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LETTER TO THE EDITOR

Polaronic transport in both the paramagnetic and ferromagnetic phases of $La_{0.95}Mg_{0.05}MnO_3$

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Abstract. Measurements of the field and temperature dependent electrical resistivity and ac susceptibility of $LaMnO_3$ doped with 5% Mg are presented. Analysis of these data reveal that while this system undergoes a ferromagnetic transition at $T_c = 147.2 \pm 0.2$ K, it remains semiconducting over the entire temperature range examined ($90 \leqslant T \leqslant 330$ K). In particular, these resistivity data are well fit by the form appropriate for adiabatic small polaron hopping for both $T > T_c$ and $T < T_c$. These fits also indicate a distinct drop in the characteristic hopping energy E_a on entering the ferromagnetic phase which presumably reflects a significant magnetoelastic influence on the polaron dynamics. Such a scenario can be accounted for specifically in recent theories involving bipolaron formation in the paramagnetic phase, however the persistence of polaronic hopping—rather than metallic transport/polaronic tunnelling—in the ordered phase would be indicative of triplet, rather than singlet, pairing at all temperatures within such a model.

Although colossal magnetoresistance (CMR) in the doped manganese perovskites was first reported nearly half a century ago [1], a comprehensive, quantitative understanding of this phenomenon is still lacking. While the double exchange (DE) model [2] provides a physically transparent, qualitative picture of such effects, it fails quantitatively. The DE model assumes a degree of itinerance is established for Mn e_g electrons by the substitution of divalent cations for trivalent lanthanide ions at A sites. However, strong Hund's rule effects (intra-site correlations) inhibit Mn^{3+}–O–Mn^{4+} hopping unless the e_g and t_{2g} (core) spins are parallel. This approach thus not only favours ferromagnetic order with an attendant increase in conductivity but also, through the field induced increase in the ordering temperature, provides a plausible explanation of CMR. It fails however, because it cannot generate the degree of scattering necessary to account for the magnitude of the resistivity present in the (spin-disordered) paramagnetic phase [3]. The consensus of current work thus supports the premise of polaronic transport in the paramagnetic regime [3, 4]. By contrast, the nature of the conduction process in the ordered phase remains contentious. Present views centre on models incorporating, respectively, not only metallic transport with carrier density consistent with doping levels (and, presumably, enhanced carrier effective mass), as opposed to the continuance of polaronic behaviour, but also a significant difference in the nature of the 'carriers'. Within the double-exchange picture current is transported by quasi-itinerant Mn e_g electrons which acquire a polaronic character in the paramagnetic phase through a combination of strong electron–phonon coupling and Jahn-Teller distortions [3]. This contrasts with proposals that the carriers are O p holes, bound into immobile (bipolaronic) pairs in the paramagnetic phase, but with the pair breaking effects of the exchange field in the ferromagnetic phase inducing increased mobility (at least for spin singlet

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pairing) through polaronic tunnelling [4]. In this latter model CMR is attributed to a collapse in the carrier density at the magnetic transition, a consequence of the marked dependence of the bipolaron pair breaking exchange coupling with localized Mn spins on field. Further, the magnetic transition in this model can be first-(discontinuous) or second-(continuous)order, depending on the polaron density which, in turn, reflects the relative magnitudes of this exchange coupling and the electron–phonon interaction.

In this letter we present measurements of the transport and magnetic properties of $La_{0.95}Mg_{0.05}MnO_3$ which reveal that this system is a ferromagnet at low temperature with strong evidence of polaronic hopping-based transport in both the disordered *and* ordered phases. Detailed fits indicate a distinct drop in the characteristic hopping energy on entering the ferromagnetic phase, supposedly reflecting a marked magnetoelastic influence on the hopping process; the magnetic transition itself is second-order. It is argued that these data provide strong support for models incorporating polaronic transport over the entire temperature range, at least for Mg doped manganese perovskites. However the specific scenario reported here, that is the occurrence of polaronic hopping—rather than 'metallic' transport/polaronic tunnelling)—in the ordered regime, can be accounted for within specific models that consider polaronic transport above and below the ferromagnetic ordering temperature by invoking triplet, rather than singlet, bipolaron pairing. Triplet pairs would, of course, not be influenced by the uniform exchange field in the ordered phase, unlike singlet pairing. The ensuing result that the magnetoresistance is moderate, rather than colossal, is in agreement with such a proposal as it essentially eliminates carrier-density collapse.

