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Evidence for non-adiabatic, small-polaron-mediated transport both above and below the ferromagnetic ordering temperature in O-depleted $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$

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Abstract

The transport and magnetic behaviours of Ar-annealed (O-depleted) bulk samples of an archetypal, ‘optimally’ doped manganese perovskite, $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, are reported, analysed and compared with those of an untreated specimen. These indicate that the transport data for both the paramagnetic *and* ferromagnetic phases of the O-depleted system are consistent with the predictions based on polaronic hopping, specifically non-adiabatic small-polaron hopping (on the basis of the internal consistency of estimates for the characteristic frequency Ω_0 from both the adiabatic and non-adiabatic formalisms). These results yield indirect support for models which attribute transport in doped perovskites in general, and the colossal-magnetoresistance phenomenon in particular, to polaronic behaviour.

1. Introduction

There appears to be general agreement at present that the double-exchange mechanism [1] alone cannot account for the colossal magnetoresistance displayed by many manganese perovskites. Double-exchange coupling—in isolation—cannot generate sufficient scattering to account for the relatively large resistivity associated with the semiconducting response displayed in the high-temperature paramagnetic phase [2]. The consensus of current models is thus to identify the transport behaviour in this magnetically disordered regime as resulting from polaron formation [2, 3], a consequence of strong electron–phonon coupling and/or Jahn–Teller distortions [4]. Several recent experiments confirm the predictions of such models [5]. Indeed evidence supporting strong electron–phonon coupling is widespread, including very large oxygen isotope effects reported for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $x \leq 0.2$ [6]. In several recent papers [7–9] experimental evidence has been presented which supports the proposal [3] that the transport behaviour of the low-temperature magnetically *ordered* regime of such systems may also be polaronic in nature. Here we present further experimental evidence supporting such a proposal for one of the most extensively studied doped manganese perovskite systems.

An interesting variant amongst some of the experiments investigating oxygen isotope effects in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $x \lesssim 0.2$ considered the influence of Ar annealing. This was shown to induce a significant depression of the ferromagnetic ordering temperature T_c , around 10–20% near $x \sim 0.2$ [6]. In this paper we summarize the effects of Ar annealing on polycrystalline ceramic samples of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$; the reduction in T_c is striking, but not as dramatic as the modifications to the transport behaviour. In the Ar-annealed sample(s) the electrical response of this archetypal, ‘optimally’ doped manganese perovskite is not only semiconducting both above and below T_c , but the resistivity is best fitted by the form predicted for charge transport by polarons over the entire temperature range investigated ($77 < T < 320$ K). Such changes are reversible and are not associated with a significant alteration to the average grain size, an important consideration as argued below. In particular, while grain boundary effects can complicate the transport behaviour of these systems, we contend that the results reported below represent the intrinsic response, in agreement with recent conclusions drawn for the $\text{LaMn}_{1-x}\text{Al}_x\text{O}_3$ system [8]. Further, while reversible changes accompanying oxygen depletion have been reported previously, these have not encompassed the situation in which a ferromagnetic semiconducting phase is produced [10].

2. Experimental details

Samples were prepared using conventional ceramic techniques from stoichiometric quantities of La_2O_3 (ultrapure), CaCO_3 and MnO_2 , with sequential sintering/refiring at 1200 °C, 950 °C and 650 °C for periods between 24 and 48 hours prior to annealing for 72 hours at 950 °C in Ar (causing O depletion). The effects of the latter could be reversed by reannealing in oxygen (specifically for 48 hours at 1200 °C followed by 24 hours at 950 °C). This procedure returned both the transport and magnetic properties of the sample(s) to values typical of the system prior to Ar annealing, within experimental uncertainty—in agreement with the behaviour reported in [10], but for somewhat smaller changes. Room temperature x-ray measurements revealed a single-phase orthorhombic structure in both the unmodified and Ar-annealed specimens with lattice parameters $a = 5.4585$ Å, $b = 5.4586$ Å and $c = 7.7026$ Å (cf. [11]), and $a = 5.5071$ Å, $b = 5.5100$ Å and $c = 7.6991$ Å respectively. A comparison of the linewidths of the more prominent lines in the XRD pattern, specifically the (020) reflection near $\theta = 32.9^\circ$, reveals an increase in the FWHM from 0.17° for the untreated specimen to 0.35° for the O-depleted state. The latter is attributed principally to strain broadening associated with an inhomogeneous distribution of the significant number of O vacancies (discussed in more detail below) produced by Ar annealing, rather than changes in the average grain size, which was found to be essentially, unchanged by the annealing process. This average size, estimated to be approximately $4 \mu\text{m}$, was found by measuring in excess of 100 grains from a series of randomly selected SEM photographs taken before and after annealing; the associated variance of typically $\pm 0.5 \mu\text{m}$ arises as much from the non-uniformity in the shape of individual grains as it does from differences between the grains in the two cases. These average sizes are comparable to those reported for other bulk specimens [10]—although they are typically fifty times larger than those for thin-film specimens [10]—on which O-depletion studies have also been reported. Susceptibility and magnetization measurements on a sample of approximate dimensions $(1 \times 1.5 \times 6) \text{ mm}^3$ were carried out in a Quantum Design PPMS model 6000 system; transport measurements on the same specimen utilized a conventional four-probe technique.

