

OBSERVATION OF A FERROMAGNETIC MODULATION IN DOPED Mn PEROVSKITES: AN ELECTRONIC PHASE SEPARATION

G. Biotteau¹, M. Hennion¹, F. Moussa¹, J. Rodriguez-Carvajal¹,
L. Pinsard² and A. Revcolevschi²

¹Laboratoire Léon Brillouin, CEA-CNRS,

²Laboratoire de Chimie des Solides, Université Paris-Sud, 91405 Orsay Cedex, France

In manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, where the divalent ions ($\text{A}=\text{Sr}, \text{Ca}, \text{Ba}$) induce a hole doping, the coupling between the hole mobility and the ferromagnetism provides spectacular effects. Close to the magnetic transition where the metal-insulator transition occurs, an applied field induces a variation of the resistivity by several orders of magnitude (giant magnetoresistance), the largest effect being for $x \approx 0.3$. On a fundamental basis, the parameters leading to these effects are still not clearly understood. For several years, the existence of magnetic inhomogeneities has been suggested^[1-3], associating the ferromagnetic transition and likely the metal-insulator transition to a percolation effect. Several experiments^[4-5] have reported unusual fluctuations close to the ferromagnetic transition $T \approx T_c$, suggesting a picture of fluctuating ferromagnetic clusters.

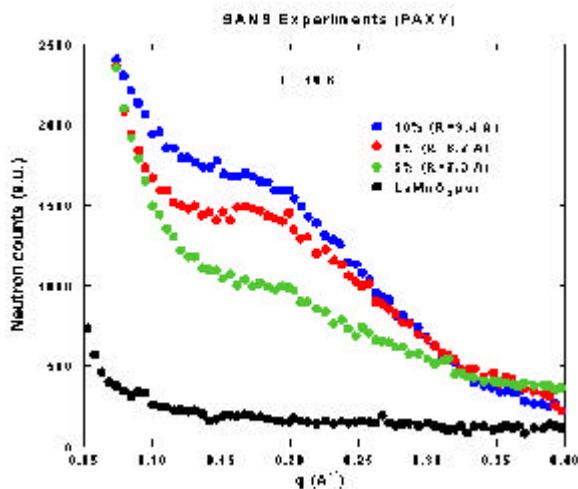


Figure 1. Scattering Intensities versus q observed using the diffractometer PAXY with an incident wavelength $\lambda=6\text{\AA}$ for $x=0, 0.05, 0.08$, and 0.1 of Ca doping. The intensities, renormalised by the volume, taking account of the sample transmission are readily comparable.

We have undertaken a small angle scattering study, using a small angle diffractometer (PAXY) in a first step, and then, a three-axis spectrometer (4F1), in an elastic configuration. The first one (PAXY), thanks to the multidetector device, provides measurements with an isotropic q resolution. However, any static ($\omega=0$) spin correlations cannot be observed as a function of temperature (contamination by the spin excitations) so that the magnetic contribution cannot be separated from the nuclear one. By contrast, the

three axis spectrometer allows to determine any $\omega \neq 0$ scattering intensity at any temperature, and, by subtracting the nuclear contribution determined at high temperature, allows to select the purely magnetic contribution.

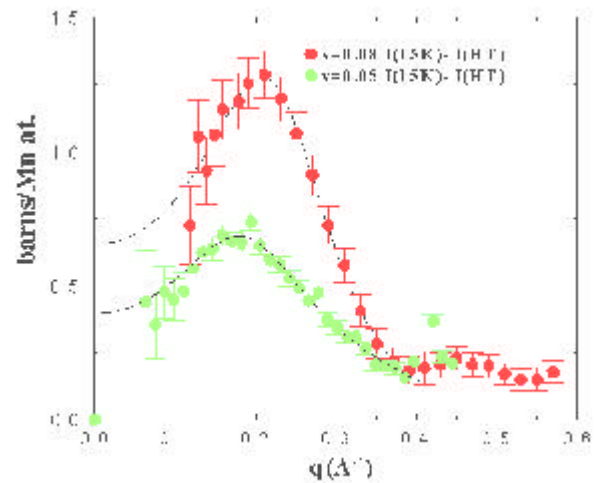


Figure 2. Scattering Intensities of magnetic origin, $I(q)=I_{15K}-I_{HT}$, versus q , calibrated in barns per Mn atom, observed using a three axis spectrometer for $x=0.05$ and $x=0.08$. The dashed line is a calculated curve according to the model described in the text

