Microphase separation in Pr$_{0.67}$Ca$_{0.33}$MnO$_3$ by small angle neutron scattering

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Abstract

We have evidenced by small angle neutron scattering at low temperature the coexistence of ferromagnetism (F) and antiferromagnetism (AF) in Pr$_{0.67}$Ca$_{0.33}$MnO$_3$. The results are compared to those obtained in Pr$_{0.80}$Ca$_{0.20}$MnO$_3$ and Pr$_{0.63}$Ca$_{0.37}$MnO$_3$, which are F and AF respectively. Quantitative analysis shows that the small angle scattering is not due to a mesoscopic mixing but to a nanoscopic electronic and magnetic ”red cabbage” structure, in which the ferromagnetic phase exists in form of thin layers in the AF matrix (stripes or 2D ”sheets”).

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It was recently proposed that the ground state of manganites which displays colossal magneto-resistive (CMR) properties\textsuperscript{1} could be an electronic phase separation\textsuperscript{2,3}. This is a very elegant manner to interpret the CMR properties by percolation of a metallic ferromagnetic phase in an insulating antiferromagnetic matrix. A small change of the fraction or of the arrangement of the domains can induce percolation. However, as pointed out by Radaelli et al.\textsuperscript{4}, if several works evidence phase separation, no clear results are published about the size and shape of the objects. Some authors have observed small (nanometric) ferromagnetic clusters by small angle neutron scattering\textsuperscript{4–6}, while others found much larger phase separation by high-resolution electron microscopy\textsuperscript{7}. Moreover, the width of the magnetic Bragg peaks in neutron diffraction experiments is not compatible with nanometric objects since the correlation length of the magnetic order $\xi$ is usually more than 100 nm\textsuperscript{8}. The origin of this phase separation can be different if it occurs on a nanoscopic or mesoscopic scale. To answer this question is one of the most important issues in this research field.

The Pr$_{1-x}$Ca$_x$MnO$_3$ series is one of prime interest, because Pr and Ca are about the same size and hence minimize the cationic size mismatch effect. For compositions close to $x=0.30$, existence of the phase separation is now well proved by magnetoresistance, magnetization and specific heat studies\textsuperscript{9,10}. Despite these numerous studies, the nature of this phase separation is not solved at the present time. To summarize the discussion, let us recall that the Pr$_{1-x}$Ca$_x$MnO$_3$ magnetic phase diagram presents different states depending on the $x$ value. For the higher Mn$^{3+}$ contents, the compounds are ferromagnetic at low temperature (typically $x=0.2$), and for larger $x$ values (typically $x=0.4$) they are orbital ordered, antiferromagnetic CE like type. In between, the composition $x=0.33$, studied here, shows a mixing of F and AF phases as shown by neutron diffraction\textsuperscript{8}. From the width of the magnetic Bragg peaks, it is clear that the order is mainly long range, typically more than 100 nm. Paradoxically, small angle neutron scattering measurements exhibit a large signal due to local inhomogeneities in the range of few nm\textsuperscript{4}. The conclusion of these previous experiments was that the sample is inhomogeneous at a macroscopic scale, different zones being at the origin of the long range order and the small angle neutron scattering signal.
Small angle neutron scattering is indeed a very powerful technique to study the phase separation between a ferromagnet and an antiferromagnet since the contrast between them is very large (the AF does not scatter at small angle). It was first used in phase separated manganites by de Teresa et al.\textsuperscript{5} and more recently by Radaelli\textsuperscript{4}, but no quantitative analysis of the scattered intensity, as we present here, was performed.

Using the floating-zone method with feeding rods of nominal compositions $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, several-cm-long single crystals were grown in a mirror furnace. Samples were cut out of the central part of these crystals and were analyzed by EDS: their cationic compositions are homogeneous and were found to be $x=0.37$, $0.33$ and $0.20$ respectively. Magnetization and transport measurements were performed to check their quality. The samples were then powdered in order to perform neutron diffraction. The powder diffraction patterns were recorded in the G41 spectrometer in Orphé reactor from 1.5K to 300K. The structures were refined using the Fullprof program, in the classical Pbnm symmetry ($a_p\sqrt{2}$, $a_p\sqrt{2}$, $2a_p$).