3. Results and discussion

3.1. Magnetic measurements

Figure 1 reproduces the zero-field ac susceptibility (measured on warming at 2.4 kHz with a driving-field amplitude of 30 mOe rms) in both the O-depleted and the untreated sample. The depression in T_c is clear and significant ($\Delta T_c \sim 90$ K, so $\Delta T_c/T_c \sim 30\%$, somewhat larger than that reported near $x \sim 0.2$). This depression in T_c is accompanied by a substantial decrease in the zero-field susceptibility; specifically the response at the principal/Hopkinson maximum falls by more than a factor of six. Since the magnetic response of ferromagnets at or below the Hopkinson maximum is governed by technical processes [12], this probably reflects the increase in coercivity reported below. The location of this maximum is related, in essence, to the temperature at which the coercive field first exceeds the ac driving field. For a given magnitude of the latter, this occurs closer to T_c in materials with larger coercive fields, as is the case for the O-depleted sample here. An ancillary effect is that the measured susceptibility at this maximum is correspondingly reduced, a consequence of which is that the transition appears broader. A similar (and related) situation arises if a large sample demagnetization factor is adopted [13]. Despite such apparent rounding resulting from an increased coercivity, the transition in the O-depleted specimen shown in figure 1 is considerably narrower than that reported by Dörr *et al* [10] for a thin-film sample of comparable T_c (sample No 5; in this sample the principal maximum in the response occurs more than 100 K below the ordering temperature, whereas here it is some 30 K below T_c). While part of this difference might arise from the larger measuring field used by Dörr *et al*, further comparison is complicated by the fact that the measuring configuration was not specified. A more quantitative investigation of these magnetic

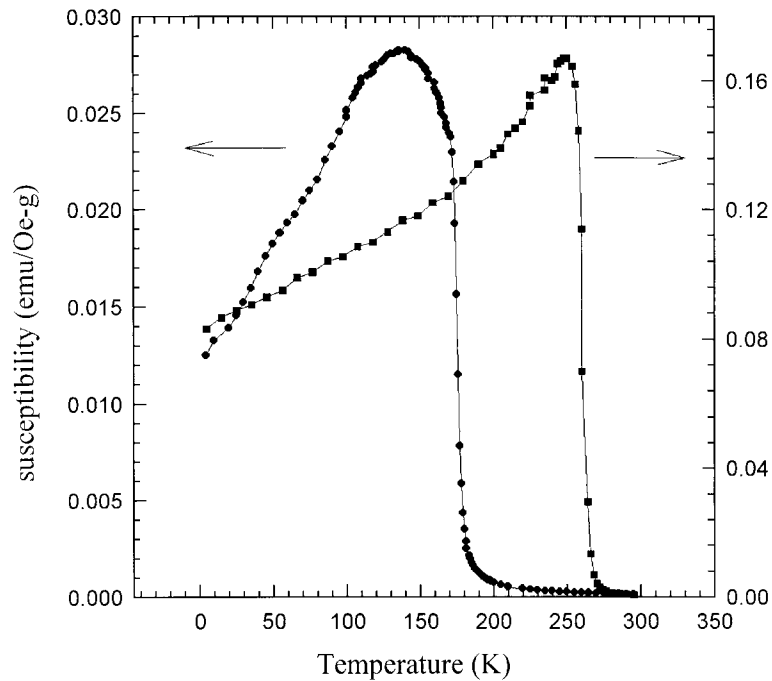


Figure 1. The zero-field susceptibility of the unmodified (right) and Ar-annealed (left) specimens plotted against temperature.

data is presented in figure 2, which summarizes the effects of superimposed static biasing fields H_a up to 3.5 kOe (both the ac driving field and the dc fields were applied along the largest specimen dimension). These latter fields suppress the Hopkinson/principal maximum in both amplitude and temperature, enabling the critical peaks evident in this figure to be resolved. In agreement with both the predictions of the static scaling law for a continuous magnetic phase transition and model calculations [14], and as reported in a number of experiments on a variety of systems [15], these critical peaks decrease in amplitude but shift upwards in temperature from T_c as H_a increases. In particular the locus of the critical maxima (at temperature T_M) displayed in figure 2 is given by [14, 15]

$$\frac{T_M - T_c}{T_c} = t_m \propto H_i^{1/\gamma+\beta} \quad (1)$$

where H_i is the internal field ($H_i = H_a - NM$, in the usual notation), with γ and β being the susceptibility and order parameter critical exponents respectively. The locus of the maxima—the crossover line (the solid line in figure 2)—separates the higher-temperature, thermally dominated regime from the lower-temperature region where the response is field dominated, hence the reference to $(\gamma + \beta)$ as the crossover exponent. A detailed analysis of the field and temperature dependence of such maxima in untreated $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ has been presented previously [16] and is therefore not repeated here, except to state that it yields $T_c \approx 260$ K. Furthermore, since applied fields in excess of 1000 Oe are needed to first resolve such critical peak structure in the O-depleted sample—more than a factor of 10^3 larger than those necessary (~ 0.4 Oe) to resolve such structure in the most favourable cases (**PdFe**) [15], and a factor of 2–3

