Evidence for the Griffiths phase in pure and Y-, Ca- and Cr-doped LaSr$_2$Mn$_2$O$_7$ manganites

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Abstract

The paramagnetic susceptibility measured on La$_{1-x}$Y$_x$Sr$_{2-y}$Ca$_y$Mn$_2$O$_7$ ($x$, $y$ or $z$ = 0, 0.03 and 0.1) manganites does not obey the Curie–Weiss law. The Curie constant exceeds the expected values by more than order of magnitude. Based on strong disorder we have compared the experimental data with predictions based on Griffith’s singularity model. We find that this model allows for consistent interpretation of the data in contrary to a model assumes that magnetic polarons make contribution akin to cluster to susceptibility. In particular the values of Curie constant agree excellently with those theoretically expected, whereas the magnetic polarons model is less satisfactory.

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Recently, the double-layered perovskites La$_{2-x}$Sr$_2$Mn$_2$O$_7$ attracted much attention due to their unusual properties [1,2]. Fascinating properties like the colossal magnetoresistance (CMR), orbital and charge ordering and phase separation were discovered which have raised new questions that have not been resolved yet [3,4]. Some of these questions call for a proper understanding of the spin dynamics above the Curie temperature ($T_C$). Similar observations are well documented in the three dimensional perovskites.

Re$_{1-x}$A$_x$MnO$_3$ (Re=La, Y, Nd,…; A=Ba, Sr or Ca; 0.1 < x <0.45). Understanding the spin dynamics above $T_C$ has become crucial for the interpretation of some unusual features observed in electron spin resonance (ESR) and magnetic-susceptibility measurements on these compounds [4–6]. The ESR measurements of Oseroff et al. [4] have provided evidence for short range ordering and the formation of spin clusters above $T_C$. On the other hand, the susceptibility of the related La$_{1-x}$Ca$_x$MnO$_3$ compounds does not to fully obey the conventional Curie–Weiss (CW) law in the paramagnetic (PM) state: above $T_C$ the $\chi^{-1}$ vs. $T$ plots do not give the straight lines representing the CW law, $\chi^{-1}=(T−θ)/C$ [6]. Moreover, the Curie constant derived from the ‘best fit’ to a straight line is found to be very large compared with the theoretically expected $C=N_Ag^2\mu_B^2[S(S+1)+(1-x)S_2(S_2+1)]/3k_B$. Here $S_1=2$ and $S_2=3/2$ stand for the moments of the Mn$^{3+}$ and Mn$^{4+}$ ions, respectively.

Numerous models were proposed to tackle the problem of the magnetic susceptibility in manganites. One of them has been proposed by Yi et al. [7], who performed Monte Carlo calculations on a single-orbital double-exchange Hamiltonian and interpreted the resulting PM susceptibility...
in terms of spin clusters and the formation of magnetic polarons. The other one we shall consider is the Griffiths phase in dilute ferromagnets [8], which was used by Salamon et al. [9] to analyse their susceptibility and heat capacity data on La$_{0.7}$(Ba, Ca, Sr)$_{0.3}$MnO$_3$ near $T_C$. This model is based on disordered (random distribution) dilute ferromagnets in the PM state [8]. The relevance of the Griffiths phase to the layered manganites has not yet been studied. In this paper we present an analysis of the PM susceptibility of the layered manganites LaSr$_2$Mn$_2$O$_7$ doped by Y$^{3+}$, Ca$^{2+}$ or Cr$^{3+}$ ions.

Polycrystalline samples were prepared following the conventional ceramic route and characterized by X-ray powder diffraction (XRD). The details of the sample preparations are given in Ref. [10]. The Rietveld refinement of the XRD data showed that all the samples are single phase and their crystal structure is tetragonal with space group 4I/MMM. The magnetic susceptibility of the samples was measured by EG and G vibrating sample magnetometer from room temperature up to 500 K at 500 Oe.

The inverse susceptibility ($\chi^{-1}$) vs. $T$ curves did not resemble the conventional CW law expected from ferromagnets in their paramagnetic state (Fig. 1). The values of the Curie (C) and Weiss ($\theta$) constants obtained from the straight line for the data above 300 K are in the range $C = 6$–15 emu K mol$^{-1}$ Oe$^{-1}$ which are large compared with 0.0244 emu K mol$^{-1}$ Oe$^{-1}$ expected from theory. On the other hand the values of $\theta$ are smaller than $T_C$ by values varying from 60 to 280 K as function of the dopant.