Classical behaviors were found:

$x=0.37$ is insulating and AF with $T_N$ at about 170K and with a structural transition associated with the doubling of cell parameter at about 245K ($T_{CO}$). At low temperature, the spins are aligned along the $c$ axis and the magnetic order is that of the pseudo CE ordering\textsuperscript{8}.

$x=0.20$ presents a ferromagnetic phase transition with $T_c$ at about 130K. The spins are oriented along the $a$ axis.

$x=0.33$ presents both a F component (similar to that of $x=0.20$) for half of the spins ($2\mu_B$) and an AF one (similar to that of $x=0.37$) with $1/4$ of the spins. $T_c$ is about 100K and $T_N$ about 115K.

Below 30K, there appears in the samples a contribution of the Pr moments ordering which will not be discussed here.

Small angle neutron scattering were performed on PAXY spectrometer at the Orphé reactor. Two different experimental configurations were used: the first is with a wavelength
of 6 Å and a sample-multidetector distance of 3.2m, allowing to study Q values between $10^{-2}$ and $10^{-1}$ Å$^{-1}$. The second one is with a wavelength of 4 Å and a sample detector distance of 1.2m, allowing to reach higher values up to 5 $10^{-1}$ Å$^{-1}$. The sample was introduced in a cryostat with aluminum windows. In order to subtract the background signal, an empty cell was measured. The calibration of the spectrometer was performed with a Plexiglas sample following the procedure given in reference$^{12}$. After subtraction of the background, normalization by the Plexiglas sample, the scattering function is presented in absolute units (cm$^{-1}$). We have systematically neglected the inelastic spin wave corrections (the fact that different neutron wavelengths give the same scattering curves supports this assumption) and the magnetic form factor of the ions (this is valid at these small Q values).

The small angle scattering in the x=0.37 sample presents the typical features of an antiferromagnet (fig. 1) and Bragg diffraction exhibits nice AF peaks which disappear at $T_N=170$K (inset of fig. 1). At small Q, the small angle scattering is dominated by the granular structure of the powder: it obeys to the classical Porod law and varies in Q$^{-4}$. In the paramagnetic phase, it is due to the nuclear and non ordered magnetic scattering. In the antiferromagnetic phase, only the nuclear contribution remains, since the antiferromagnetic phase does not contribute to the small angle scattering. The intensity of the Q$^{-4}$ signal can be calculated from the grain size R by using

$$I(Q) = \frac{4\pi}{R} \Delta\rho^2 Q^{-4}$$

where $\Delta\rho$ is the difference between the scattering length densities ($\Delta\rho^2=3.2 10^{21}$ cm$^{-4}$) between the two phases (here the sample and the vacuum). Direct electron microscopy observations show that the smallest grains are observed to be small flat grains of thickness about R=3 µm. Then IQ$^4$ can be calculated to be $10^{27}$ cm$^{-5}$ at room temperature. There is a perfect agreement with the value measured by small angle neutron scattering of figure 1. At higher Q, the signal measured is a paramagnetic contribution at high temperature, which disappears completely in an antiferromagnetic phase. The low temperature signal can be thus considered as the non magnetic signal even at high Q and will be used as a background.
for the x=0.33 and the x=0.20 samples. Such an assumption is verified since I(Q) at room
temperature is exactly the same for the three samples (not shown here).

The x=0.20 sample is ferromagnetic below 130K. The ferromagnetic component of the
diffraction peaks disappears at Tc (inset of fig. 2). The Q$^{-4}$ signal due to the granular
structure of the sample is clearly observed above and below Tc (fig. 2). In the neighborhood
of Tc, the Lorentzian shape (Q$^{2}$+ξ$^{-2}$)$^{-1}$ in which ξ is the correlation length of the order was
previously used to describe this phase transition and is here adequate$^5$. At low temperature,
ξ is very small (about few nm, not shown in the figures).

