Field-Induced Ferromagnetic Metallic State in the Bilayer Manganite $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$, Probed by Neutron Scattering

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The bilayer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ exhibits a phase transition from a paramagnetic insulating (PI) to a ferromagnetic metallic (FM) state with a colossal magnetoresistance (CMR) effect. Upon 60% Pr substitution, magnetic order and PI to FM transition are suppressed. Application of a moderate magnetic field restores an FM state with a CMR effect. Neutron scattering by a single crystal of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$, under a magnetic field of 5 T, has revealed a long-range and homogeneous ferromagnetic order. In the PI phase, under zero field, correlated lattice polarons have been detected. At 28 K, under 5 T, the spin wave dispersion curve determines an in-plane isotropic spin wave stiffness constant of 146 meV Å^2. So the magnetic field not only generates a homogeneous ferromagnetic ground state, but also restores a magnetic coupling characteristic of FM CMR manganites.

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The manganese perovskites $A_{1-x}B_xMnO_3$, with $A =$ La, Nd, etc., and $B =$ Ca, Sr, etc., have attracted a great deal of attention recently, both from applications as well as fundamental points of view [1,2]. Their remarkable properties, such as their colossal magnetoresistance (CMR) effect, are mainly due to the interplay between charge, lattice, orbital, and spin degrees of freedom. Understanding the physical origin of these spectacular experimental results is a true challenge for solid state theorists. Among several models proposed, we mention here the three most popular ones: (i) The double exchange model proposed by Zener as early as 1951 [3] explains the metal-insulator transition but not quantitatively the CMR effect. (ii) A modified Zener model taking into account the Jahn-Teller distortion due to the Mn^{3+} ions has been proposed [4] and accounts for the observed intrinsically inhomogeneous insulating state, often described as polaronic. (iii) The so-called phase separation models [5–7] are appropriate to explain the peculiar inhomogeneous ground states of the manganites at low doping ($x \ll 1$) and close to $x \approx 0.5$. In this latter case, upon application of a magnetic field, some systems can easily switch from a phase-separated state to a single phase one [1]. It seemed therefore very interesting to design new materials which could be tuned directly to a ferromagnetic and metallic state from a paramagnetic and an insulating one by application of a moderate field.

In fact, recently, such a field-induced transition was reported in the Pr-substituted bilayer manganite $(La_{1-z}Pr_z)_{1.2}Sr_{1.8}Mn_2O_7$, with $z = 0.6$. This compound is a paramagnetic insulator (PI) but shows a magnetic field-induced first-order PI ferromagnetic metallic (FM) transition accompanied by a magnetoresistance ratio $\frac{R(0)-R(H)}{R(H)} \sim 10^6$ [8,9]. This bilayer manganite, studied in the present work, derives from the $n = 2$ member of the Ruddlesden-Popper series expressed generally as $(La_{1-x}Sr_x)_{n+1}Mn_nO_{3n+1}$. The bilayer compound with $n = 2$ and $x = 0.4$ shows a PI-FM transition at $T_C = 126$ K with a magnetoresistance ratio of $\sim$180 [10,11]. However, for the same hole count ($x = 0.4$), but with an additional substitution of Pr on the La site, viz., $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$, the sample becomes a paramagnetic insulator at all temperatures. The bilayer manganites crystallize in a tetragonal structure *I4/mmm*, and single crystals are not twinned; this is a major advantage over the well studied nearly cubic perovskite manganites. Moreover, the highly anisotropic properties arising from this quasi-2D structure make the study of this compound very attractive.

In addition to the detection of the long-range ferromagnetic order induced by field application in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$, neutron scattering has allowed us to determine the coupling between the spins. The measured spin wave stiffness constant has nearly the value found in the FM phase of the Pr-free bilayer and the perovskite manganites. Our data demonstrate convincingly that the magnetic field induces not only a long-range ferromagnetic order but also a strong magnetic coupling, probably of double exchange nature. Moreover, thanks to neutron diffuse scattering, we could also establish the polaronic character of the PI phase of the Pr-substituted bilayer compound. This feature is often mentioned as a possible origin of the CMR effect. Correlated lattice polarons do exist in the PI state and vanish in the field-induced FM phase.