Dc magnetization and ac susceptibility data as a function of both field and temperature were acquired using a Quantum Design PPMS (model 6000) system on a sample of approximate dimensions $(0.8 \times 1.3 \times 7)$ mm^3 prepared by standard ceramic techniques. X-ray diffraction data acquired using a Philips PW1710 automated diffraction system with a Bragg–Brentano goniometer confirmed a single-phased orthorhombic structure (Pbnm). The latter could be fitted using $a = 5.4907$ Å, $b = 5.7097$ Å and $c = 7.7254$ Å (i.e. $c/\sqrt{2} < a < b$) with no indication of impurity phases—specifically various oxides of manganese—above background. Full details of the preparation method and analysis of the magnetic measurements are presented elsewhere [5].

For the purpose of this letter it is sufficient to examine the behaviour of the ac susceptibility displayed as a function of temperature in various (fixed) static biasing fields (measured on warming, following zero-field cooling, at 2.4 kHz with a driving field amplitude of 3 μT) in figure 1. The peak structure reproduced in the inset in this figure is evidence of critical fluctuations accompanying a second-order (continuous) phase transition. The locus of such peaks in the (H–T) plane—the crossover line—separates a regime where the response is field dominated from a higher temperature, thermally dominated region, as discussed in detail recently for the pyrochlore system $Tl_2Mn_2O_7$ [6]. The usual scaling law equation of state for such a transition, relating the (reduced) magnetization m to the linear scaling fields and $h \sim H_i/T_c$ (H_i being the internal field), namely

$$m = t^{\beta} F(h/t^{\gamma+\beta}) \tag{1}$$

yields a susceptibility $\chi(h, t) = \partial m/\partial h$ of the form

$$\chi(h, t) = t^{-\gamma} G(h/t^{\gamma+\beta} = h^{1-1/\delta} H(h/t^{\gamma+\beta}) \tag{2}$$

where G is the derivative of the scaling function F with respect to its argument, X, and $H(X) = X^{\gamma/\gamma+\beta} G(X)$ (assuming the validity of the Widom equality, $\gamma = \beta(\delta - 1)$). Equation (2) predicts that the susceptibility measured along each isokap or constant field curve, normalized to its peak value, should scale onto a single curve when plotted against this

argument $X = (h/t^{\gamma+\beta})$ if the scaling hypothesis is correct, as the following argument shows. From the final expression in equation (2)

$$\chi(h,t)/\chi(h,t_m) = H(X)/H(X_m) \propto H(X) \tag{3}$$

with the last step resulting from the scaling theory assertion that $H(X)$ is a universal function of its argument, i.e. any feature in $\chi(h, t_m)$—such as the maxima evident in the inset in figure 1—occur at the same value of this argument ($X_m = h/t_m^{\gamma+\beta}$)—in which case the function itself, $H(X_m)$, is also a constant. The main body of this figure shows a plot of these data normalized to each peak value, against the argument X (actually its inverse $t^{\gamma+\beta}/H_i$, to preserve the peak structure). The data collapse onto a single curve, confirming the scaling hypothesis, using isotropic 3D Heisenberg model exponents, $\gamma + \beta = 1.75$ [7], and $T_c = 147.2$ K. As mentioned above, a complete analysis of these susceptibility data and related magnetization measurements confirm this [5].

