Coexistence of ferromagnetic and antiferromagnetic spin correlations in $La_{1.2}Sr_{1.8}Mn_2O_7$

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We have investigated the antiferromagnetic (AF) spin correlations which coexist with the ferromagnetic spin excitations close to the Curie temperature $T_C \approx 128$ K in the bilayer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ that shows colossal magnetoresistance (CMR) behavior, by inelastic neutron scattering both on a cold triple-axis and a time-of-flight neutron spectrometer. The scattered neutron intensity at $Q=(0.5,0,0)$ could be detected at $T=120$ K. This intensity grows rapidly to become maximum at about $T \approx 128$ K. Upon increasing the temperature, the intensity decreases very slowly and can be easily detected up to $T=200$ K. The temperature variation of AF correlations strongly suggests that they are of intrinsic origin. The scattered neutron intensity due to the AF correlations decreases under applied magnetic field in a very similar way as the resistivity, suggesting that the AF correlations are relevant to the CMR effect.

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Following the discovery of colossal magnetoresistance (CMR) in the bilayer ferromagnetic manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ by Moritomo *et al.*,[1] its spin dynamics have been investigated quite intensively[2–10] by inelastic neutron scattering. Due to the reduced dimensionality, the electronic and magnetic properties of this bilayered manganite are expected to be different from those of the well-studied three-dimensional manganites $A_{1-x}A'_xMnO_3$ (A=La,Pr,Nd; A'=Ca,Sr,Ba). The reduced dimensionality in fact enhances the CMR effect, albeit at the cost of decreasing the ferromagnetic transition temperature. Further, novel features concern the observation of the coexistence of ferromagnetic and antiferromagnetic short-range-ordered spin correlations[2,11] above $T_C \approx 128$ K. Figure 1 illustrates the crystal structure and the important exchange paths. Also shown in the figure is the temperature dependence of the resistivity in zero field and applied magnetic field. In CMR manganites, there are two species of electrons, which contribute to the low energy physics: Mn t_{2g} electrons form the localized spins with high-spin state $S=3/2$, while itinerant electrons occupy the Mn e_g bands. A simple model which captures the physics of CMR ferromagnetic manganites is the double-exchange (DE) Hamiltonian first introduced by Zener.[12] Zener argued that, in order to gain maximum kinetic energy, the hopping (t_{ij}) of the itinerant Mn e_g electrons, spins of which are parallel to the localized t_{2g} electrons by Hund's coupling (J_H), will cause through O (double exchange) the localized spins to align in a parallel way, leading to the ferromagnetic ground state. The magnetic excitation for the double exchange model has been discussed by Furukawa[13,14] who showed that, for a strong Hund's coupling, $J_H \to \infty$ and in the classical spin limit $S \to \infty$, the spin waves in a DE model can be mapped into an effective Heisenberg model. Shannon and co-workers[15,16] have discussed the quantum and thermal corrections of the minimal DE model and have shown that part of the experimentally observed zone-boundary softening and damping can be qualitatively accounted for by these corrections. In order to explain quantitatively the spin wave softening and damping effects, it may be necessary to include orbital and lattice degrees of freedom to the minimum DE Hamiltonian. The above theoretical conclusions are equally valid for perovskitelike three-dimensional (3D) as well as

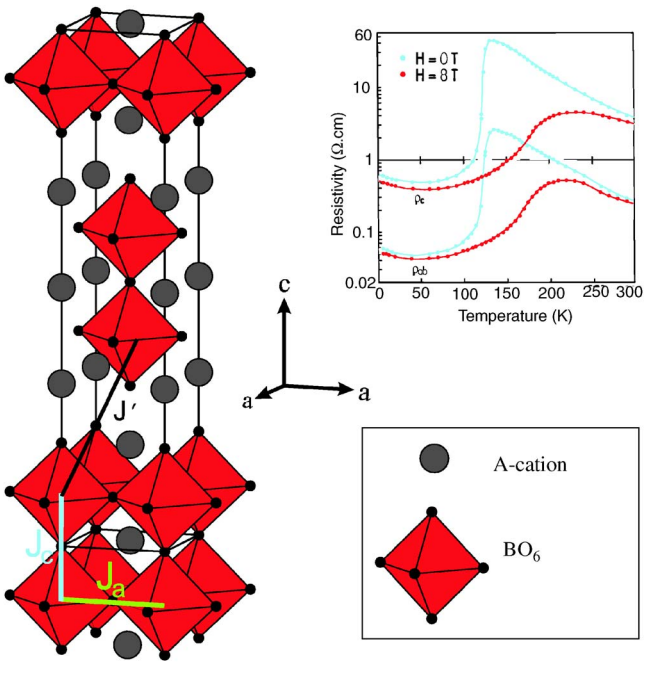

FIG. 1. (Color online) Crystal structure of $La_{1.2}Sr_{1.8}Mn_2O_7$ and the important exchange interactions. Temperature dependence of the resistivity of the $La_{1.2}Sr_{1.8}Mn_2O_7$ single crystal measured in the a-b plane and parallel to the c axis under applied magnetic fields of $H=0$ and 7 T, respectively.

