Two-fluid behaviour at the origin of the resistivity peak in doped manganites

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Abstract. - We report a series of magnetic and transport measurements on high-quality single crystal samples of colossal magnetoresistive manganites, La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} and Pr\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}. 1 % Fe doping allows a Mössbauer spectroscopy study, which shows (i) unusual line broadening within the ferromagnetic phase and (ii) a coexistence of ferro- and paramagnetic contributions in a region, $T_1 < T < T_2$, around the Curie point $T_C$. In the case of Pr\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}, the resistivity peak occurs at a considerably higher temperature, $T_{MI} > T_2$. This shows that phase separation into metallic (ferromagnetic) and insulating (paramagnetic) phases cannot be generally responsible for the resistivity peak (and hence for the associated colossal magnetoresistance). Our results can be understood phenomenologically within the two-fluid approach, which also allows for a difference between $T_C$ and $T_{MI}$. Our data indeed imply that while magnetic and transport properties of the manganites are closely interrelated, the two transitions at $T_C$ and $T_{MI}$ can be viewed as distinct phenomena.

Introduction. – The phenomenon of colossal magnetoresistance (CMR) in doped manganese oxides continues to attract extensive research effort [1]. While the physical mechanism underlying the CMR phenomenon remains elusive, one can expect it to be generic for the entire family of the CMR compounds, spanning a broad range of chemical compositions, dopant levels, and lattice properties. This natural suggestion is corroborated by the fact that, in addition to the CMR itself, other generic unusual features of the CMR compounds have been found in recent years. These include the formation of a “pseudogap” in the carrier density of states on increasing temperature toward $T_C$ [2] (arguably responsible for the peak in the resistivity, $\rho(T)$, which in turn gives rise to the CMR effect), and the unusual short-range magnetic correlations in the critical region (“central peak”), observed in the inelastic neutron scattering experiments [5]. Although these findings testify to the anomalous electronic and magnetic properties respectively, the relationship between the two remains unclear. While it is generally understood that the metal-insulator transition (at $T_{MI}$, corresponding to the resistivity peak) and the ferro- to paramagnetic transition (at the Curie temperature $T_C$) lie close to each other, the consensus does not go much further. Indeed, questions regarding the mutual location of the two transitions [6, 7] (whether $T_C$ actually equals $T_{MI}$), as well as to their character, remain largely open. This situation is partly due to sample preparation issues, which make it difficult to draw a quantitative connexion between results of different measurements, carried out on different samples.

On the theory side, the picture is similarly uncertain. Current ideas on the mechanism of the CMR mainly fall within two general categories, which can be referred to phenomenologically without specifying the microscopic models or even the relevant degrees of freedom. The first one is the so-called phase separation scenario [8, 9], whereby the metallic (ferromagnetic) and insulating (paramagnetic) phases coexist in the temperature region around $T_C$. With decreasing temperature, the volume fraction of ferromagnetic “droplets” grows, resulting in an eventual percolation and metallic behaviour at low $T$. The

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\footnotetext{Note also the optical [3] and transport [4] data, suggesting that the effective carrier number decreases with $T$ increasing toward $T_C$.}
long-range ferromagnetic order is also linked to connectivity between the ferromagnetic clusters and is established at about the same point.

The second theoretical view is that of the two-fluid model [10], based on the coexistence [11] of (i) localised carriers (or polarons [12]) and (ii) itinerant conduction electrons (present below $T_{MI}$), in a spatially homogeneous (on a submicron scale) system. While the high-temperature insulating properties are accounted for by the fact that all carriers are localised, lowering the temperature leads to an increase of the itinerant carrier population. This in turn results in (i) the resistivity passing through a maximum and decreasing toward lower $T$ and (ii) strengthening the ferromagnetic interaction in the system via the double exchange mechanism [13], which is more effective for the itinerant electrons than for the localised ones.

