} \, \Omega \text{cm K}^{-1} \) (figures 7 and 8), \( J \approx 85 \, \text{meV} \) and reasonable values for the phonon dispersion of 1 (10) meV, we obtain \( D_p \approx 7.5 \) (2.4) meV. This corresponds to \( \alpha \approx 2.2 \) (2.5).

The polaronic bandwidth seems to be rather small and comparable to the phonon energy, also in well annealed samples and at high magnetic fields. Since band-like mobility requires
$D_p > E_{ph}$, reduction of $D_p$ due to spin misalignment and octahedral misalignments would eventually even give rise to the emergence of hopping conductivity, as observed experimentally in as-prepared samples at high fields or in well annealed samples at low fields.

In addition, the polaron mass $m_p$ is expected to increase with decreasing bandwidth. Remarkably, the defect-related residual resistivity and the pre-exponential factor of phonon scattering reveal the same dependence on post-annealing time and magnetic field resulting in a universal dependence of the parameters $\rho_{LT}$ on the residual resistivity $\rho_R$ (figure 8(b)). This implies, that both field and disorder related changes in the low-temperature resistivity are governed by the change of the scattered particle mass $m_p$. However, the coupling constant $\lambda$ is rather small in the paramagnetic phase. The increase of the bandwidth $D$ in the FMM phase could therefore result in a state, where small polarons are not stable, i.e., new quasiparticles are formed. It is worthwhile to note, that the observed correlation between $\rho_{LT}$ and $\rho_R$ does not depend on the applied model of phonon scattering.

7. Summary and conclusions

Octahedral disorder has only a minor effect on the magneto-electric transport behavior in the paramagnetic Pbnm phase with an activation barrier $E_A \approx 130$ meV. The disorder contribution is of the order of $W_D \approx 10–15$ meV. Magnetic fields significantly reduce the activation energy because of a strong additional double exchange contribution $J_M$ of about 30 meV to the zero field electronic overlap integral of $J \approx 85$ meV, but this effect depends on the disorder.

Due to the structural change and the modification of the Coulomb interactions, the emergence of charge ordering increases the polaron formation energy from about $E_p \approx 370$ meV to about 400 meV. The activation barrier $E_A$ amounts to about 200 meV in the CO state of well-annealed samples. The absence of CMR in samples, where the formation of P2$_1$mn phase is suppressed by crystallographic defects like nano-twins and octahedral tilt disorder, clearly shows, that in small bandwidth manganites with strong electron–phonon coupling, the FMM phase can only evolve via long range ordering of small polarons. The field-induced increase of the transfer integral seems to be counteracted by octahedral disorder, giving rise to a polaron mass, which decreases with increasing field strength and increasing post-annealing time. The estimate of the ratio of polaron bandwidth to scattering induced fluctuations show that the CMR state seems to be at the stability limit of small polaron band conduction and is thus extremely sensitive to magnetic field or disorder induced change of the transfer integral.

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