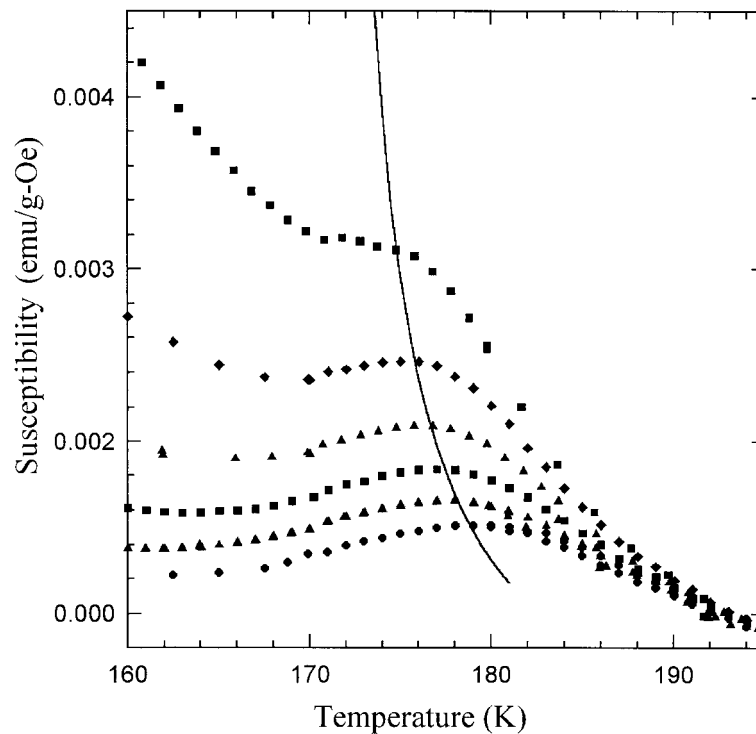


Figure 2. The temperature dependence of the susceptibility of the O-depleted sample measured in static biasing fields increasing from 1 kOe (top) to 3.5 kOe (bottom). The solid line represents the crossover line discussed in the text.

higher than in the untreated sample [16]—an extended analysis of the present data to determine true, *asymptotic* critical exponents is precluded. This result reflects the substantially higher coercive field—actually a combination of an elevated coercivity and a large reversible moment [15]—in the O-depleted specimen, as can be seen in figure 3 and its inset. Here the coercive field is close to 550 Oe, more than an order of magnitude larger than estimates made at the same temperature for untreated samples [16] ($H_c \gtrsim 50$ Oe at 4.2 K). The solid line in figure 2 nevertheless demonstrates consistency with the occurrence of a thermodynamic transition to a ferromagnetic state characterized by Heisenberg model exponents [17], $\gamma + \beta = 1.75$, with $T_c \simeq 170$ K.

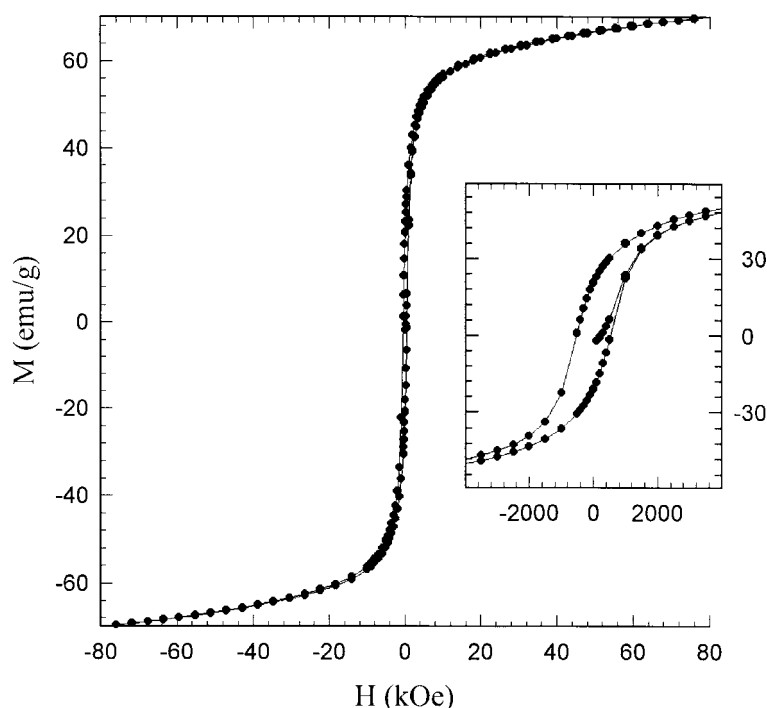
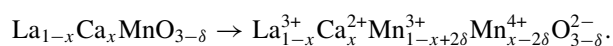


Figure 3. The hysteresis loop at 4.2 K for the O-depleted specimen; the inset shows the behaviour near $H_a \simeq 0$ on an enlarged scale, from which the coercive field is estimated.