We note that the prevalent view [14] is that the double exchange mechanism on its own cannot lead to localisation of carriers above certain temperature, hence a microscopic model of colossal magnetoresistance must include additional interactions and/or additional degrees of freedom. In principle, the ferromagnetic order can be established above or below the downturn of the resistivity. Thus, while the physics behind the magnetic transition at $T_C$ can be that of thermal fluctuations overpowering the ferromagnetism, the electronic transition at $T_{MI}$ is due to a (presumably strongly correlated) mechanism leading to the disappearance of itinerant carriers at higher $T$. One may expect this latter mechanism to become operational only in the presence of sufficiently strong magnetic fluctuations (as found near $T_C$), so that ultimately the two transitions are inter-related.

In the present letter, we report a series of magnetic and transport measurements. All of these were performed on the same high-quality manganite single crystals. Our findings appear incompatible with the percolative nature of the metal-insulator transition (as in the phase separation scenario) being a general property. They also imply that the ferro- to paramagnetic and electronic (metal-insulator) transitions are two distinct phenomena with no rigid interconnection. Indeed, the metal-insulator transition at $T_{MI} \neq T_C$ leads to a change of the Curie–Weiss temperature and therefore to a separate feature in the magnetic properties of the system at $T = T_{MI}$. These results can be understood in the framework of the two-fluid approach.

While the two compounds, Pr$_{1-x}$Sr$_x$MnO$_3$ (PSMO) and La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) with $0.2 \approx x \approx 0.5$ show metallic behaviour at low $T$ and CMR near $T_C$, their properties differ significantly. The unconventional magnetic behaviour (giving rise to the central peak as observed near $T_C$ in the neutron scattering experiments [5]), first found in LCMO, is much less pronounced in the PSMO [5]. The underlying unusual short-range magnetic correlations should also be accessible via a local (i.e., momentum-integrated) magnetic probe, such as Mössbauer spectroscopy of iron-doped samples. Earlier Mössbauer studies of the CMR manganites [15–17] indeed uncovered an unusual coexistence of para- and ferromagnetic contributions to the hyperfine field near $T_C$, which can be expected to be a manifestation of the same phenomenon. Other local magnetic probes, such as neutron scattering [18] and nuclear magnetic resonance [19], also find several different contributions in the region around $T_C$.

**Experimental.** – Single crystals of pure and $^{57}$Fe-doped PSMO and LCMO (with $x = 0.3$) were grown by non-crucible floating-zone melting with radiation heating [20]. X-ray diffraction and EPMA (Electron Probe Micro Analysis) measurements were performed to verify that the samples are single phase crystals of the nominal compositions. Properties of the samples are summarised in table II. As expected [21], the 1% substitution of Mn by enriched $^{57}$Fe (needed for Mössbauer spectroscopy) in the two samples, PSMO-F and LCMO-F, does not significantly change the respective system properties.

Magnetisation measurements were performed in a commercial (Quantum Design) SQUID magnetometer. The in-phase component of the zero-field ac susceptibility (measured at 1065 Hz, amplitude 0.05 Oe) and the standard four contact resistivity were measured by homemade probes inserted into the magnetometer. Pieces of LCMO-F and PSMO-F crystals were crushed to powder for the Mössbauer measurements. These were performed using a constant acceleration drive in transmission mode and a 50 mCi $^{57}$Co : Rh source. Measurements taken at 4.2 K revealed well-defined sextet spectra (fig. 1 bottom), indicating that the Fe ions were located at a specific lattice site (presumably that of Mn). Further measurements were performed between 90K and 300K. Mössbauer spectra were fitted to a superposition of magnetic (with an asymmetric Gaussian distribution of hyperfine fields) and paramagnetic (quadrupole doublet) components.