A high quality single crystal of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$, with a 0.3 cm^3 volume and a 0.5° mosaic spread, was grown by the floating-zone technique [8]. The sample was attached to the cold finger in a 6 T vertical field superconducting magnet. The sample was aligned with its (**a**, **b**) scattering plane horizontal and **c** axis parallel to the magnetic field. The space group is

I4/mmm, with, at room temperature, $a = b = 3.85$ Å and $c = 20.15$ Å.

Elastic and inelastic neutron scattering measurements were carried out on the triple axis spectrometer 4F2, installed on a cold neutron source at the Orphée reactor of the Laboratoire Léon Brillouin in Saclay. The elastic spectra of the Bragg peaks were analyzed with a Gaussian law. The diffuse scattering due to the lattice polarons was modelized by a Lorentzian law. The inelastic spectra were described as the sum of several components, convoluted with the instrumental resolution function: a delta function for the elastic incoherent scattering $C_0\delta(\omega)$ and a Lorentzian law for the inelastic part: $\frac{C}{[\omega-\omega(q)]^2+\Gamma(q)^2}$ multiplied by $1 + n(\hbar\omega)$, $n(\hbar\omega)$ being the Bose factor.

$\mathbf{Q} = \boldsymbol{\tau} + \mathbf{q}$, and $\boldsymbol{\tau}$ is defined in the *I4/mmm* indexation, $\omega(q)$ represents the spin wave dispersion law and $\Gamma(\mathbf{q})$, the damping of the spin wave (half width at half maximum). The fitting process of the data takes into account the Lorentzian line centered at $-\omega(q)$, which spreads in the positive energy side because of the damping. In all the spectra represented, the lines through the points are the results of the fitting process.

Figure 1 shows the temperature evolution of the integrated intensity of the (110) Bragg peak without and with the magnetic field applied parallel to the **c** axis. In the absence of a magnetic field (open circles), the intensity has a purely nuclear origin clearly indicating the absence of any long-range magnetic ordering. Then, upon application of a field of 5 T at high temperatures, one detects, on cooling down, below 100 K, a magnetic intensity, superposed to the nuclear one (solid circles). This intensity saturates at low temperatures, with an inflexion point at $T_C \sim 75$ K. This agrees well with the field-cooled magnetization measurements [8]. No extra diffuse scattering was detected at the foot of the magnetic Bragg peak, indicating that, at least in the (**a**, **b**) layer plane, the FM state appears homogeneous.

Now we present the dynamical study of this spin system, especially the determination of the spin wave dispersion in the low energy range (0–6 meV). For that we have measured the propagation of spin waves in the basal plane (**a**, **b**). Because of the 2D character of the structure, the magnetic coupling is expected to be maximum in this plane. We have performed this study at 28 K (~2.5 meV), a good compromise between a significant increase of the population factor and a moderate increase of the spin wave damping. An example of the spectacular effect of the field on magnetic excitations is shown in Fig. 2, where the spectra are measured at $\mathbf{Q} = (1.035, 1, 0)$. Under $H = 0$ T, the spectrum (open circles) is centered on the zero energy value, characteristic of the quasielastic spin fluctuations in a paramagnetic state. Upon application of a field of 5 T, a well resolved spin wave mode, centered on the energy value of 1.3 meV, appears. We have repeated this measurement at different **q** values, parallel to **a** or to **a** + **b**. The results are displayed in Fig. 3(a). The energy of the spin waves follows an isotropic law, characteristic of ferromagnetic systems: $\omega = \omega_0 + Dq^2$, with $\omega_0 = 0.87 \pm 0.04$ meV and a spin wave stiffness constant $D = 146 \pm 5$ meV Å^2. Since the double exchange model, in the infinite Hund coupling limit, can be represented by a Heisenberg model [12], we deduced from our measurements the equivalent superexchange integral between in-plane first neighbors: $J_{\parallel} = 5 \pm 0.15$ meV. The gap ω_0 is the sum of a gap due to the intrinsic anisotropy of the system Δ and the Zeeman frequency $g\mu_B H$ [13]. The shape of the single crystal is nearly isotropic, so $g\mu_B H$ is a good approximation for the Zeeman frequency [14]. For $H = 5$ T, $g\mu_B H = 0.58$ meV, and $\Delta = 0.29$ meV. The value of D (or $J_{\parallel}$) fairly agrees with the value measured in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.4$) [15–20]. *In the Pr-substituted system, the magnetic field has restored a ferromagnetic and metallic state very similar to that found*