It is well established that annealing in Ar—equivalent to reducing the O_2 partial pressure—causes oxygen depletion [10, 18]. While no direct means of quantifying this depletion is currently available to us, making an indirect estimate is possible by considering charge compensation, usually assessed through changes in the compositional dependence of the Mn valence, namely



If the modified Mn^{4+} concentration, $x - 2\delta$, is equated to that Mn^{4+} composition in the untreated system yielding the measured T_c of 170 K, one finds $\delta \sim 0.09$; this estimate is necessarily approximate, probably an upper limit. This estimate for δ is nevertheless consistent with that made by Dörr *et al* [10] for a sample of comparable T_c , although the transport properties of that thin-film specimen are rather different.

3.2. Transport data

The principal results of the present investigation are summarized in figures 4 and 5. The first of these figures reproduces the zero-field resistivity of the two samples in question; while the unmodified sample displays a response (in both zero field and an applied field of 1.5 kOe) typical for variously reported polycrystalline ceramic specimens of similar composition [19], the O-depleted sample remains semiconducting over the entire temperature range examined ($77 \leq T \leq 300$ K), i.e. both above and below T_c ; furthermore, no obvious anomaly in the behaviour of the resistivity itself or its temperature derivative in this latter specimen is apparent at T_c , as is evident from figure 4. The changes through T_c are quite smooth (as emphasized in the inset in figure 6).

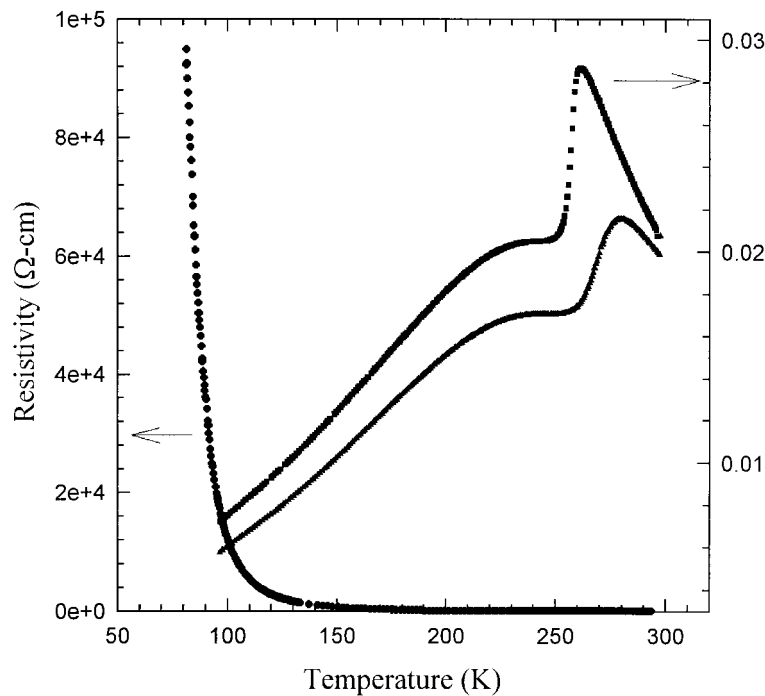


Figure 4. The zero-field resistivity of the O-depleted sample (left) and the resistivity of the unmodified sample (right) (in both zero field and a field of 1.5 T) plotted against temperature.

3.2.1. High temperature: paramagnetic regime ($T > T_c$)

Untreated specimen Several previous studies of the paramagnetic (high-temperature) phase of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system with $x \sim 0.33\text{--}0.35$, have concluded that the behaviour in this regime is well described by small-polaron transport [5, 6, 20]. This includes the associated resistivity $\rho(T)$ which is well fitted by the predictions for charge transport by such polarons, namely [21]

$$\rho(T) = \rho_0 T^n e^{E_a/k_B T}. \quad (2)$$

Since such a consensus exists, a comparison with the present data appropriately begins there. In equation (2) the ‘activation’ energy E_a is related to the polaron formation energy,