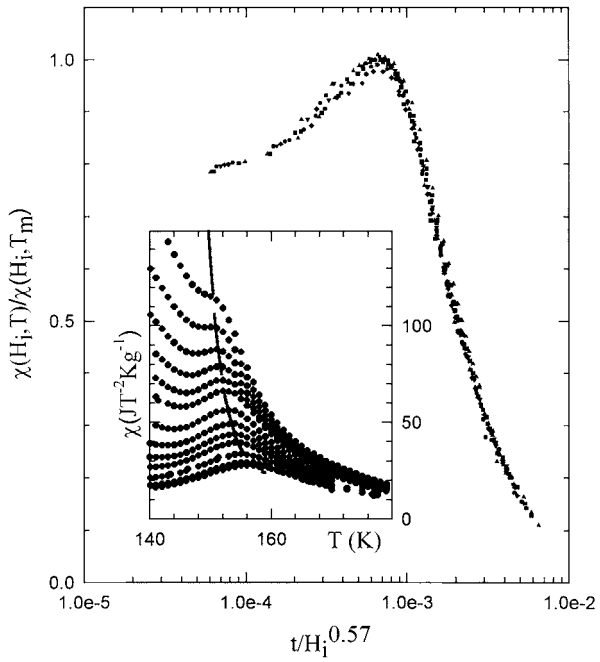

Figure 1. The inset shows the ac susceptibility (corrected for background and demagnetizing effects) plotted as a function of temperature for a sequence of superimposed dc biasing fields between 0.04 and 0.28 T. The main body of this figure shows the collapse of similar data onto a scaling curve using Heisenberg model exponents, as discussed in the text.

The transport data are presented in figure 2. The zero-field resistivity, $\rho(T)$, is displayed in the inset in this figure in the form of a $\ln \rho(T)$ versus T plot; from this it can be seen that the system remains semiconducting over the entire temperature range examined ($90 \leqslant T \leqslant 330$ K; there is no evidence in the magnetic data of a second transition at lower temperature). In particular, no metal–insulator transition occurs in the vicinity of the paramagnetic to ferromagnetic transition temperature. Indeed no anomaly is evident in this $\ln \rho(T)$ versus T plot. This changes, however, when these data are replotted in the form suggested by the theory of adiabatic small polaron hopping, namely [4, 8]

$$\rho(T) = \rho_0 T \mathrm{e}^{E_a/k_B T} \tag{4}$$

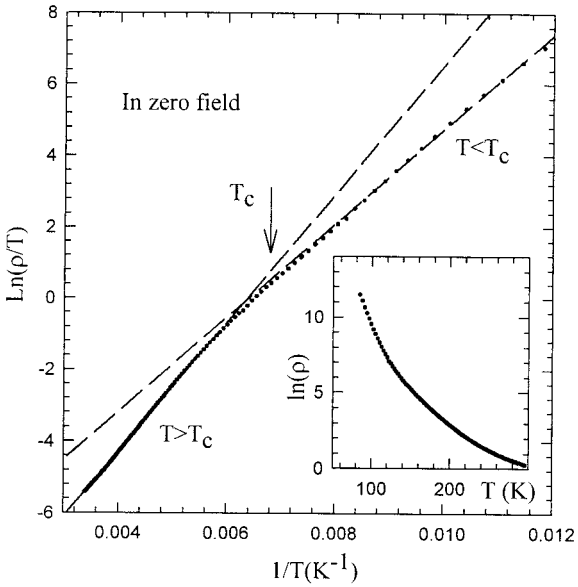

Figure 2. The inset reproduces the resistivity of the $La_{0.95}Mg_{0.05}MnO_3$ sample in the form of a $\ln(\rho)$ versus temperature (T) plot. The main body shows these data replotted in a form consistent with the predictions for adiabatic small (bi)polaron hopping, equation (3).