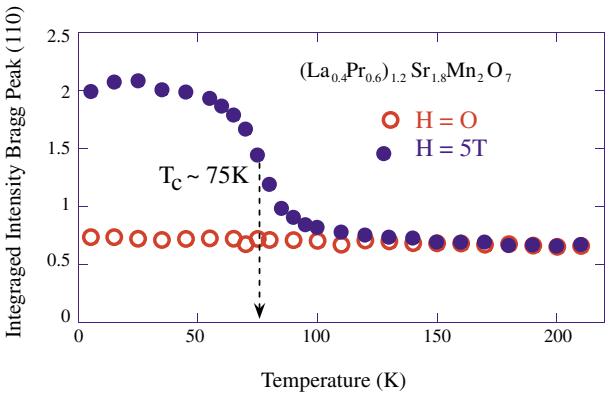

FIG. 1 (color online). Integrated intensity of the Bragg peak (110). Open (solid) circles represent measurements in zero (5 T) field. The arrow represents the inflexion point of the field-induced ferromagnetic transition.

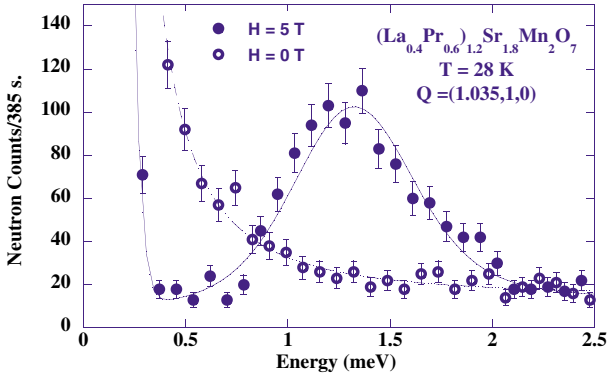

FIG. 2 (color online). Comparison of energy spectra at $\mathbf{Q} = (1.035, 1, 0)$, $T = 28$ K, in zero (open circles) and applied field (solid circles). The spin wave mode appearing under a 5 T applied field disappears when the field is turned off. The lines are the result of the fitting process; see the text.

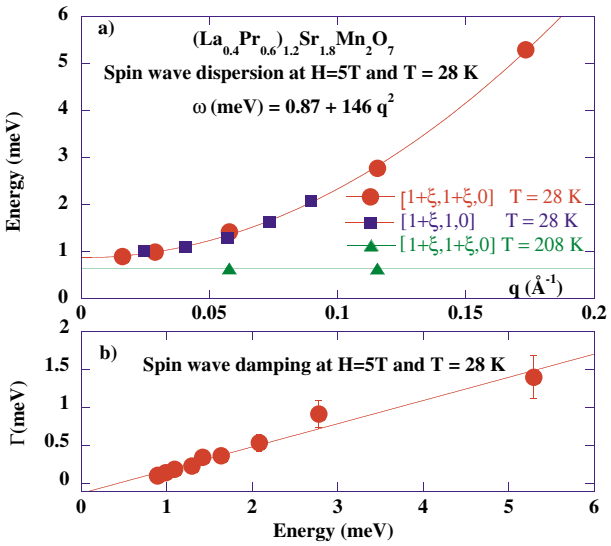

FIG. 3 (color online). (a) Spin wave dispersion at 5 T and $T = 28$ K along [100] (squares) and [110] (circles). Measurements at 208 K are reported as triangles. (b) Spin wave damping at $H = 5$ T and at $T = 28$ K. $\Gamma(\omega)$ is nearly linear, with a slope of ~ 0.3.

in the Pr-free compound. However, the gap Δ, characteristic of the intrinsic anisotropy of this field-induced FM phase, is 10 times larger than in the Pr-free system [16], where the Mn ion spins lie spontaneously in the basal plane [11] . This large anisotropy, surely related to the spin-orbital coupling, reveals a strong spin-lattice interaction. One will see below yet another effect of this coupling.