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quasi-two-dimensional (2D) manganites such as bilayered $La_{1.2}Sr_{1.8}Mn_2O_7$. The superexchange interaction between the core t_{2g} spins have been left out completely in the above-mentioned theories. The superexchange interaction is, however, present in all concentrations but is dominated by the double exchange ferromagnetic exchange interaction for the present 40% hole doping. Antiferromagnetism is known to dominate in the bilayer manganite $La_{1-2x}Sr_{1+2x}Mn_2O_7$, both for $x<0.3$ and $x>0.5$ doping.[17] But the ordering temperature of the AF phases for doping $x=0.3$ is smaller than that of the ferromagnetic phase. This suggests that the strength of the antiferromagnetic exchange interaction is, however, somewhat smaller than that of the ferromagnetic interaction at the doping for which CMR effect is dominant. In the optimally doped metallic ferromagnet, the existence of antiferromagnetic spin correlations is therefore not entirely unexpected. In fact antiferromagnetic spin correlations were observed at the very early stage of the neutron scattering investigation[2,11] of the spin dynamics of $La_{1.2}Sr_{1.8}Mn_2O_7$. However, the scattered neutron intensity due to the antiferromagnetic spin correlations was about only 10% of that of ferromagnetic excitations and therefore was not investigated much further. We have studied the antiferromagnetic correlations in $La_{1.2}Sr_{1.8}Mn_2O_7$ in some detail during the investigation reported here.

A cylindrical single crystal of $La_{1.2}Sr_{1.8}Mn_2O_7$ of diameter 5 mm and length 25 mm already studied in our previous investigations[2–5] was used for the present investigations. The Curie temperature of this crystal was determined both by magnetization and neutron diffraction and was found to be $T_C \approx 128$ K which is somewhat larger than $T_C=116$ K reported by Potter *et al.*,[18] but is very close to $T_C \approx 126$ K originally reported by Moritomo *et al.*[1] The low-energy part of the spin dynamics of $La_{1.2}Sr_{1.8}Mn_2O_7$ has been studied on the cold time-of-flight neutron spectrometer IN6 of the Institut Laue Langevin in Grenoble. The crystal was measured inside a helium cryostat with its [010] crystallographic axis vertical such that the scattering plane was $(h0l)$. A wavelength of 4.6 Å was applied resulting in an energy resolution of 120 μeV, and an elastic Q range of 0.3–2.4 $Å^{-1}$ with a Q resolution of 0.02 $Å^{-1}$. A set of measurements in a temperature range varying from 2 up to 150 K was performed.

As a direct time-of-flight spectrometer IN6 is characterized by a constant $\vec{k}_i$ of neutrons and a fixed scattering angle range of 10°–115°. Consequently, the determination of excitations along a distinguished $\vec{Q}$ necessitates measurements at different orientations of the sample with respect to $\vec{k}_i$, taking into account the energy dependence of the studied mode. Here, we primarily report results from measurements with the sample aligned for $\vec{Q}=(1,0,0)$ at $E=0$ meV.

Figure 2 shows the spin dynamics of $La_{1.2}Sr_{1.8}Mn_2O_7$ measured at this orientation. The upper panel of the figure illustrates the complex geometry of the time-of-flight experiment. The lower panel of the same figure shows the mapping of the spin excitations from $La_{1.2}Sr_{1.8}Mn_2O_7$ at $T=50$, 120, 130, and 150 K. At $T=50$ K, we see relatively a well-defined ferromagnetic spin wave dispersion starting from $Q=(1,0,0)$ with a spin gap of about 0.2 meV. There is no scattering at the AF position $Q=(0.5,0,0)$ at this temperature. The scattering starting from $Q=(1,0,0)$ becomes much broader at $T=120$ K which is about 8 K below T_C. One also observes the development of quasielastic scattering at the AF position $Q=(0.5,0,0)$ already at this temperature. At $T=130$ K, the scattering at $Q=(1,0,0)$ in the (Q,ω) is still broader but remains qualitatively similar to that at $T=120$ K. The scattering at $Q=(0.5,0,0)$ has become much stronger at this temperature. Similar scattering is observed at $T=150$ K which is 22 K above T_C. Figure 3 shows constant-energy slices of the scattering shown in the lower panel of Fig. 2 after subtracting the elastic background measured at $T=50$ K. We note that in constant-energy slices, dispersing ferromagnetic signals at $Q=(1,0,0)$ are observed, not only below T_C but also at $T=130$ and 150 K which are 8 and 22 K above T_C, respectively. The constant-Q slices (not shown) also show spin-wave peaks at $T=50$ and 120 K, but, at temperatures 130 and 150 K, which are above T_C, no peaks are observed at finite energy transfer. The scattering