in which E_a is the characteristic polaron activation energy. From the $\ln[\rho(T)/T]$ versus $1/T$ plot shown in the main body of this figure it can be seen that these data are well fit by this expression, *both above and below* T_c. This provides strong evidence supporting the contention that polaronic processes control the transport behaviour in both the magnetically disordered *and* ordered phases of this system. As might be anticipated, these data also indicate a distinct reduction in the hopping energy E_a in the ordered phase; the lines drawn in figure 2 are the results of least-squares fits of equation (3) to these data, yielding

$$T > T_c : E_a^p = 157 \text{ meV} \qquad \rho_0 = 9.2 \times 10^{-6} \Omega \text{ cm K}^{-1}$$
$$T < T_c : E_a^f = 115 \text{ meV} \qquad \rho_0 = 1.97 \times 10^{-4} \ \Omega \text{ cm K}^{-1}$$

so that $\Delta E = E_a^p - E_a^f \simeq 2k_B T_c$.

Data acquired for $T > T_c$ are in general agreement with the results of similar fits carried out on the paramagnetic/semiconducting phase of bulk samples and sputtered films of $La_{1-x}Ca_xMnO_3$ for $x \simeq 0.35$ and $x = 0.30$ respectively [9, 10]. Further, while this is the first report of polaronic *hopping* behaviour in the ordered phase of doped manganese perovskites, a recent analysis of the resistivity of $La_{1-x}Ca_xMnO_3$ ($x \simeq 0.25, 0.4$) films has demonstrated convincing fits [11] to a form consistent with polaronic *tunnelling* below 100 K in the ferromagnetic phase. Thus, both types of response (i.e. $d\rho/dT > 0$ and $d\rho/dT < 0$) have been demonstrated to be consistent with the occurrence of polaronic transport below T_c, at least qualitatively. Quantitative comparisons however reveal some differences. The activation energy $E_a^p(T > T_c)$ deduced above for the paramagnetic phase is roughly twice that estimated for the corresponding phase in Ca doped samples (with $x \sim 0.33$), so that deduced for the *ordered* phase, E_a^f, being smaller, is closer in magnitude. Neither estimate for E_a however appear unphysical. Comparisons based on the characteristic resistivity ρ_0 are, however, very

different. This parameter is generally written as [9, 10]

$$\rho_0 + \frac{ak_B}{g_d \nu_0 e^2}$$

where a is the average hopping distance, g_d a numerical constant ($\gtrsim 1$) reflective of the hopping topology while ν_0 is a characteristic frequency usually associated with a typical optic mode phonon frequency. With the often made assumption that $g_d \simeq 1$ and $a \simeq 3.9$ Å (the Mn–Mn separation), the above fits yield $\nu_0 \simeq 3.2 \times 10^{13}$ Hz ($\simeq 1500$ K), reasonably close to typical literature values for the paramagnetic phase of other doped manganites [9, 10]. Below T_c a corresponding analysis yields $\nu_0 \simeq 10^{11}$ Hz (~ 5 K), a much lower value. In the case of $La_{1-x}Ca_xMnO_3$ ($x \simeq 0.25, 0.4$) films, a significant reduction in characteristic frequency was also reported below T_c. There mode energies of some 75–80 K were estimated and could be linked to the occurrence of low-lying optical excitations associated with the tilt/rotation of the oxygen octahedra [11]. By contrast the very low-energy mode corresponding to $\nu_0 \sim 10^{11}$ Hz—assuming, of course, that equation (4) continues to be applicable over the entire temperature range to the Mg doped sample surveyed here—has no clearly identifiable origin currently.