The x=0.33 sample is a mixing of F and AF components below 110K. In the upper inset
of fig. 3, we have reported the temperature dependence of both F and AF components on
the Bragg peaks, showing this coexistence. In the lower insets of fig. 3, it is shown that
these Bragg peaks are narrow, close to experimental resolution and certainly not typical of
short range order. The small angle scattering shown in fig. 3 is, at a first glance, very similar
to that of a ferromagnetic sample (compare to fig. 2). However, at low temperature, the
magnetic signal obtained by subtracting the signal of the sample x=0.37 is very different
for the two ferromagnetic samples as presented in fig. 4. In addition to the Q$^{-4}$ Porod
contribution$^{11}$ due to the granular structure which exists in both samples, there is a clear
Q$^{-2}$ contribution in the high Q regime in the only x=0.33 sample. This Q dependence is that
of infinite 2D sheets$^{12}$. This analysis was introduced first in the soft matter field by Nallet
et al.$^{13}$. In the present case, it corresponds to 2D ferromagnetic sheets in antiferromagnetic
matrix which plays the role of the vacuum. The adjustable parameter in this model is the
thickness of the 2D sheets "t". For such a 2D object, the scattering function is I(Q)= 2π
ϕ(1 − ϕ)t ∆ρ$^{2}_{m}$ Q$^{-2}$|1−cos Qt| Q$^{-2}$ (Qt)$^{2}$ which reduces in the small Q limit to:

I(Q)= πϕ(1 − ϕ) t ∆ρ$^{2}_{m}$ Q$^{-2}$

∆ρ$^{2}_{m}$ is here proportional to the magnetization M: ∆ρ$^{2}_{m}$ =αM. M can be determined
from the diffraction data or from the small Q values as shown in the inset of fig. 3. (the
proportional constant α is 0.27 10$^{-12}$ cm/µB divided by the unit volume of a Mn cation
0.57 10$^{-22}$ cm$^{3}$, so ∆ρ$^{2}_{m}$ =0.4 10$^{21}$ cm$^{-4}$). ϕ is the ferromagnetic fraction (ϕ=0.5 here).
Experimentally, \( IQ^2 = 10^{14} \text{ cm}^{-3} \). This drives to a parameter value \( t \), which is about 2.5 nm. Moreover, it can be stated that \( t \) does not vary significantly with temperature up to the Curie phase transition. Close to the critical temperature \( T_c \), the shape of the scattering function changes, turning to the Lorentzian function \((Q^2 + \xi^{-2})^{-1}\), classical of critical fluctuations close to a phase transition\(^5\).

Note that spherical domains would have given a \( Q^{-4} \) variation and linear domains a \( Q^{-1} \) dependence\(^{12}\). The Lorentzian function \((Q^2 + \xi^{-2})^{-1}\) which was previously used to describe this phase separation\(^5\) is clearly not adequate below \( T_c \). It would have driven to very small \( \xi \) values (smaller than 1 Å), and has not physical meaning. Note also that this \( Q^{-2} \) contribution is very hard to observe directly on the Bragg peaks since the convolution of this \( Q^{-2} \) contribution with the lorentzian resolution of the spectrometer does not broaden them, contrary to what is observed if \( \xi \) is not zero. This explains why there is no important broadening of the Bragg peaks, even with this very large small angle neutron scattering (inset b of fig. 3). This situation is also very different from that of uncorrelated 2D sheets which should present asymmetrical Warren shapes of the Bragg peaks\(^{14}\). An image of this microphase separation can be proposed in a ”red cabbage illustration” in which the ferromagnetic phase is the cabbage itself whereas the antiferromagnetic part is the vacuum (inset of fig. 4). Such an image can both explain the long range of the magnetic order and the very large small angle signal with this specific Q dependence.

The phase separation occurs at about \( x=0.33 \), in between \( x=0.37 \) which is purely AF and \( x=0.2 \) which is purely F. By looking to the magnetic properties of the two phases and to the phase diagram, it can be suggested that a charge transfer between the two phases can drive to a modulation of the charge density (the cationic composition is not modified) from \( x=0.2 \) to \( x=0.4 \). \( x=0.2 \ (1/5) \) is possibly an insulating ferromagnetic phase similar to \( x=0.125 \ (1/8) \). Some recent theoretical work supports this point of view, considering possible orbital ordering in \( x=1/8 \)\(^{15}\). For the antiferromagnetic phase, the CE structure of \( x=0.50 \) is not a possible candidate because the antiferromagnetic phase of the \( x=0.33 \) is pseudo CE type. Since it was shown that the \( x=0.37 \) sample presents about 2% of
ferromagnetism\textsuperscript{9}, x=0.40 is probably typical of the charge density of the F phase in x=0.33. Some more experimental work is needed to see in the non powdered single crystal itself if the small angle scattering is isotropic or not. It will be also very important to test the role of the magnetic field on this striped phase. The nanoscopic structure proposed here to interpret the apparent discrepancy between long range ferromagnetic order and strong small angle scattering in x=0.33 sample was first proposed from electrostatic arguments, due to the high Coulomb energy cost of the charge separation\textsuperscript{2}. However, as pointed out by Khomskii et al.\textsuperscript{15}, electrostatic interaction is not enough to understand the existence of the 2D sheets of the ”red cabbage” system. Pure electrostatic interactions should drive to charge and/or orbital ordering with a superstructure (as it is observed in the x>0.5 part of the phase diagram), but not to 2D sheets structure. For x<0.5, elastic interactions would be the crucial ingredient to obtain such a striped structure for the electronic phase separation.