Yi et al. [7] analysed a similar behaviour observed in the results of their Monte Carlo calculations. Following Oseroff et al. [4], they assumed that the deviation from the CW law defined by

$$\chi = C/(T - \theta) + \Delta \chi$$

(1)

can be represented by the function

$$\Delta \chi = \chi_0 \exp(E_a/T)$$

(2)

where $E_a$ is ‘an activation energy’. In our case, the ln $\Delta \chi$ vs. $1/T$ plots are by no means straight, indicating that this parameterisation does not work. Nor is there any reason to expect that Eq. (2) be valid. To begin with, $E_a$ would be a negative activation energy, the graphical representation of Eq. (2) gives an Arrhenius plot, which slopes in the wrong direction. Furthermore, no matter what kind of ‘magnetic entities’ are postulated to account for the enhanced susceptibility above $T_C$, the constituents of such entities must be the same magnetic moments that determine the Curie constant $C$ in the high-temperature limit. Therefore, the decomposition of the susceptibility according to Eq. (1) has no physical justification: while $\Delta \chi$ increases upon lowering the temperature towards $T_C$, $C$ in the first term must decrease.

The anomalously large values of the high-temperature CW constant can be taken as a signature of spin-cluster formation. The question arises, whether the further enhancement of the susceptibility at lower temperature, which is evident in the downturn of the $\chi^{-1}$ vs. $T$ curves, can be attributed to the Griffiths phase. Salamon and Chun [9] have successfully analysed their data on Ba-, Sr- and Ca-doped LaMnO$_3$ perovskites in terms of Griffiths singularities.

Bray [11] has provided a formula for the susceptibility in the Griffiths phase,

$$\chi = C \int \frac{T}{\beta} \mu^{-1} p(\mu) d\mu \int \frac{T}{\beta} p(\mu) d\mu$$

(3)

where $p(\mu)$ is the density of the eigenvalues of the inverse susceptibility matrix, for which he gave $p(\mu) \propto \mu^{-\gamma} \exp(-A(T)/\mu)$ with $A(T) = (T/T_C - 1)^{\xi - 2\beta}(1 - T/T_C)^{-2\beta}$, where $T_C$ is the disordered alloy’s Curie temperature and $T_G$ the Griffiths temperature, is the highest possible Curie temperature in the alloy system. In our attempts to fit the susceptibility data with expression (3), we have varied the parameters $\beta$, $\gamma$, $\alpha$, $T_G$ and $T_C$.

The general shape of the curves calculated with Eq. (3) is in accord with the measured results in as much as there is a downturn in $\chi^{-1}$ as $T$ approaches $T_C$. However, there is an extended linear region seen above $T = 1.3T_C$ in all calculated curves, which is not observed experimentally. In fact, all experimental curves maintain a significant downward curvature throughout the measure temperature range. Also, the measured downturn is more pronounced than the calculated one. This observation can be made quantitative, if one compares $\theta_{\text{ext}}$ values, the paramagnetic Curie temperatures extrapolated from the high-temperature end.

![Fig. 1. The temperature dependence of the inverse susceptibility as function of temperature for (a) the Cr-doped samples; (b) for Y- and Ca-doped samples. The solid lines are the theoretical fit of Eq. (4).](image-url)
Fig. 2. Calculated inverse susceptibility as function of temperature using Eq. (3) for fixed $T_0$ and $\beta$ while $\gamma$ varied. The general behaviour reproduces the observed inverse magnetic susceptibility. The inset shows the change of the slope just above $T_C$ for measured susceptibility.

of the curves, see Fig. 2. To evaluate this comparison, we have carried out least-square-deviation fits on all measured and some typical calculated curves, matching the points with a straight line above $500 \, K$. The intercepts of these straight lines with the $T$ axis gives the $\vartheta_{\text{extr}}$ values tabulated in Table 1. Evidently, the measured curves give much lower, (sometimes negative) values for $\vartheta_{\text{extr}}$ than any of the calculated ones. We have to conclude that, not withstanding the large number of options provided by the free parameters contained in $\mu$ in Eq. (3), a successful fitting of the experimental curves throughout the measured range of temperatures is not possible.

Salamon et al. [12] have pointed out that the inverse of the susceptibility calculated from Bray’s formula is quite close to the power law

$$\chi^{-1} \propto (T - T_C)^{1-\gamma}, \quad 0 < \gamma < 1$$  \hspace{1cm} (4)

The curvature of such a power law being always negative, this is a promising option for the analysis of our experimental data. Castro Neto et al. [13] have suggested that the non-Fermi liquid behaviour observed in some $f$-electron compounds is due to the development of the Griffiths phase at quantum phase transitions, i.e. for $T_C = 0$. However, Millis et al. [14] have shown that in metallic materials no Griffiths behaviour can be expected at the quantum critical point. Clearly, on this basis we cannot justify the use of Eq. (4) for perovskites on the metallic side of the metal-insulator transition, having $T_C \approx 300 \, K$. Our motivation remains thus the simplicity of Eq. (4) and its similarity to the Bray formula in the parameter range relevant to our case.

