This study concerns the physics of metal-insulator transition in manganites with colossal magnetoresistance (CMR). This topic still provides a challenge for theories. The possibility of mixed-phases to explain the CMR properties in La$_{1-x}$Ca$_x$MnO$_3$ at hole doping $x \approx 0.2$, has been pointed out by numerical studies [1]. However, in this doping range, the experiments are not conclusive. We have investigated two compounds at $x=0.17$ and $x=0.2$, close to $x=0.22$ where the ferromagnetic metallic (FM) phase with CMR properties occurs [2]. The compounds, which are ferromagnetic (F), exhibit a “quasi-metallic” behaviour below $T_C$ ($T_C=175K$ and $180K$ for $x=0.17$ and $0.2$ resp.) as expected from double-exchange coupling. At lower temperature, however, they become insulating, which reveals additional processes not accounted by double-exchange. Inelastic neutron scattering performed in the quasi-metallic state, reveals that the spin-wave spectrum is strongly anomalous. Instead of a continuous cosine law as for a F spin wave dispersion (cf the dashed line in Fig. 1), nearly dispersionless levels are observed at large $q$ values. They can be quantitatively described by spin waves confined inside finite-size clusters [3,4]. This analysis allows us to determine (i) the shape (evolving from two-dimensional for $x=0.17$ to three-dimensional for $x=0.2$), (ii) the size (decreasing from 4 to 2 lattice spacings with increasing $x$) and (iii) the super-exchange (SE) coupling constants inside the clusters. The use of SE coupling constants, in a Heisenberg model, indicates that the clusters are “hole-poor” or orbital-ordered, implying hole-rich and orbital-disordered boundaries. These observations could be crucial for clarifying CMR. Moreover, confined spin waves inside ultra-fine domains are observed for the first time.

Let us first focus on the $x=0.2$ compound, the results on $x=0.17$ being summarized below. Fig 1 displays the spin-wave spectrum in the quasi-metallic state ($T=150K$, left panel) and in the insulating state (right panel) along the [001], [010],[001] axis, superimposed because of twinning, in cubic indexation. At 150K, at small $q$ up to $q=0.25$, the spectrum consists of a dispersed curve. Beyond, the intensity is divided into three levels moderately dispersed, numbered from (1) to (3). At low temperature, in the insulating state, the dispersion of the levels increases and the low-energy level (3) disappears. The same type of dispersionless modes are observed along all symmetry directions. The spin-wave spectrum along the [110],[011],[101] directions (diagonal of the cubic face) and along [111] (main diagonal of the cube for which all domains are equivalent) are reported in Fig. 2 at $T=150K$. Beyond a dispersed curve at small $q$ values, only two levels are observed along [111] whereas several can be determined along [110]. From the expression for the energy of a propagating spin wave in a Heisenberg model, one gets relations between the zone boundary energies $E_B$, along each symmetry direction, and the superexchange (SE) magnetic coupling constants, $J_{ab}$ along the $a$ or $b$ axis (equivalent) and $J_c$ along the $c$ axis of the perovskite cube. These relations are also valid for finite-size clusters, where $E_B$ is the largest energy level. According to predictions [3], the lowest energy confined wave corresponds to a half-wave and its energy should be a sub-multiple of $E_B$. The cluster size $\xi$ is deduced from
the ratio between this lowest energy level and $E_B$. In Figure 1, the largest energy level at $E_B=18$ meV and the level at 9 meV, are attributed to a full-wave and half-wave along [100] or [010], whereas the same level at 9 meV (accidental coincidence) and that at 4.5 meV are attributed to the full and half waves along [001] (see drawing in Fig 4). This assignment defines $J_{ab}$ and $J_c$ (reported in Fig 3) and the values of all energy levels along the other three symmetry directions (indicated by hatched areas, instead of lines, due to the experimental uncertainty), labeled (1) and (2) for [110], (3) and (4) for [011]+[101], in Fig 2-left panel, and (1) and (2) for [111] in Fig 2-right panel. The good agreement with experiment supports this attribution. A cluster size $\xi$ of 2 lattice spacings is obtained. The small-q dispersed curve implies that the small domains are ferromagnetically coupled together.

A similar study for $x=0.17$ where the flat levels exist only in the $(a, b)$ plane and not along the $c$ direction, leads to the $J_{ab}$ value reported in Fig 3 and determines a cluster size of 4 lattice spacings within the $(a, b)$ plane. The general evolution of $J_{ab}$ and $J_c$ deduced from the dispersionless levels for $x>0.125$ (for $x=0.17$, $J_c$ is obtained from $E_B^{110}$ and $E_B^{111}$) and from the “normal” spin wave branch for $x<0.125$ (in the canted antiferromagnetic insulating state or CAFI) are reported in Fig 3. It shows a monotonic effect of the hole-doping on the SE coupling constants, starting from undoped LaMnO$_3$. These constants characterize an orbital-ordered or “hole-poor” spin system. A general evolution of the charge segregation with hole doping is displayed in Fig 4. The hole-rich domains, strongly anisotropic, embedded in an orbital-ordered matrix observed for $x<0.125$[5], percolate at $x=0.125$ ($J_c=0$), whereas small orbital-ordered domains with 2D ($x=0.17$) and 3D ($x=0.2$) character are formed as $x$ increases beyond 0.125.

References