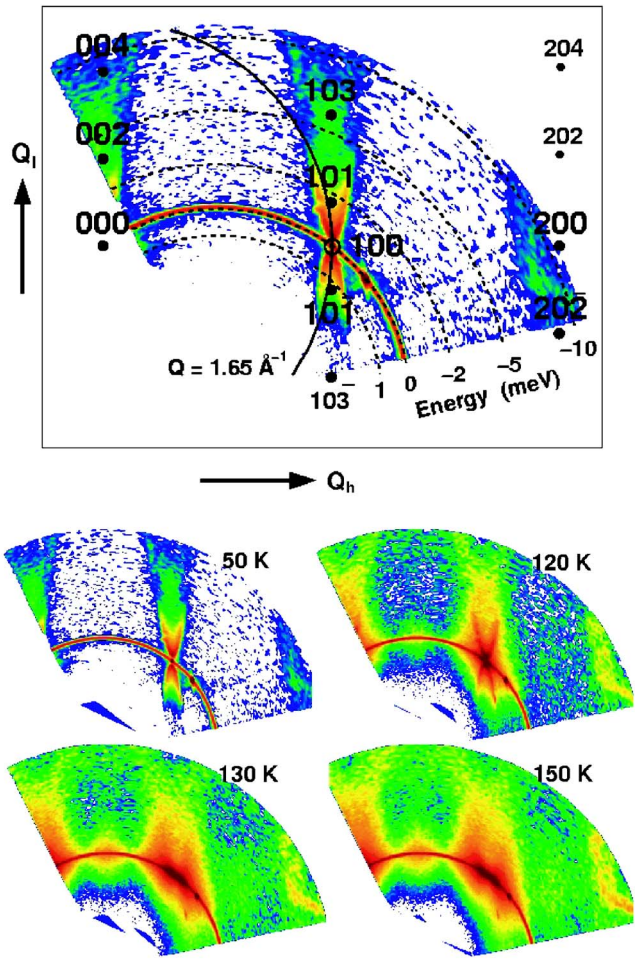

FIG. 2. (Color online) Spin wave excitations of $La_{1.2}Sr_{1.8}Mn_2O_7$ at $T=50$, 120, and 150 K, measured with a time-of-flight spectrometer using cold neutrons. The upper panel of the figure illustrates the complex geometry of the time-of-flight experiment. The lower panel of the figure shows the mapping of the spin excitations from $La_{1.2}Sr_{1.8}Mn_2O_7$ at $T=50$, 120, 130, and 150 K. The coordinates of the individual figures of the lower panel are the same as those of the upper panel.