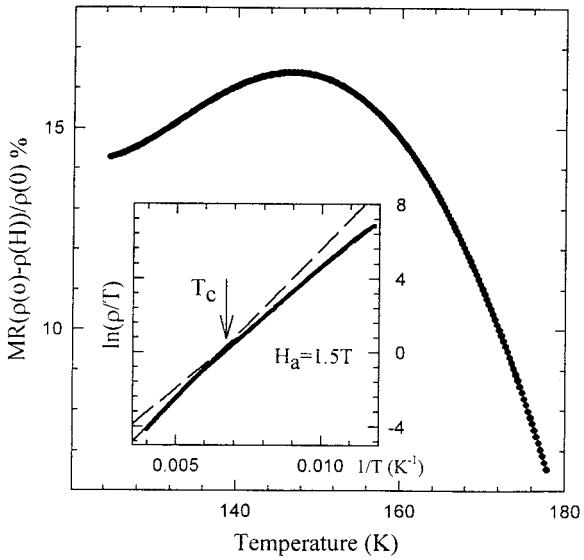

Figure 3. The percentage magnetoresistance measured in an applied field of 1.5 T plotted against temperature. The inset displays the resistivity data acquired in 1.5 T; here the solid lines are again fits to equation (3) with $E_a^p = 138$ meV, $\rho_0 = 2.9 \times 10^{-5} \Omega$ cm K^{-1} ($T > T_c$); $E_a^f = 111$ meV, $\rho_0 = 2.48 \times 10^{-4} \Omega$ cm K^{-1}.

The effects of an applied magnetic field $\mu_0 H_a \sim 1.5$ T are shown in the inset in figure 3 in a form consistent with equation (3). Not unexpectedly, while a change in slope above and below T_c is evident, it is not as distinct as in the zero field data, although there is a similar reduction in the hopping energy below T_c (as detailed in the caption for this figure). The main body of this figure displays the associated magnetoresistance, $\Delta\rho(T) = (\rho(0, T) - \rho(H, T))/\rho(0, T)$, as a function of temperature. This magnetoresistance is moderate, not colossal, displaying a broad maximum of some 20% near T_c.

The above results were obtained on a specimen with low divalent cation doping, significantly below the levels necessary to enable Mn e_g electrons to delocalize in a double

exchange picture (due to the emergence of an e_g–O($2\rho_\sigma$) band for x, typically, > 0.1 [12]). Nevertheless, the agreement with the predictions for polaronic transport above and below T_c and an enhanced mobility in the ordered phase here is unequivocal (this ordered phase is ferromagnetic here, as opposed to canted antiferromagnetism at similar doping levels in canonical double exchange systems such as $La_{1-x}Ca_xMnO_3$ [12]). The present data are clearly consistent with models invoking polaronic transport both above and below T_c, with the reduction in the characteristic hopping energy E_a being indicative of a significant magnetoelastic influence on the hopping process. The specific nature of the current results are, however, atypical. They represent a particular aspect of models invoking polaronic transport above and below T_c that is not generally observed in the doped perovskites (namely, the persistence of polaronic hopping ($d\rho/dT < 0$), as opposed to polaronic tunnelling ($d\rho/dT > 0$), in the ferromagnetic phase). Such a situation could result if the triplet bipolaron states lie *below* that of the singlet state (that is, the exchange coupling, J_{st} in the notation of Alexandrov and Bratkovsky [4] favours ferromagnetic bipolaron coupling), indicative of a more delocalized bipolaronic formation, i.e. an inter-site pairing of neighbouring O p holes rather than an intra-site/nearest-neighbour pairing. In this case, the triplet bound pairs formed in the paramagnetic phase would remain bound in the ferromagnetic phase where the exchange field would not induce pair breaking, unlike the case of singlet pairing, as shown schematically in figure 4. This would, correspondingly, eliminate carrier-density collapse and the CMR, as is observed here. This contrasts markedly with the case where $0 < |J_{st}| \leqslant |\Delta|$ (where Δ is the singlet pair binding energy), in which a thermal population of the (higher energy) triplet states leads—through their increased degeneracy—to a further depression in the carrier density and an enhancement of the already colossal magnetoresistance [4].