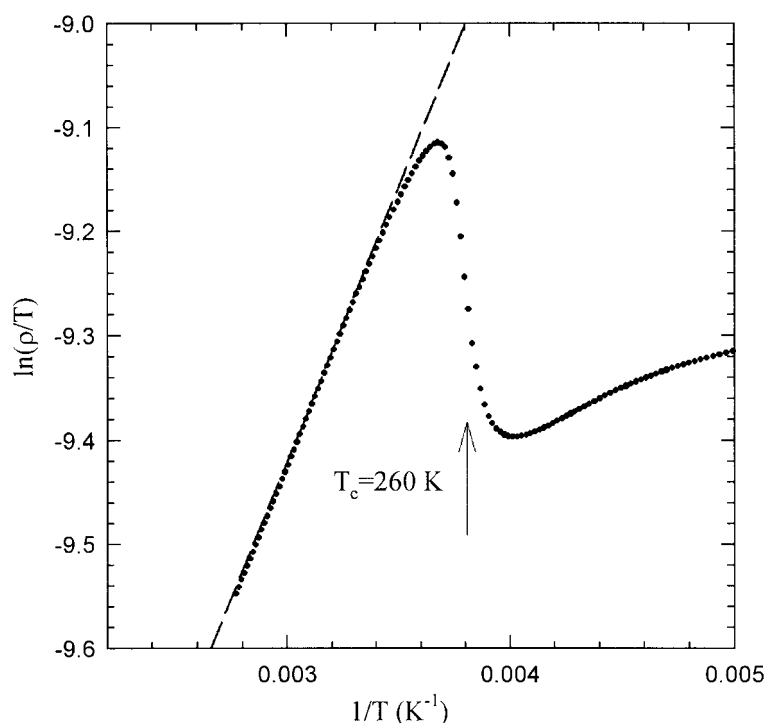


Figure 5. The data for the unmodified specimen plotted in a form consistent with adiabatic small-polaron transport, namely $\ln(\rho/T)$ versus T^{-1} .

while $n = 1$ or $3/2$, depending on whether the adiabatic or non-adiabatic regime is appropriate (discussed in more detail below, along with the significance of the ρ_0 -values). Several existing investigations [5, 6] have, furthermore, been unable to distinguish conclusively between the appropriateness of fits provided by these two choices for the index n . A similar situation exists here; a least-squares fit of equation (2) to the present data yields comparable fits for $n = 1$ and for $n = 3/2$. Figure 5 replots the data contained in figure 4 for the untreated sample in a form consistent with such predictions—actually the adiabatic expression, $\ln(\rho/T)$ versus $1/T$, as this affords the more direct comparison with previous work [5, 6]. The line drawn in figure 5 utilizes

$$E_a^p = 89 \text{ meV} \quad \rho_0 = 2.15 \times 10^{-6} \Omega \text{ cm K}^{-1}$$

(these parameters, along with the those characterizing the non-adiabatic fit and the corresponding standard errors, are summarized in table 1). Both sets of parameters are in good agreement with previously reported values, particularly thin-film data [5]. This is an important result in the present context since it demonstrates that the presence of grain boundaries in these bulk ceramic samples does *not* influence significantly the transport behaviour in this *semiconducting* regime. Hence the claim that the behaviour reported here is indeed intrinsic.

O-depleted specimen. The data for the same specimen annealed in Ar, figure 6, are markedly different. This figure demonstrates that the predictions for polaronic transport fit these data both above and *below* T_c . The data on this oxygen-depleted sample, being not only semiconducting in nature over the entire temperature range examined, but also for a treated system with the

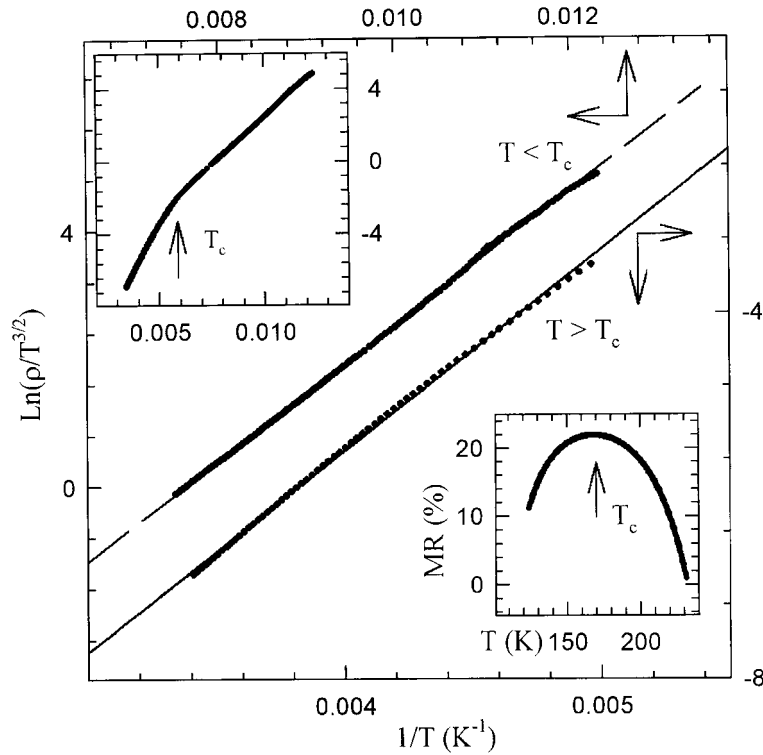


Figure 6. The data for the O-depleted specimen in a form consistent with predictions for non-adiabatic small-polaron transport, i.e. $\ln(\rho/T^{3/2})$ versus T^{-1} , for temperatures above and below T_c . The upper inset shows these data over the entire temperature range, while the lower inset reproduces the (moderate) magnetoresistance in a field of 1.5 T.

Table 1. Parameters characterizing small-polaron fits in the paramagnetic regime. ‘Std Err’ stands for standard error.