This result agrees well with the fact that, when the field is along **c**, a lower value of the field could produce the FM state and a stronger saturation value of the magnetization, in comparison with the case where the field is applied in the basal plane [8]. The values of the spin wave damping, $\Gamma(\omega)$, at 28 K, are displayed in Fig. 3(b). In the energy range studied, it appears that $\Gamma(\omega)$ follows a nearly linear law, with a slope $\frac{\Gamma(\omega)}{\omega} \sim 0.3 \pm 0.02$. In that case too, the results compare pretty well with those measured on $La_{1.2}Sr_{1.8}Mn_2O_7$ [19] in a larger energy range. This spin wave damping is also comparable to the damping measured on pseudocubic manganites [21]. We have also checked the response of the system at high temperature, in the paramagnetic and the insulating state, with and without magnetic field. Examples of the spectra measured at $\mathbf{Q} = (1.025, 1.025, 0)$, at $T = 208$ K, are presented in Fig. 4. Under a field of 5 T (solid circles), we observe a resonance at 0.64 ± 0.04 meV, very close to $g\mu_B H = 0.58$ meV, the value expected in a paramagnetic system under such a magnetic field. Under zero field (open circles), this mode is replaced by a quasielastic scattering characteristic of paramagnetic fluctuations, as in the case $T = 28$ K and $H = 0$ (Fig. 2).

Finally, let us consider lattice polarons in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. It is well established that the localization of the charges in the insulating phases of manganites of orthorhombic structure and with CMR effect leads to the formation of lattice distortions, also called lattice polarons. Furthermore, the high Mn^{4+} concentration at these doping rates makes correlations between polarons unavoidable [22–26]. We measured the neutron diffuse scattering around the (220) Bragg point, scanning in the $[-\zeta, \zeta, 0]$ direction. The choice of this Bragg peak was motivated by the absence of variation of its intensity with field and with temperature. Figure 5 shows a typical spectrum measured along the $[2 - \zeta, 2 + \zeta, 0]$ direction at $T = 28$ K in the PI state under a zero field, and the same measurement along a half path under $H = 5$ T in the FM state. In the PI phase, in addition to the Bragg peak, three Lorentzian modes are clearly seen, a huge one and a narrow one, centered on the Bragg peak position, and two modes, symmetrically centered at $\zeta = \pm 0.2$, on each side of the Bragg peak (220). This modulated scattering can be explained as follows: the first mode can be related to lattice defects giving rise to a large Huang scattering (the corresponding Lorentzian distribution has a very small width, so the intensity varies as $\sim \frac{1}{q^2}$), while the two symmetric modes correspond to correlated polarons. From their symmetric positions, we can determine a mean distance of ~ 5 lattice parameters between them. The width of both symmetric lines indicates that these polarons are correlated on a very short range. The localization of the charges on a short range results partly from the competition between the double exchange coupling and the long-range charge ordering. When applying a field of 5 T at 28 K, the system shifts towards the field-induced FM state. We observe then a strong change in the diffuse scattering. As seen in Fig. 5, the intensity attributed to correlated polarons completely

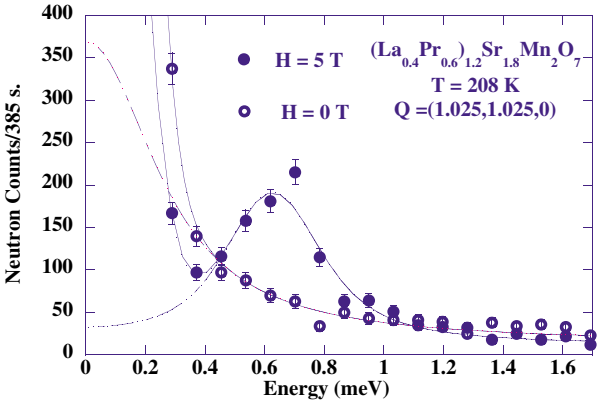

FIG. 4 (color online). Comparison of energy spectra at $\mathbf{Q} = (1.025, 1.025, 0)$, and at $T = 208$ K (paramagnetic phase) in zero (open circles) and applied field (solid circles). The Zeeman mode at $\omega = 0.64$ meV, under a 5 T applied field, disappears when the field is turned off; the lines are the result of the fitting process.

