Correlation between the Nucleation of a Griffiths-like Phase and Colossal Magnetoresistance Across the Compositional Metal-Insulator Boundary in La$_{1-x}$Ca$_x$MnO$_3$

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Abstract. Detailed measurements of the magnetic and transport properties of single crystals La$_{1-x}$Ca$_x$MnO$_3$ (0.18 $\leq$ x $\leq$ 0.27) are summarized; comparisons between which (i) not only confirm that Griffiths Phase-like (GP) features are not a prerequisite for CMR, but also demonstrate that the presence of GP-like characteristics do not guarantee the appearance of CMR; (ii) indicate that whereas continuous magnetic transitions occur for 0.18 $\leq$ x $\leq$ 0.25, the universality class of these transitions belongs to that of nearest-neighbour 3D Heisenberg model only for x $\leq$ 0.20, beyond which complications due to GP-like behaviour occur.

Transition metal oxides exhibit a range of fascinating properties that include multiferroicity, superconductivity, and colossal magnetoresistance (CMR). Many of these appear to be critically sensitive to differing types/levels of ion substitutions, particularly striking in the case of CMR perovskites manganites [1-3] in which dramatic changes in resistivity result from a metal-insulator (M-I) transition, the temperature of which exhibits a marked field-dependence (the latter often occurring in close proximity to a paramagnetic-ferromagnetic (PM-FM) transition).

Below we summarize a study of single-crystal La$_{1-x}$Ca$_x$MnO$_3$ with 0.18 $\leq$ x $\leq$ 0.27, spanning the compositionally driven M-I boundary region, 0.18 $\leq$ x $\leq$ 0.22 [2-3]. The appearance of CMR in manganites was initially considered within the framework of a spin-dependent Double Exchange (DE) model [4] in which FM interactions between the localized Mn $t_{2g}$ spins are mediated by the hopping of itinerant $e_g$ spins. The onset of metallicity is thus linked with the establishment of an infinite (percolation) pathway of DE metallic bonds, the same bonds that establish an infinite FM “backbone”, so that the occurrence of metallicity and ferromagnetism are coincident. Subsequent discussions/studies have emphasized the necessity of including the Jahn-Teller effect and the electron-phonon interaction [5]. Currently, the role of spontaneous electronic phase separation [6] and relationship between the occurrence of a Griffiths-like Phase (GP) and CMR [7-9], amongst others, are regarded as pivotal ingredients in this context. The physical mechanism underlying CMR nevertheless remains controversial. That FM and metallicity are governed by percolative mechanisms appears generally agreed, however questions have arisen recently as to whether they emerge coincidental. The present study focuses on the doping range
where both ferromagnetism and metallicity first emerge, although not, as detailed measurements confirm, coincidentally.

Measurements of the magnetic and transport behaviour of high quality La$_{1-x}$Ca$_x$MnO$_3$ single crystals with the nominal compositions $x = 0.18, 0.19, 0.20, 0.21, 0.23, 0.25,$ and $0.27,$ grown using the floating zone technique [10], were carried out using standard techniques [8]. Fig. 1 reproduces the temperature dependent resistivity $\rho(T,H)$ measured in static magnetic fields of 0, 30 kOe, and 90 kOe; the insets display the associated magnetoresistance ($\Delta \rho = (\rho(0) - \rho(H))/\rho(H)$). These data confirm that the M-I boundary lies between $0.19 \leq x_c \leq 0.20$ in the series studied. In Fig. 2 the inverse ac susceptibilities $\chi_{ac}$ of these same samples (measured in both zero-field and in various static biasing fields up to 1 kOe) are plotted as a function of temperature. The characteristic depression of some of these data below the higher temperature Curie-Weiss line are clearly evident, a symptom of so-called GP behaviour [7-9, 11-16], viz., an inverse susceptibility of the form:

$$\chi^{-1} \propto (T - T_C)^\lambda \quad \lambda < 0 < 1$$

The occurrence of GP-like features have been reported in range of doped perovskites based on a various physical measurements [7-9, 11-16]; their presence has been attributed to the influence of disorder on the phase complexity in the magnanites and related systems [7-9, 11-16]. Whereas GP-like features have been shown to correlate closely with CMR in this system near optimal doping [7], a comparison of the data in Figs 1 and 2 provide (i) further confirmation of the earlier conclusion [8] that GP-like features are not a prerequisite for CMR – the $x = 0.20$ and 0.21 samples both exhibit CMR, whereas only the latter displays GP-like features, and (ii) allows the important additional caveat that the appearance of GP-like features do
not guarantee the emergence of CMR – the x = 0.19 specimen exhibits GP-like features but has an insulating ground state and hence no appreciable magnetoresistance. These data raise further questions regarding our current understanding of the fundamental mechanism(s) underlying CMR [8-9].