$T > T_c$	O-depleted sample			Untreated sample		
	E_a (meV)	ρ_0 (Ω cm)	Std Err	E_a (meV)	ρ_0 (Ω cm)	Std Err*
$\rho = \rho_0 T \exp(E_a/k_B T)$	179	1.60×10^{-5}	0.028	89	2.15×10^{-6}	0.0003
$\rho = \rho_0 T^{3/2} \exp(E_a/k_B T)$	189	6.22×10^{-7}	0.031	105	6.76×10^{-8}	0.0003

* The low standard error reflects the small fitting range.

same average grain size as the untreated specimen is consequently, we contend, also intrinsic in nature. While it must be stated that no direct means of separating grain boundary from intrinsic effects is currently available to us, significant indirect evidence supports this contention. Using a comparable analysis to Akther Hossain *et al* [10] based on available oxygen self-diffusion coefficients for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($\sim 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ [22]), the annealing procedures adopted here result in an estimated diffusion length in excess of $100 \mu\text{m}$. The latter is more than an order of magnitude larger than the average grain size, making any preferential depletion of O from grain boundaries (rather than the grains themselves) quite unlikely. This is supported by the fact that T_c , a bulk property, is depressed by the annealing process, supporting the contention (also made by Akther Hossain *et al* [10]) that such a depression reflects O removal from the grain interior. Furthermore, a decreased magnetoresistance (discussed in section 3.2.2) has also been claimed

to reflect the intrinsic properties of grains [10] since it agrees with the results of deoxygenation effects in single-crystal $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{3-\delta}$ [23]. The latter contrasts with results reported for the low-temperature, ferromagnetic *metallic* phase of ceramic $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$, in which the low-field magnetoresistance is strongly influenced by grain boundary scattering [24].

The least-squares fits that have been carried out of equation (2) to data in the paramagnetic regime are again unable to distinguish conclusively between the adiabatic ($n = 1$) and non-adiabatic ($n = 3/2$) forms. The parameters deduced from such fits are also listed in table 1. Despite the comparability of the fits to these data provided by the two choices for the exponent n , an examination of the appropriateness of the fitting parameters—particularly ρ_0 —in terms of the self-consistency that they demonstrate with the regime of validity of the associated model enables a clear choice to be made, as the following analysis demonstrates.

In the frequently discussed adiabatic limit, the prefactor ρ_0 assumes the form [5, 25]

$$\rho_0 = \frac{k_B}{g_d n a^2 e^2 \Omega_0}. \quad (3)$$

In this equation the hopping distance a has been identified with the nearest-neighbour Mn separation, while the carrier density $n = (4/V)x(1-x)$ incorporates the factor $x(1-x)$ to account for site occupation effects (x being the hole/Mn⁴⁺ fraction) with V being the double-cell volume (found from the listed lattice parameters); g_d is a numerical constant ($\gtrsim 1$) reflecting the polaron hopping geometry and Ω_0 is an attempt frequency, identified with a characteristic optical phonon frequency ω_0 in this (adiabatic) limit. The corresponding expression for this prefactor in the non-adiabatic regime is [25]

$$\rho_0 = \frac{k_B}{n a^2 e^2} \frac{\hbar}{J^2} \left[\frac{4E_a k_B}{\pi} \right]^{1/2} = \frac{k_B}{n a^2 e^2 \Omega_0 T^{1/2}}. \quad (4)$$

This is an expression which is valid when two conditions are satisfied:

- (i) the electronic coupling factor J (the transfer matrix element) is much smaller than the polaron formation energy (related, but not equal, to E_a), and
- (ii) the condition

$$\Omega_0 = \frac{J^2}{\hbar} \left[\frac{\pi}{4E_a k_B T} \right]^{1/2} \ll \omega_0 \quad (5)$$

where the characteristic optical phonon frequency ω_0 is generally in the range 10^{13} – 10^{14} Hz for such materials [25, 26].

For the untreated sample (with $x \simeq 0.33$), the listed ρ_0 -value (table 1) from the adiabatic fit used in conjunction with equation (3) and $g_d \simeq 1$ yields

$$\Omega_0 \simeq 4.5 \times 10^{13} \text{ Hz.}$$

The corresponding analysis within the framework of the non-adiabatic approach, equation (4), for a ‘typical’ temperature $T \simeq 250$ K (a choice which is not crucial), is in good agreement, suggesting

$$\Omega_0 \simeq 9 \times 10^{13} \text{ Hz.}$$

Both estimates fall within the range $\omega_0 \simeq 10^{13}$ – 10^{14} Hz indicating that the adiabatic small-polaron limit does provide an appropriate description of this untreated sample. This conclusion agrees with that drawn from previous measurements on this system at comparable doping levels, particularly data on thin films [5], acquired in some cases over a wider temperature range extending up to 1200 °C [20]. It also justifies the presentation of these data in the form of figure 5.