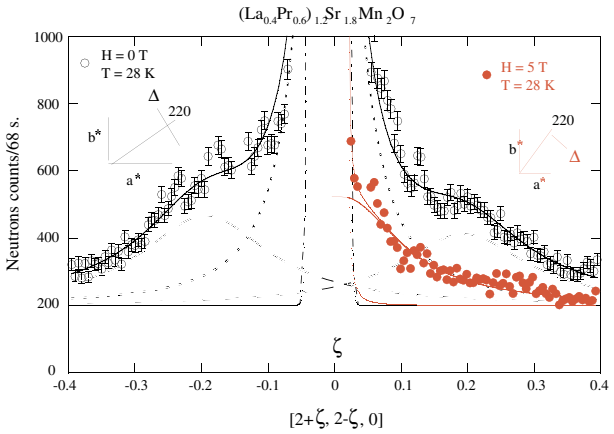

FIG. 5 (color online). Elastic spectra along $[2+\zeta, 2-\zeta, 0]$, at $T = 28$ K and $H = 0$ T, in the PI phase (path Δ in the left inset and open circles) and at $T = 28$ K and $H = 5$ T, in the FM phase (path Δ in the right inset and solid circles). The same dashed and dotted lines fit the (220) Bragg peak in each spectrum. The dotted line fits the huge diffuse scattering centered at $\zeta = 0$ in the PI state. The broken lines fit the correlated polarons only in the PI phase. Note the huge change from the PI to the FM state.

vanishes. Only central scattering remains, but with a very small intensity. Thus, the field induces first a full melting of the correlated polarons as expected in a metallic state. More surprising is the considerable reduction of the Huang scattering, which is further proof of the strong lattice-spin coupling. Magnetostriction measurements [8] had already established such a coupling.

In $Pr_{0.7}Ca_{0.3}MnO_3$, such a first-order field-tuned insulator to metal transition also occurs. Under an applied field, this system evolves from a magnetic phase-separated insulating state to a homogeneous FM state. The spin wave stiffness constant exhibits a jump from a value characteristic of the ferromagnetic and insulating state to a value characteristic of the FM state [27]. In the present experiment, the jump is even more spectacular. It goes from zero, under zero field, to $\sim$150 meV Å^2, under a 5 T field. The following scenario may help toward understanding this phenomenon. Pr substitution on the La sites distorts the structure by a steric effect and makes the O $-$ Mn $-$ O bond angle very different from 180°. Hence the electronic band width narrows. A gap opens and a paramagnetic and insulating state becomes energetically favorable. However, due to an interplay between many degrees of freedom (spin, charge, orbital, lattice), the energies of different possible ground states are very close to each other. The delicate balance that exists between these phases is easily tipped by a magnetic field. Thus, a moderate magnetic field applied on the polaronic PI phase induces a ferromagnetic order and, through the spin-dependent double exchange interaction, restores a strong ferromagnetic coupling, favoring the charge mobility, so that the system becomes metallic. The present PI-FM transition is certainly assisted by the change of the magnetic state of the Pr ions under field, revealed by recent polarized neutron scattering measurements on the same sample. When the field is applied along **c**, the Pr ions acquire a significant magnetic moment ($2\mu_B$) [28]. The same experiment has also demonstrated that the $3d_{3z^2-r^2}$ orbitals are preferentially occupied in this FM state.

These measurements have contributed to an understanding of the spectacular effect of magnetic field on $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. The polaronic inhomogeneous phase present in the PI state is suppressed by the field which induces a true long-range ferromagnetic order. Spin-lattice interaction and double exchange are certainly responsible for restoring this homogeneous FM state.

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