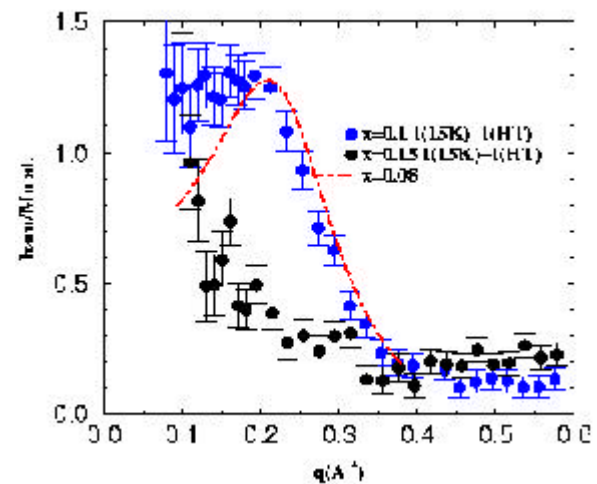


Figure 3. Scattering Intensities of magnetic origin $I(q)=I_{15K}-I_{HT}$, versus q , calibrated in barns per Mn, observed using a three-axis spectrometer for $x=0.1$ and $x=0.15$. The dashed line is a guide for the eye.

In the $0 \leq x \leq 0.15$ range studied, both experiments reveal the occurrence of a ferromagnetic modulation, in all the q directions. We have shown that it can be interpreted in terms of magnetic inhomogeneities,

with a liquid-like distribution, and therefore in repulsive interaction. Both the size of the inhomogeneities and their characteristic distance can be quantitatively determined. Such an experimental result, observed for the first time, likely originates from a purely electronic effect^[6].

In the range $0 \leq x \leq 0.15$, the compounds are insulating at all temperatures and, depending on x , undergo either a transition from a paramagnetic to a canted-antiferromagnetic state at T_{CA} ($T_{CA}=122\text{K}$ at $x=0.08$) or a transition from a paramagnetic to a ferromagnetic state at $T_C=155\text{K}$ for $x=0.15$.

In figure 1, the SANS scattering intensities obtained at 10K for $x=0, 0.05, 0.08$ and 0.1 are compared. The new experimental feature occurring in doped samples is a q -modulation, growing with x and superposed on a large scattering intensity (see the weak scattering intensity in the pure LaMnO_3). The multidetector device allows in principle, to check the q -isotropy of this modulation, but here, the complication related to the twinning domains prevents any definitive conclusion. A similar study on a three-axis spectrometer allows to separate the contribution of nuclear origin (dislocations or any structural defects induced by Ca doping) determined above the magnetic transition T_{CA} , where the intensity $I(q)$ is temperature independent, from the intensity of magnetic origin that grows below T_{CA} . This magnetic contribution is reported in figure 2 at 15K, for $x=0.05$ and $x=0.08$ of Ca. It reveals clearly that the modulation observed around $q \approx 0.2 \text{ \AA}^{-1}$ using PAXY has a magnetic origin and its intensity evolves strongly in this small concentration range. The magnetic contribution is also shown at higher doping value in figure 3. At $x=0.1$ the scattering intensity is close to that observed for $x=0.08$ (represented by the red dot-dashed line) except at small q , where a flat plateau instead of a true modulation is observed. At $x=0.15$, the modulation is no more observed in our experimental window. We have also studied the temperature evolution of the scattering. In figure 4, the evolution with temperature observed in the sample with $x=0.05$ is reported. It shows that as the intensity decreases, there is a slight shift of the modulation towards smaller q values. Since the studied samples are single crystals, all the experimental features observed close to the direct beam also exist around Bragg peaks. For example, in Figure 5, the intensity observed around (110) Bragg peak is reported for $x=0.08$ at several temperatures. There, the q -modulation is clearly observed, without any subtraction. It disappears above the magnetic transition ($T_{CA}=122\text{K}$), where a monotoneous decreasing scattering intensity, nearly temperature independent, persists. In addition, a study at small angle scattering using X-rays, for which a large contrast between La and Ca scattering exists, has been performed. It allows to check that there is no scattering in this small q range, which

excludes any chemical clustering related to Ca impurities associated to the magnetic scattering observed by neutrons.

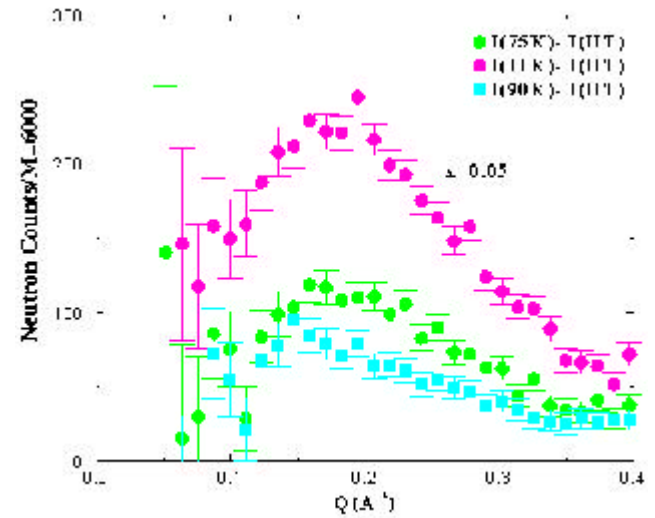


Figure 4. Diffuse scattering intensity versus Q along $[110]$ at several temperatures obtained at $x=0.08$ of Ca doping.