By contrast, for the oxygen-depleted specimen (with δ taken as 0.09, although this estimate is *not* pivotal) similar analyses produce substantially lower values for Ω_0 . These are

$$\Omega_0 \simeq 10^{13} \text{ Hz} \quad (\text{with } g_d = 1 \text{ in the adiabatic expression})$$

and

$$\Omega_0 = 1.6 \times 10^{13} \text{ Hz} \quad (\text{non-adiabatic regime, equation (4), with } T = 250 \text{ K}).$$

These indicate that the situation is marginal as the estimates of Ω_0 are at the lower limit of typical optical frequencies, but falling below such frequencies if polaronic hopping beyond nearest neighbours is operative ($g_d > 1$) [5, 20], or if the δ -estimate is indeed an upper limit. For these reasons, coupled with the results of the following section, the non-adiabatic form of equation (2) has been utilized in this regime for this sample, and this is the format shown in figure 6.

3.2.2. Ordered regime ($T < T_c$): O-depleted sample. While some consensus exists as regards the question of (small-) polaron-mediated transport in the high-temperature paramagnetic phase of doped manganese perovskite systems, there are differing reports on the applicability of such processes in the low-temperature/ferromagnetic regime. Consequently, in addition to equation (2), two further forms have been fitted to these data. The first of these:

$$\rho(T) = \rho_0 e^{(T_0/T)^{1/4}} \quad (6)$$

has been associated with both phonon-assisted hopping for temperatures at or below half the Debye temperature θ_D [25] (appropriate for this lower-temperature region) and variable-range hopping [26] in which T_0 measures the localization length. The second is

$$\rho(T) = \rho_0 e^{E_a/k_B T}. \quad (7)$$

This direct exponential dependence could result from a form of charge ordering; in the present context, inhomogeneous spontaneous electronic phase separation into electron-rich antiferromagnetic insulating regions coexisting with hole-rich ferromagnetic conducting regions might occur. While it is argued below that this is probably unphysical in the case of ferromagnetic semiconducting behaviour, it is considered here as it has been the focus of some considerable theoretical and experimental debate recently [27].

We find that equation (6) is quite inappropriate for fitting these data (a similar conclusion has been reached for an *untreated* sample for temperatures well *above* T_c [20]), and while equation (7) provides a significantly better fit, it is still statistically inferior to those provided by equation (2) with either choice for the exponent n . For completeness, table 2 lists the parameters characterizing all four fitting schemes in the regime $T < T_c$; however, due to the superior quality of fits provided by the small-polaron approaches, our subsequent discussion is focused on them. Additionally, while equation (7) does provide a reasonable (though statistically inferior) fit, the occurrence of a ferromagnetic ground state, within an inhomogeneous electronic phase-segregation picture, would probably reflect the formation of an infinite, percolating ferromagnetic cluster, of the type originally proposed for the **AuFe** system [28]. While some approaches claim that such phase separation can occur with equal-density clusters, the ferromagnetic regions still retain metallic characteristics; such features are predicted to appear near $x \sim 0.5$ [29]. At the lower doping levels of the present experiment, the hole-rich ferromagnetic metallic regions would predominate. Since the ranges of the interactions responsible for magnetic coupling and charge transport appear comparable in these systems, the presence of an infinite, percolating cluster of this type would be inconsistent, in general, with the continuation of semiconducting behaviour (the occurrence of a ferromagnetic insulating phase in the specific case of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for $x \sim 0.1$ notwithstanding [30]).

Table 2. Fitting parameters extracted for the ferromagnetic phase.

$T < T_c$	O-depleted sample		
	E_a (meV)	ρ_0 (Ω cm)	Std Err
$\rho = \rho_0 T \exp(E_a/k_B T)$	86	5.53×10^{-3}	0.025
$\rho = \rho_0 T^{3/2} \exp(E_a/k_B T)$	91	3.28×10^{-4}	0.024
$\rho = \rho_0 \exp(E_a/k_B T)$	78	1.57	0.029
$\rho = \rho_0 \exp(T_0/T)^{1/4}$	1.29×10^7	8.51×10^{-12}	0.081

To turn, therefore, to an analysis of the parameters characterizing the fits to equation (2), the most obvious result is the decrease in the activation energy E_a on entering the ferromagnetic phase for both the adiabatic and non-adiabatic models. In both model approaches $E_a^p \sim 2E_a^f$, demonstrating a marked decrease in the characteristic energy E_a in the ferromagnetic regime, probably reflecting a significant magnetoelastic influence on polaron formation and its subsequent dynamics. From the adiabatic fit, the listed ρ_0 -value (table 2 and equation (3) with $g_d = 1$) yields an estimate of Ω_0 —following the procedure outlined above—of

$$\Omega_0 \simeq 3 \times 10^{10} \text{ Hz} \quad (T < T_c).$$

The non-adiabatic formalism (equation (4) with $\simeq 100$ K) yields a comparably low value of

$$\Omega_0 \simeq 5 \times 10^{10} \text{ Hz} \quad (T < T_c).$$

Both estimates fall more than two orders of magnitude below the characteristic optical frequencies ω_0 , provided, of course, that the numerical values of other parameters appearing in equations (3) and (4) remain unaltered, an assumption discussed in more detail below. Nevertheless these estimates satisfy the inequality of equation (5), thus supporting not only the applicability of the non-adiabatic limit to this O-depleted sample but also the use of the corresponding form of equation (2) in plotting figure 6.