**Results and discussion.** – Our Mössbauer results are represented in figs. 1 and 2. Fig. 1 shows a sequence of Mössbauer spectra for the PSMO-F sample (our spectra for LCMO-F look similar to those shown in refs. [15, 16]). While the spectra at 90 K and 230 K show the magnetically ordered (sextet) and paramagnetic (doublet, also shown on a larger scale at 300K) behaviour, respectively, a superposition of the two contributions is clearly observed between $T_1 \approx 180K$ and $T_2 \approx 230K$ (cf. fig. 2). Above $T_1$, both the relative intensity of the ferromagnetic component (fraction of magnetically ordered sites, fig. 2, shown also for LCMO-F) and the value of the hyperfine field (for both PSMO-F and LCMO-F) characterising the ferromagnetic contribution decrease and ultimately vanish at $T_2$. The

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2Unless the electron is localised on a single lattice site, the localised carriers also contribute to double exchange ferromagnetism. This effect is however weaker than for the itinerant electrons.

3The resistivity of PSMO (fig. 2 top) is indeed very close to that of PSMO-F; see also table II.
Table 1: Samples – compositions and measured properties, including: Curie and paramagnetic Curie–Weiss temperatures, \(T_C\) and \(T_{CW}\) (from magnetic measurements); metal-insulator transition temperature, \(T_{MI}\) and transport gap \(\Delta\), from the transport experiments. Coexistence of ferro- and paramagnetic contributions to Mössbauer spectra takes place at \(T_1 < T < T_2\).

| Sample  | Composition       | \(T_1, K\) | \(T_2, K\) | \(T_C, K\) | \(T_{MI}, K\) | \(\Delta, \text{eV}\) | \(T_{CW}, K\) |
|---------|-------------------|------------|------------|------------|----------------|----------------|--------------|
| PSMO    | \(\text{Pr}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) |            |            |            |                |                |              |
| PSMO-F  | \(\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3\) | 180        | 230        | 223        | 244            | 0.064          | 221          |
| LCMO-F  | \(\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.99}\text{Fe}_{0.01}\text{O}_3\) | 190        | 230        | 221        | 231            | 0.078          | 222          |

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Fig. 1: A selection of Mössbauer spectra obtained for PSMO-F at various temperatures. Thin solid lines represent the simulated sub-spectra; notice the coexistence of ferro- and paramagnetic contributions at 210K and 215 K.

long-range magnetic order, on the other hand, disappears\(^4\) at \(T_C = 223\), \(T_1 < T_C < T_2\).

We find that for PSMO-F the ferromagnetic fraction disappears more abruptly (mostly at \(210K < T < 230K\), see fig. 2 top) than for LCMO-F, in agreement with the more conventional critical properties found by neutron scattering [5]. Note that the increase of resistivity \(\rho\) with \(T\) (for \(T \approx T_{MI}\)) is steeper in the case of LCMO-F (figs 2 and 3). Phase separation scenario would imply the opposite trend. We will now consider the behaviour of \(\rho(T)\) in more detail.

Our low-\(T\) resistivity data are best fitted by [22]

\[
\rho = \rho_0 + \rho_1 T^{3/2}
\]

With increasing temperature, \(\rho(T)\) passes through a maximum at \(T = T_{MI}\), followed by an activated-type dependence, \(\rho \sim \exp(\Delta/k_B T)\) with \(\Delta \approx 0.07\) eV at higher \(T\). In the case of PSMO-F, magnetically ordered sites are absent already at \(T_2 = 230K\), some 15 K below \(T_{MI}\). This is similar to earlier results for \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\) (with \(T_{MI} - T_2 \approx 7K\)) [16]. Such behaviour is impossible to reconcile with the phase separation scenario, which implies that the disappearance of metallic ferromagnetic areas occurs at or above \(T_{MI}\). Indeed, the effective-medium calculation [23, 24] for resistivity at a given value of metallic fraction suggests that \(T_{MI}\) is well below the actual value (figs. 2 and 3).