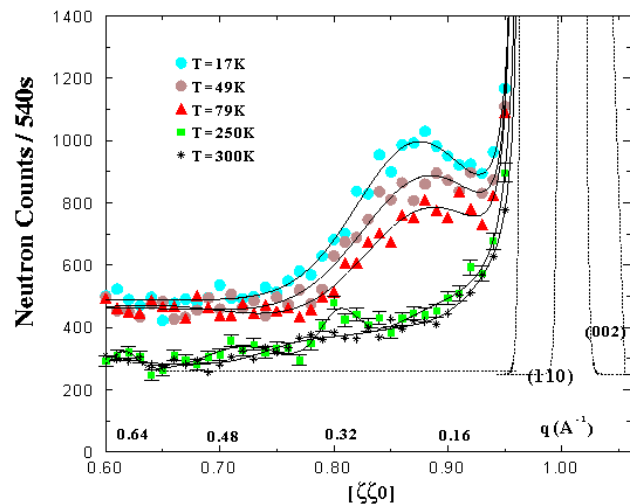


Figure 5. Diffuse scattering intensity versus Q along $[110]$ at several temperatures obtained at $x=0.08$ of Ca doping.

The existence of such an isotropic modulation, suggests a typical characteristic distance between similar magnetic inhomogeneities as in a liquid-like distribution. These inhomogeneities can be seen thanks to the contrast between their magnetization density and that of the surrounding matrix. To get a more quantitative description, a hard sphere model has been used with a liquid function for the distribution and excluded volumes, assuming a perfect isotropy. The corresponding calculated curves which fit the experimental data are shown also in Figure 2 for $x=0.05$ and $x=0.08$. They determine a typical size of 15 \AA for $x=0.05$, increasing to 18 \AA for $x=0.08$ with a typical distance of 38 \AA . The most striking result is that the density of these inhomogeneities, or "droplets", is smaller by more

than an order of magnitude than the density of Ca atoms. Such a result gets rid of a picture of magnetic polarisation surrounding each Ca or hole defects, but rather suggests a purely electronic effect of hole rich regions in repulsive interaction within a hole poor medium. This segregation would occur on a small spatial scale of some tens of Å. The temperature dependence reported for $x=0.05$ reflects a decrease of the size of the inhomogeneity and of their spatial density. However, the fall down of the intensity may be also related to a change of the magnetic contrast which must become nul in the paramagnetic state. The calibration of the intensities in barns per Mn atom, allows in principle, an estimation of the difference between the magnetization densities of the two magnetic regions at low temperature. This determination is model dependent. In particular, the isotropy of the structure, which could not be checked with accuracy because of twinned domains, is assumed.

The present determination of the magnetic contrast, $0.7 \mu_B$, does not agree with a ferromagnetic state within the hole rich regions. This conclusion apparently disagrees with NMR experiments performed on the same samples. These latter experiments indicate that some Mn spins follow the applied field as expected for spins within a

ferromagnetic state. Both findings can be conciliated in a more complex picture of magnetic clusters with a small ferromagnetic core, therefore not observable by neutrons (the intensity is proportional to the square of the volume).

Very recently, a similar study has also been performed in a $x=0.06$ Sr doped compound. A ferromagnetic modulation with characteristics close to those found for Ca doping has been also observed. This suggests the general character of these observations.

The disappearance of the modulation in the scattering intensity for $x=0.15$, where the compound is fully ferromagnetic, could be explained by a percolation of the magnetic inhomogeneities or by an homogeneization of the electronic density. In the first case, one expects the intensity to be restricted within a much smaller q scale, out of the present experimental window.

The role of such an electronic phase separation in the metal-insulating transition, is still unclear. At $x=0.15$, where one can expect a percolation of these inhomogeneities, the compound keeps insulating properties. This stresses out that the magnetic state alone is insufficient to explain the metal-insulating transition.

References

- [1] E. L. Nagaev, *Phys. Status Solidi B* **186**, 9 (1994)
- [2] M.Kagan, M.Mostovoy and D.Khomskii, cond-mat/9804213 Los Alamos April 1998
- [3] S. Yunoki, J. Hu, A.L. Malvezzi, A. Moreo, N. Furukawa and E. Dagotto, *Phys. Rev. Lett.* **80**, 845 (1998)
- [4] J. M. De Teresa M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. Del Moral, Z. Arnold, *Nature* **386**, 256 (1997)
- [5] J. W. Lynn, R. W. Erwin, J. A. Borchers, Q. Huang and A. Satoro, *Phys. Rev. Lett.* **76**, 4046 (1996)
- [6] M. Hennion, F. Moussa, G. Biotteau, J. Rodriguez-Carvajal, L. Pinsard, A. Revcolevschi, *Phys. Rev. Lett.* **81**, 1957 (1998)