In conclusion, we have shown that magnetic small angle neutron scattering is particularly adapted to this study of phase separation in manganites. The excellent contrast between ferromagnetism and antiferromagnetism provides large signals. The analysis of the Q dependence associated with absolute measurements allow to determine the shape and the size of the ferromagnetic objects. In Pr\textsubscript{0.67}Ca\textsubscript{0.33}MnO\textsubscript{3}, the prototype of electronic phase separation, it appears a strong Q\textsuperscript{−2} signal, characteristic of 2D ferromagnetic stripes, which suggests a red cabbage structure. The thickness of the stripes is about 2.5nm at 10K. This model also explains why there is no significant broadening of the magnetic Bragg peaks. This technique offers the possibility to investigate in details this new and important research field and provides experimental data about the size and the shape of the phase separation.

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Figure Captions

Figure 1: The small angle scattering functions of the x=0.37 sample (AF with
$T_N \simeq 170\,\text{K}$ at two temperatures below and above $T_N$. The two different Q ranges are evidenced by a small gap in the curves at about 0.1 Å$^{-1}$. Inset: the antiferromagnetic magnetization given by the integration of the intensity of the antiferromagnetic 110 peak of powder pattern obtained on G41.

Figure 2 : The small angle scattering functions of the $x=0.20$ sample ($F$ with $T_C \simeq 130\,\text{K}$) at three temperatures below, above and close to $T_C$. Inset: the ferromagnetic magnetization given by the ferromagnetic 002 peak intensity of powder pattern obtained on G41.

Figure 3: The small angle scattering functions of the $x=0.33$ sample ($F$+AF with $T_N \simeq T_C \simeq 110\,\text{K}$) at three temperatures below, above and close to the critical temperature. The antiferromagnetic and the ferromagnetic magnetizations given by the intensities of the 110 and 002 peaks of powder pattern obtained on G41 are shown in the inset (a), as well as the intensity in $10^{-2}$ Å$^{-1}$. In the inset (b), these typical ferromagnetic or antiferromagnetic Bragg peaks show the absence of any important broadening.

Figure 4 : The magnetic scattering function $I_m(Q)$ for $x=0.33$ ($F$+AF with $T_N \simeq T_C \simeq 110\,\text{K}$) and $x=0.20$ ($F$ with $T_C \simeq 130\,\text{K}$) at $T=10\,\text{K}$, showing the $Q^{-4}$ and the $Q^{-2}$ behaviors. In the inset, a schematic drawing of a cut of the nanoscopic electronic red cabbage model.
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$Pr_{0.63} Ca_{0.37} MnO_3$

$Q^{-4}$

$I(\text{cm}^{-1})$

$Q (\text{Å}^{-1})$

$180K$

$10K$

$M(\mu_B)$
Pr$_{0.8}$Ca$_{0.2}$MnO$_3$

$Q^{-4}$

$10K$

$115K$

$285K$

$I$ (cm$^{-1}$)

$Q$ (Å$^{-1}$)

$M$ ($\mu_B$)

$T$ (K)

0 0 2
\( \text{Pr}_{0.67} \text{Ca}_{0.33} \text{MnO}_3 \)

10K
150K
285K

\( I(\text{cm}^{-1}) \)

\( Q(\text{Å}^{-1}) \)

(a) $M(\mu_B)$

(b) $I(\text{arb. units})$

Pr $0.67$ Ca $0.33$ MnO$_3$
$I_m (\text{cm}^{-1})$ vs. $Q (\text{Å}^{-1})$

- $Pr_{0.67}Ca_{0.33}MnO_3$
- $Pr_{0.8}Ca_{0.2}MnO_3$

Lines:
- $Q^{-4}$
- $Q^{-2}$