In the case of LCMO-F, Mössbauer spectra at 230 K (only slightly below \(T_{MI}\) still indicate some presence of magnetically ordered sites [1(±1)% fraction]. The resistivity data are in a perfect agreement with the effective medium description. This is in line with earlier results [17] for \(\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.99}\text{Sn}_{0.01}\text{O}_3\). However, our results for PSMO-F (see above) prove that this situation is not generic. The apparent success of phase-separation scenario in describing LCMO-F should be viewed as incidental, reflecting the relatively low value of \(T_{MI} - T_C\) for this case (table 1). It is plausible that the (nearly) first-order transition [5, 25] observed in LCMO (with \(x \geq 0.3\))
at $T_C$ circumvents a more generic behaviour and is indeed accompanied by phase separation, thereby masking the physics behind the resistivity peak.

We note an earlier suggestion [16] that in the case of $T_2 < T_{MI}$ (realised in La$_{0.8}$Ca$_{0.2}$MnO$_3$ [16] and in our PSMO-F), ferromagnetic phase (assumed metallic) may form filaments, which facilitate metallic conductance down to a low value of their relative volume. While this view appears to allow for an interpretation of the results in terms of phase separation scenario, we find that in the case of PSMO-F, the metallic volume fraction at $T > 230$K would have to be well below 1%. Such behaviour does not seem plausible both on energy grounds (large surface energy term) and because one would expect such a structure to show a hysteretic behaviour and/or history dependence. These, however, were not found in our transport and magnetisation measurements. In addition, the effective media equation [23,24] which is so successful in quantitatively describing the resistivity peak in LSMO-F (fig. 2) assumes spherical inclusions of minority phase, and it is extremely unlikely that geometry of such inclusions should change so drastically in the case of PSMO-F or La$_{0.8}$Ca$_{0.2}$MnO$_3$. We therefore conclude that both in our PSMO-F sample and in the La$_{0.8}$Ca$_{0.2}$MnO$_3$ ceramics of ref. [16] phase separation scenario cannot account for the resistivity peak.

An alternative interpretation is provided by the two-fluid approach, which allows for the itinerant electrons in the paramagnetic phase. On the other hand, continued presence of localised electrons below $T_2$ may explain the origin of the paramagnetic contribution to the Mössbauer spectra. Between the sites where the wave function of a localised electron is centred, the ferromagnetic double exchange coupling is weaker than elsewhere$^2$, hence the corresponding spins order at a lower $T < T_2$. Even below $T_1$, when uniform ferromagnetic order is maintained, thermal fluctuations of these spins will be stronger, corresponding to a broad distribution of the hyperfine field values. Indeed, we observe an asymmetric line broadening in the Mössbauer spectra of both LCMO-F and PSMO-F at 90K $< T < T_2$ (with linewidths, for $T > 150$K, reaching over 50% of the hyperfine field value). While inhomogeneities, which appear inherent in the single crystals of doped manganites, might result in smearing of the Curie transition by a few degrees K (i.e., in a distribution of $T_C$ values within the sample, see, e.g., ref. [7]), this cannot possibly account for such strong line broadening well below $T_C$. We note that the earlier Mössbauer studies [15–17], carried out typically on ceramic samples (whose measured properties can be affected by the inter-grain boundaries$^3$ suggested the coexistence of ferro- and paramagnetic contributions down to lower $T$, and/or the presence of several distinct ferro- (at low $T$) or paramagnetic (at high $T$) phases. The continuous hyperfine field distribution observed in our samples (also at $T < T_1$) is, on the other hand, most probably due to either the continuous (static) distribution of ferromagnetic interaction strengths (due to the presence of localised electrons) or to spin fluctuations in the single ordered phase, with the fluctuation rate comparable to the nuclear magnetic Larmor frequency [27]. We note that the slow relaxation processes (also reported earlier, see e.g., ref. [25]) may also be due to the presence of nearly-localised electrons.