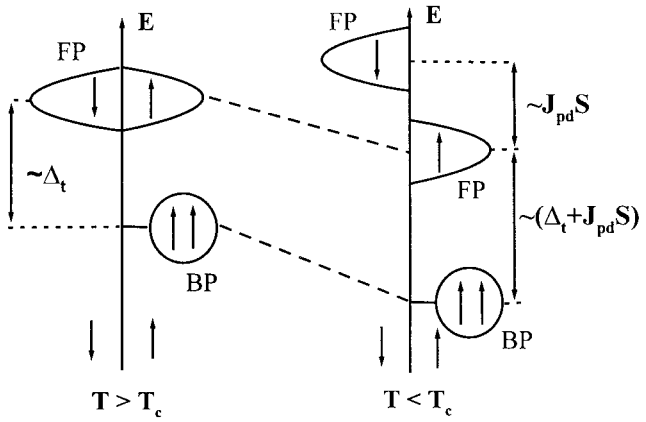

Figure 4. A schematic diagram of the spin-up (↑) and spin-down (↓) free polaron (FP) and the (triplet) polaron bound pair (BP) density of states at temperatures above and below T_c. Δ_t measures the triplet binding energy (relative to a free pair). The exchange interaction of the polarons with localized Mn spins (S) causes the energy of both the spin-up free polaron sub-band and the triplet bound pair to fall at temperatures below T_c.

There are, of course, several interesting questions raised by the present measurements. If indeed the bipolaronic model is demonstrated to have broad applicability, then the possible influence of the dopant species on the singlet/triplet character of the polaron pairing would require further investigation, as would be its relationship to the magnetic transition. For the present system, the magnetic transition is continuous, with exponent values falling in the universality class of the near-neighbour, isotropic 3D Heisenberg model.

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References

[1] Jonkers G H and van Santen J H 1950 *Physica* **16** 337
Jonkers G H and van Santen J H 1950 *Physica* **16** 599
Searle C W and Wang S T 1969 *Can. J. Phys.* **47** 2703 Searle C W and Wang S T 1969 *Can. J. Phys.* **48** 2023
[2] Zener C 1951 *Phys. Rev.* **81** 440
Anderseon P W and Hasegawa H 1955 *Phys. Rev.* **100** 675
Furukawa N 1994 *J. Phys. Soc. Japan* **63** 3214
Furukawa N 1995 *J. Phys. Soc. Japan* **64** 3164
Furukawa N 1995 *J. Phys. Soc. Japan* **64** 4321
[3] Millis A J, Littlewood P B and Shraiman B I 1995 *Phys. Rev. Lett.* **74** 5144
Millis A J, Shraiman B J and Mueller R 1996 *Phys. Rev. Lett.* **77** 175
Li Q, Zang J, Bishop A R and Soukoulis C M 1997 *Phys. Rev.* B **56** 4541
[4] Alexandrov A S and Bratkovsky A M 1998 *Phys. Rev. Lett.* **82** 141 Alexandrov A S and Bratkovsky A M 1999 *J. Phys.: Condens. Matter* **11** 1989
Alexandrov A S and Bratkovsky A M 1999 *J. Phys.: Condens. Matter* **11** L531
[5] Zhao J H, Song T, Kunkel H P, Zhou X Z, Roshko R M and Williams Gwyn 2000 *J. Phys.: Condens. Matter* **12** 6903
[6] Zhao J H, Kunkel H P, Zhou X Z, Williams Gwyn and Subramanian M A 1999 *Phys. Rev. Lett.* **83** 219
[7] Le Guillon L C and Zinn-Justin J 1980 *Phys. Rev.* B **21** 3976
[8] Emin D and Holstein T 1959 *Ann. Phys., NY* **53** 439
[9] Franck J P, Isaac I, Chen W, Chrzanowski J and Irwin J C 1998 *Phys. Rev.* B **58** 5189
[10] Jamie M, Hardner H T, Salamon M B, Rubinstein M, Dorsey P and Emin D 1997 *Phys. Rev. Lett.* **78** 951
[11] Zhao G, Keller H and Prellier W 2000 *J. Phys.: Condens. Matter* **12** L361
[12] Schiffer P, Ramirez A P, Bao W and Cheong S-W 1995 *Phys. Rev. Lett.* **75** 3336
Tomioka Y, Asamitsu A, Kuwahara H, Morimoto Y and Tokura Y 1996 *Phys. Rev.* B **53** R1689