A more detailed examination of these data is provided by conventional analysis of critical behaviour in the vicinity of a continuous PM-FM transition; this is based on the scaling law equation of state relating the reduced magnetisation, \( m(h, t) \), and susceptibility \( \chi(h, t) \), to the usual (reduced) linear scaling fields \( t = (T-T_C)/T_C \) and \( h \sim H_i/T_C \) (where the internal field \( H_i = H_u - N_d M \), in the usual notation) [17-18], viz.,

\[
\begin{align*}
\frac{\partial m}{\partial h} = & H_0 \left( \frac{h}{H_0} \right)^{1-\gamma} \\
\chi(h, t) = & \frac{\gamma}{t} \left( \frac{h}{H_0} \right)^{1-\delta} \frac{1}{Y_{\delta}} \left( \frac{h}{H_0} \right)
\end{align*}
\]  

(2)

\( G_\delta(x) \) being the derivative of \( F_\delta(x) \) wrt its argument. Fig. 3a reproduces scaling plots of the magnetization and Fig. 3b of the susceptibility for all samples; only the 0.18, 0.19 and 0.20 samples are fit using isotropic 3-D Heisenberg model exponent values (\( \gamma = 1.387, \beta = 0.365, \) and \( \delta = 4.783 \)) [19]. As the static applied field is the conjugate field for uniform ferromagnetism, rather than its disorder GP counterpart, the GP-like features appearing in the \( x=0.19 \) sample are rapidly suppressed by small external fields – as in \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) (\( x = 0.27 \)) [20] – and “conventional” critical behaviour ensues [20]. In contrast, in samples with \( x > 0.20 \), complications from GP-like behaviour yield non-universal exponent values (\( 5 < \delta < 19 \), for example).

The present data provide a careful delineation of the compositionally driven M-I boundary as lying between 19 and 20% Ca substitution in this series of single crystals, thereby supplying incontrovertible evidence supporting the conclusion that the emergence of metallicity and ferromagnetism is not coincidental in \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \). An immediate corollary to this conclusion is the question of what are the principal mechanisms underlying ferromagnetism in this composition range. The answer to this latter question, as argued recently [21], is that whereas ferromagnetic DE, stabilized by hole delocalization, dominates in the metallic regime immediately above the compositionally controlled M-I boundary, the relevant interaction below this boundary is ferromagnetic super exchange (SE).

Returning to GP-like behaviour, with the adoption of a working definition of the Griffiths temperature, \( T_G \), as the temperature at which a marked onset depression in the inverse zero-field ac susceptibility first occurs [11-13] (marked by vertical arrows in Fig. 2), a phase diagram for \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) (\( x < 0.33 \)) can be
constructed, Fig. 4. This affords comparisons with those reported previously for La_{1-x}Sr_xMnO_3 (0.075 ≤ x ≤ 0.175) [11] and La_{1-x}Ba_xMnO_3 (0.10 ≤ x ≤ 0.33) [12]. In the present system, the GP-like regime terminates in close proximity to the M-I boundary, but the emergence of such features near this boundary may be particularly sensitive to various aspects of the underlying “disorder”, possibly including the oxygen stoichiometry (precise measurements of which are not currently available to us). The latter may play a role in both the lack of GP-like features at x = 0.2 and their reappearance at x = 0.19, as well as in the variation evident in T_G and T_C estimates for x > 0.21. The termination of this region is consequently marked as hatched, the latter also delineating – likely non-coincidentally – the M-I boundary at 0.19 ≤ x_c ≤ 0.20 in the series studied. The remaining lines – drawn as guides for the eye – joining the T_G (upper) and T_C (lower) estimates appear somewhat different from the essentially triangular structure predicted by both Griffiths’ original diluted FM Ising model and the ±J random bond approach [22]. The present data clearly exhibit scatter around such model predicted boundaries, although what is consistent with such predictions is the narrowing gap between T_C and T_G as the Ca doping is increased toward “optimal” levels, x = 0.33. Additional evidence supporting the narrowing gap between T_C and T_G around x = 0.25 can be seen in data reported by Belevtsev et. al., [14]. Elements of such scatter are evident in data from other systems. In La_{1-x}Ba_xMnO_3 [14], for example, T_C estimates also displays some structure near x = 0.27, while in Sm_{1-x}Ca_xMnO_3 [15] the reported T_G values are neither constant - they decline by some 6% between x = 0.85 and 0.92 – nor is the corresponding phase diagram reminiscent of the model predicted forms mentioned above. All of the latter attest to the yet unresolved subtleties displayed by GP-like behaviour and CMR in the manganites.

Support for this work by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the University of Manitoba (in the form of a Fellowship to WJ), and MISIS are gratefully acknowledged.

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