We next turn to the temperature dependence of the inverse magnetisation (shown in fig. 3 for PSMO and PSMO-F) and notice that it deviates downward from the Curie–Weiss law, $H/M \propto T - T_{CW}$, when approaching $T_C$ from the paramagnetic side (cf. “magnetisation kink” [11]). In all cases, the inverse ac susceptibility shows the same feature (see fig. 3, bottom panel). This deviation starts at a point which can be recognised as the metallic-insulator transition temperature, $T_{MI}$ (within 2-K accuracy). We emphasise that this (and not the Curie ferro-paramagnetic transition) is a manifestation of the resistivity peak in the magnetic properties of the system.

This downturn of $1/M(T)$ is often identified [23] as a Griffiths singularity (denoted $T_G$). This implies that at $T_C < T < T_G$, the inhomogeneity of effective exchange couplings gives rise to (fluctuating) ferromagnetic metallic clusters, resulting in the resistivity downturn at $T = T_{MI} < T_G$. We note that one does expect an inhomogeneity of exchanges in a system where carrier localisation leads to an inhomogeneous (on the atomic length scale) charge distribution; this probably accounts for the deviation of $1/M$ from the high-temperature Curie–Weiss law, characterised by $T_{CW} > T_{CW}$.

$^2$We are aware of a sole exception [26], reporting emission Mössbauer data for a single crystal of La$_{0.9}$Ca$_{0.1}$MnO$_3$, which is well outside the metallic doping range.
occurs at much higher temperatures, \( T/T_C \sim 1.5 - 2 \) [28].
As for the ferromagnetic cluster formation (and hence for the possibility of the Griffiths phase), our results as outlined above allow for this only below the temperature \( T_2 \), which in the case of PSMO-F is well below \( T_{MI} \) (see table [1]).

This behaviour of \( 1/M(T) \) is, on the other hand, easy to understand within the two-fluid approach. The itinerant carriers, which would appear once the temperature approaches \( T_{MI} \) from above, strengthen the double-exchange ferromagnetism\(^2\). This gives rise\(^6\) to the increase of \( T_{CW} \) below \( T_{MI} \); we note that our plots of \( 1/M(T) \) suggest the possible presence at \( T_C < T < T_{MI} \) of an intermediate Curie–Weiss behaviour, \( 1/M \propto T - T_{CW} ' \) (with \( T_{CW} ' \) slightly larger than \( T_C \), as expected for a Curie–Weiss temperature in a conventional magnet).

While the abrupt change of \( T_{CW} \) at \( T = T_{MI} \) would suggest the first-order nature of the metal-insulator transition, we leave this question for future study.

Conclusion. – The results presented here shed light on the nature of the electronic states in the ferro- and paramagnetic phases of colossal magnetoresistive manganites. In the ferromagnetic phase, the unusual strong Mössbauer line broadening (observed in both PSMO and LCMO at \( T > 90\text{K} \)) is compatible with the presence of some localised carriers in a homogeneous metallic system. As for the paramagnetic phase, our data for PSMO show that in the vicinity of transition, the presence of some extended carrier states does not necessarily lead to inhomogeneity and phase separation.

It should be stressed that our results do not imply different physics underlying the resistivity peak in the two compounds, PSMO and LCMO. Indeed, the peak is a generic consequence of metallic and insulating behaviour below and above the critical temperature region respectively. Whether the actual transition has prominent first-order characteristics and may be accompanied by phase separation (as in the case of LCMO) or occurs smoothly without breaking the homogeneity of the system (PSMO) depends on the chemical composition and doping level of the sample. The critical behaviour of a system with multiple degrees of freedom can be expected to vary depending on the details of the balance between different interactions. In the case of manganites, such variation has already been uncovered by the neutron scattering measurements and magnetometry [25].

In summary, we found strong evidence against phase separation being a generic mechanism for the resistivity peak (and hence for the CMR phenomenon). We suggest that the relationship between Mössbauer and transport data, as well as the presence of two distinct transitions at \( T_C \) and \( T_{MI} \) (the latter also affecting the magnetic properties) can be understood within the two-fluid model.