Fig. 1 shows the experimental results fitted with Eq. (4). The optimal fitting parameters are given in Table 2. The quality of the fit is good; the general behaviour of the susceptibility is reproduced. The obtained values of the Curie constant are found to be of the order of 0.02–0.03 emu K mol$^{-1}$ Oe$^{-1}$, which is in excellent agreement with that expected from theory. It is seen that upon partial substitution of La$^{3+}$ by $Y^{3+}$ ions $\chi^{-1}$ changes and the quality of the fit improves which is clear just above $T_C$. The Cr$^{3+}$ ions, on the other hand, are supposed to go to the Mn-sites. This would inhibit the double exchange interaction and hence we expect to observe a change in the susceptibility. The clearest change is observed just above $T_C$, see the inset of Fig. 2.

The wide range of validity of the power law is remarkable. Salamon and Chun [9] had found on a single crystal of La$_{0.7}$Ca$_{0.3}$MnO$_3$ that the power law holds, with $\gamma = 0.37$, up to $T = 1.06T_C$. Though this is reasonably close to $T_C$ to expect critical behaviour, this would be a very curious critical exponent. In the conventional notation of the critical exponent, $\chi^{-1} \propto (T - T_C)^{\gamma}$, we expect normally $\gamma \geq 1$, whereas, the above value of $\gamma$ corresponds to $\gamma = 0.63$. Our analysis shows that the experimental data fit a power law with $\gamma \approx 2/3$, that is, $y \approx 1/3$, in a much broader range than can be expected from critical behaviour.

In conclusion, we have found that the paramagnetic susceptibility of our doped LaSr$_2$Mn$_2$O$_7$ samples is well described by the power law (4), with $\gamma \approx 2/3$, for temperatures between $T_C$ and $\approx 2T_C$. In as much as the rather complicated expression for the susceptibility in the

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi_C$ (emu K mol$^{-1}$ Oe$^{-1}$)</th>
<th>$\theta_{\text{extr, Cal.}}$</th>
<th>$\theta_{\text{extr, Exp.}}$</th>
<th>$T_0$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaSr$_{2}$Mn$_2$O$_7$</td>
<td>60.430</td>
<td>25.15</td>
<td>4.5</td>
<td>0.38</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.97}$Y$</em>{0.03}$Sr$_2$Mn$_2$O$_7$</td>
<td>-163.830</td>
<td>215.10</td>
<td>10.5</td>
<td>0.38</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.9}$Y$</em>{0.1}$Sr$_2$Mn$_2$O$_7$</td>
<td>-136.630</td>
<td>228.19</td>
<td>16.5</td>
<td>0.38</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>LaSr$<em>{1.97}$Ca$</em>{0.03}$Mn$_2$O$_7$</td>
<td>133.130</td>
<td>171.14</td>
<td>4.5</td>
<td>0.38</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.95}$Ca$</em>{0.05}$Mn$_2$O$_7$</td>
<td>74.610</td>
<td>194.11</td>
<td>4.5</td>
<td>0.38</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>LaSr$<em>{2}$Mn$</em>{1.97}$Cr$_{0.03}$O$_7$</td>
<td>-222.130</td>
<td>250.46</td>
<td>4.5</td>
<td>0.38</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>
Griffiths phase given by Bray [11] qualitatively resembles Eq. (4), we can say that this result supports the claim [9,12] that Griffiths singularities occur in perovskites. The validity of Eq. (4) in a broad temperature range justifies a search for the conditions, under which this expression follows from the Griffiths scenario.

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References


Table 2
The optimal fitting parameters obtained by using Eq. (4) to fit the experimental data

<table>
<thead>
<tr>
<th>$T_C$ (K)</th>
<th>$y$</th>
<th>$a$ (Oe mol K$^{-1}$ emu$^{-1}$)</th>
<th>$C$ (emu Oe$^{-1}$ mol$^{-1}$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaSr$_2$Mn$_2$O$_7$</td>
<td>321.95</td>
<td>0.64</td>
<td>42.44</td>
</tr>
<tr>
<td>La$<em>{0.97}$Y$</em>{0.03}$Sr$_2$Mn$_2$O$_7$</td>
<td>309.71</td>
<td>0.69</td>
<td>38.52</td>
</tr>
<tr>
<td>La$<em>{0.9}$Y$</em>{0.1}$Sr$_2$Mn$_2$O$_7$</td>
<td>317.52</td>
<td>0.66</td>
<td>35.75</td>
</tr>
<tr>
<td>LaSr$<em>{1.97}$Ca$</em>{0.03}$Mn$_2$O$_7$</td>
<td>298.55</td>
<td>0.64</td>
<td>46.98</td>
</tr>
<tr>
<td>LaSr$<em>{1.9}$Ca$</em>{0.1}$Mn$_2$O$_7$</td>
<td>296.56</td>
<td>0.63</td>
<td>56.77</td>
</tr>
<tr>
<td>LaSr$<em>2$Mn$</em>{1.97}$Cr$_{0.03}$O$_7$</td>
<td>319.49</td>
<td>0.70</td>
<td>32.34</td>
</tr>
<tr>
<td>LaSr$<em>2$Mn$</em>{1.9}$Cr$_{0.1}$O$_7$</td>
<td>305.74</td>
<td>0.66</td>
<td>35.87</td>
</tr>
</tbody>
</table>