These results indicate a significant modification to both E_a and the ‘dynamics’ associated with polaronic motion in this ordered phase, as do estimates of other characteristic parameters. The coupling factor J can be found directly from the non-adiabatic model expression, equation (4), and the corresponding ρ_0 - and E_a -values listed in tables 1 and 2. These yield

$$|J| \simeq 28 \text{ meV} \quad (T > T_c)$$

falling to

$$|J| \simeq 1 \text{ meV} \quad (T < T_c).$$

This low value for $|J|$ at $T < T_c$ directly reflects the estimate of Ω_0 given above. Both estimates satisfy the inequality $|J| \ll E_a$, providing support for the conditions necessary for the validity of equation (4) in the high-temperature disordered and the low-temperature ordered phases.

The estimate for J at temperatures $T > T_c$ is comparable to those calculated from available high-temperature data [25] on LaMnO_3 ($|J| \approx 26$ meV) and LaCrO_3 ($|J| \simeq 8$ meV), which are also well described by, and are internally consistent with, the non-adiabatic formalism. In this latter context it is interesting to note that the corresponding estimates for E_a ($\simeq 190$ meV and 180 meV respectively) are also close to that found here for the O-depleted specimen above T_c ($E_a \simeq 189$ meV). The relevance of this comparison is that the resistivity of LaCrO_3 is close to three orders of magnitude larger than that for LaMnO_3 which, given the similarity in the activation energy E_a , is only partially accounted for by a reduced value for the electronic coupling factor $|J|$ in the former. Differences in the small-polaron concentration—suggested to be close to a factor of 50—play a more significant role [25]. We suggest that analogous

considerations apply here, namely, that a substantial drop in the small-polaron concentration occurs in the Ar-treated sample below T_c . That ρ_0 in equation (2) increases below T_c is a natural consequence of a decrease in E_a below, and the continuity of the resistivity through, the transition temperature. The associated marked decrease in Ω_0 (and hence $|J|$) results only if the polaron density remains unmodified in the ordered phase. We think that this is unlikely.

One *possible* model for such a decrease is provided by approaches which attribute transport in doped perovskites in general, and colossal magnetoresistance (CMR) in particular, to polaronic behaviour [3]. Specifically, these approaches attribute the metal–insulator transition to the formation of immobile bipolarons in the paramagnetic regime, the number density of which increases with decreasing temperature. Below T_c , the emergence of an exchange field results in pair breaking—at least for spin-singlet bipolaron pairing—with a dramatic increase in the free-polaron density, resulting in metallic behaviour (actually associated with polaronic tunnelling rather than hopping). However, as recently suggested for $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ [9]¹, the persistence of semiconducting behaviour *below* T_c would be consistent, within such a picture, with spin-triplet bipolaron formation. The number density for the latter would not decrease dramatically below T_c —rather the opposite, as illustrated in figure 4 in reference [9]—in contrast to the case for spin-singlet bipolaron formation. The observation that the magnetoresistance in $\text{La}_{0.95}\text{Mg}_{0.05}\text{MnO}_3$ and the present O-depleted specimen (inset, figure 6) is moderate, not colossal, is in agreement with such a proposal. In the present context (uncertainties in the nature of the charge carriers—Mn e_g rather than O 2p holes [3]—notwithstanding), triplet pairing would increase the energy separation between the triplet bound pair and the ‘free’-polaron band below T_c (figure 4 in [9]), so the occupation of the latter would fall. Such a decrease would mean that Ω_0 (and hence $|J|$) would assume values closer to those found in the paramagnetic region. That Ω_0 and $|J|$ should be modified in the ordered phase is not unreasonable; however, changes in these parameters by several orders of magnitude appear less likely, and the mechanism that could produce such changes is not clear currently. The situation characterized by bipolaron formation is therefore likely to lead to more physically realistic changes.

4. Summary and conclusions

Transport and magnetic data on O-depleted $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$ are presented and contrasted with data for an untreated specimen. Detailed analyses indicate that the transport data for both the magnetically disordered *and* ordered regimes of the O-depleted sample are consistent with the predictions based on small-polaron hopping, in particular—on the basis of the consistency of model parameters extracted—non-adiabatic hopping. These results yield indirect support to the modelling of the metal–insulator transition and CMR in doped perovskites as polaronic behaviour.

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¹ A reanalysis of the data in [9] using the more appropriate expressions for ρ_0 —equations (3) and (4)—leads to: (a) $T > T_c$, $\Omega_0 \approx 6 \times 10^{13}$ (adiabatic), $\Omega_0 \approx 9 \times 10^{13}$ (non-adiabatic), a result that supports the use of the adiabatic formalism in the paramagnetic regime; however, for (b) $T < T_c$ these estimates fall by a factor of 20–30, probably reflecting a crossover to a non-adiabatic regime, and a situation similar to that discussed in the main text regarding the polaron concentration. Here the non-adiabatic fit yields $|J| \approx 11$ meV.

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