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\( ^{6}\)We note that in ref. [11], the “magnetization kinks” were attributed to the appearance of metallic islands (cf. our \( T_2 \)).

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**REFERENCES**

[1] Tokura Y. (Editor). Colossal Magnetoresistive Oxides (Gordon and Breach, New York) 2000, and references therein.
[2] Saitoh T. et al., Phys. Rev. B, 62 (2000) 1039;
Dessau D. S. and Shen Z.-X., in ref. [1];
Chuang Y.-D. et al., Science, 292 (2001) 1509;
Biswas A. et al., Phys. Rev. B, 59 (1999) 5368;
Mitra J. et al., Phys. Rev. B, 71 (2005) 094426.
[3] Okimoto Y. et al., Phys. Rev. Lett., 75 (1995) 109.
[4] Chun S. H. et al., Physica B, 284-288 (2001) 1442.
[5] Lynn J. W. et al., Phys. Rev. B, 76 (1996) 4046;
Fernandez-Baca J. A. et al., Phys. Rev. Lett., 80 (1998) 4012;
Zhang J. et al., J. Phys.: Condens. Matter, 19 (2007) 315204.
[6] Nagaev E. L., Phys. Rep., 346 (2001) 388.
[7] Lofland S. E. et al., Phys. Rev. B, 56 (1997) 13705.
[8] Moreo A., Yunoki S. and Dagotto E., Science, 283 (1999) 2034;
Uehara M. et al., Nature, 399 (1999) 560.
[9] Dagotto E., Hotta T. and Moreo A., Phys. Rep., 344 (2001) 1.
[10] Ramakrishnan T. V. et al., Phys. Rev. Lett., 92 (2004) 157203;
Ramakrishnan T. V., J. Phys.: Condens. Matter, 19 (2007) 125211.
[11] Jaime M. et al., Phys. Rev. B, 60 (1999) 1028.
[12] Millis A. J., Mueller R. and Shraiman B. I., Phys. Rev. B, 54 (1996) 5405.
[13] de Gennes P.-G., Phys. Rev., 118 (1960) 141.
[14] Millis A. J., Littlewood P. B. and Shraiman B. I., Phys. Rev. Lett., 74 (1995) 5144.
[15] See, e.g.,
Chechersky V. et al., Phys. Rev. B, 62 (2000) 5316;
Goya F. et al., J. Appl. Phys., 91 (2002) 7932.
[16] Chechersky V. et al., Low Temp. Phys., 23 (1997) 549.
[17] Assaridis et al., Phys. Rev. B, 75 (2007) 224412.
[18] Heffner R. H. et al., Phys. Rev. Lett., 85 (2000) 3285.
[19] Papavassiliou G. et al., Phys. Rev. Lett., 84 (2000) 761;
Savosta M. M. and Novák P., Phys. Rev. Lett., 87 (2001) 137204.
[20] Shulyatev D. A. et al., J. Crystal Growth, 237-239 (2002) 810.
[21] Ogale S. B. et al., Phys. Rev. B, B57 (1998) 7841;
Li J. et al., J. Phys.: Condens. Matt., 16 (2004) 2839.
[22] Schiffer P. et al., Phys. Rev. Lett., 75 (1995) 3336.
[23] Salamon M. B. and Chun S. H., Phys. Rev. B, 68 (2003) 014411.
[24] McLachlan D. S., Blaskiewicz M. and Newnham R. E., *J. Amer. Ceram. Soc.*, **73** (1990) 2187.

[25] Adams C. P. et al., *Phys. Rev. B*, **70** (2004) 134414; Li W. et al., *J. Phys.: Condens. Matt.*, **16** (2004) L109.

[26] Chechersky V. et al., *Phys. Rev. B*, **63** (2001) 214401.

[27] Nowik I. and Wickman H. H., *Phys. Rev. Lett.*, **17** (1966) 949.

[28] De Teresa J. M. et al., *Nature*, **386** (1997) 256.