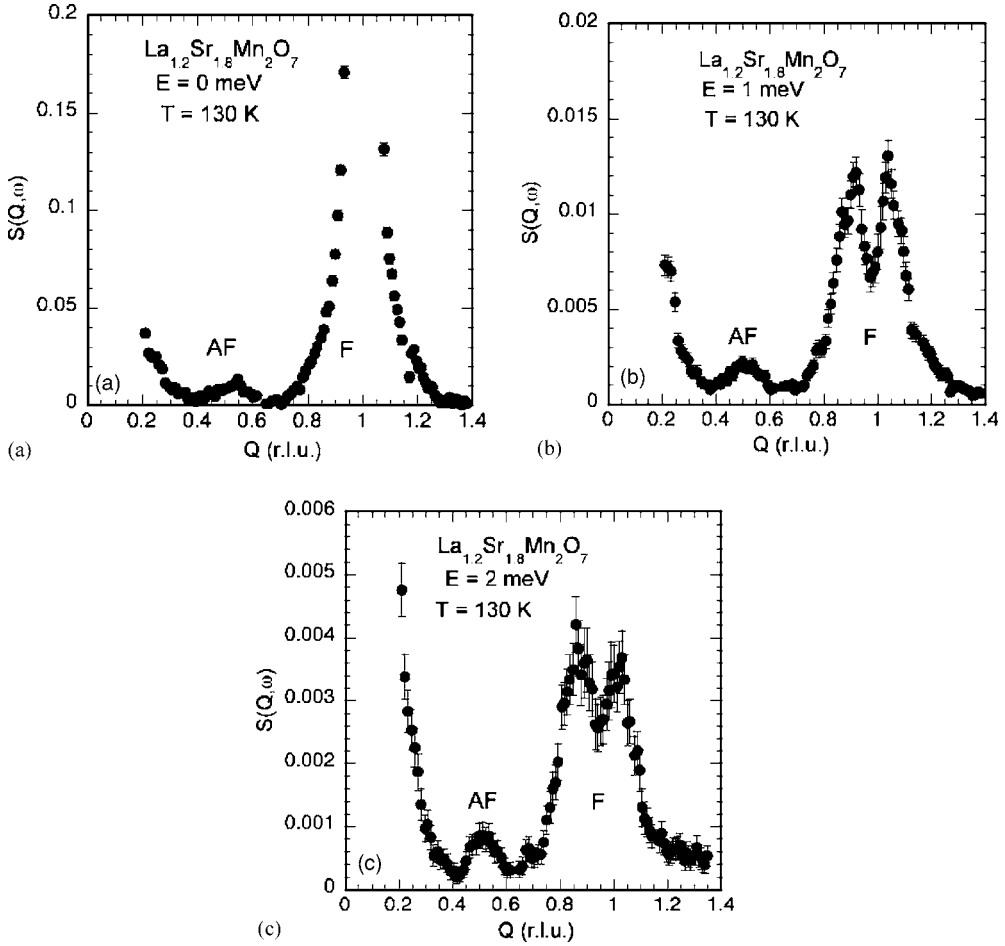

FIG. 3. Constant-E slices of the (Q,ω) mapping of Fig. 2 at $T=130$ for energy transfers of (a) 0 meV, (b) 1 meV, and (c) 2 meV. The elastic background measured at $T=50$ K has been subtracted from the data. The two strong peaks at $Q=1\pm q$ are due to the ferromagnetic spin excitations and the relatively small peak at $Q=(0.5,0,0)$ is due to the antiferromagnetic spin correlations. The intensity goes again up for small Q due to the proximity of the strong scattering due to ferromagnetic excitations at $Q=(0,0,0)$.

peaks at $E=0$ at these temperatures. This was also observed in our previous study[5] of the spin excitations close to T_C with a thermal triple-axis spectrometer using a multianalyzer detector (MAD). The other remarkable result is the scattering which appears at the position $Q=(0.5,0,0)$ close to T_C, implying the coexistence of antiferromagnetic spin correlations with the ferromagnetic spin excitations.

In order to study further the antiferromagnetic spin correlations in $La_{1.2}Sr_{1.8}Mn_2O_7$, we performed constant-Q scans at $Q=(0.5,0,0)$ at several temperatures close to T_C on the cold triple-axis spectrometer IN12 of the Institut Laue-Langevin. We placed the same crystal inside the helium cryostat with the b crystallographic axis vertical so that the scattering plane was $(h,0,l)$. Figure 4 shows the constant-Q scans of the antiferromagnetic fluctuations in $La_{1.2}Sr_{1.8}Mn_2O_7$ at $Q=(0.5,0,0)$ at $T=120$, 129.9, and 199.5 K. We see clear evidence of the antiferromagnetic fluctuations in these scans. The continuous curves are the least-squares fit of the data with a Lorentzian function for the quasielastic scattering plus a Gaussian function for the incoherent elastic scattering. From the least-squares fits we determined the intensity and half-widths of the antiferromagnetic fluctuations close to T_C. Figure 5 shows the temperature variation of the intensity and the half-width at half maximum (HWHM) of the AF scattering. The quasielastic intensity at $Q=(0.5,0,0)$ is small but measurable at $T=120$ K. It then grows rapidly to become maximum at about 130 K. At higher temperature, the intensity decreases very slowly and could be easily detected up to $T=200$ K. We note that the intensity becomes maximum at about the same temperature as the ferromagnetic $T_C\approx 128$ K. So the AF spin correlations seem to be intrinsic and are not due to the presence of some neighboring AF impurity phase. The half-width at half maximum (HWHM) of the AF fluctuations is about 1.86 meV at $T=200$ K. The HWHM decreases to about 1.27 meV at $T=120$ K. The typical decay time for the local antiferromagnetism at $T=200$ K is of the order of $\tau=\frac{\hbar}{HWHM}=0.35\times10^{-12}$ s and that at $T=120$ K is $\tau=0.52\times10^{-12}$ s. The characteristic time scale of the AF fluctuations determined here is in agreement with that determined by Perring *et al.*[11]

We have determined the magnetic field dependence of the AF correlations on the flat-cone diffractometer E2 of the Berlin Neutron Scattering Centre (BENSC). The crystal was placed inside a superconducting cryomagnet capable of generating a maximum field of 6.5 T. The vertical axis of the

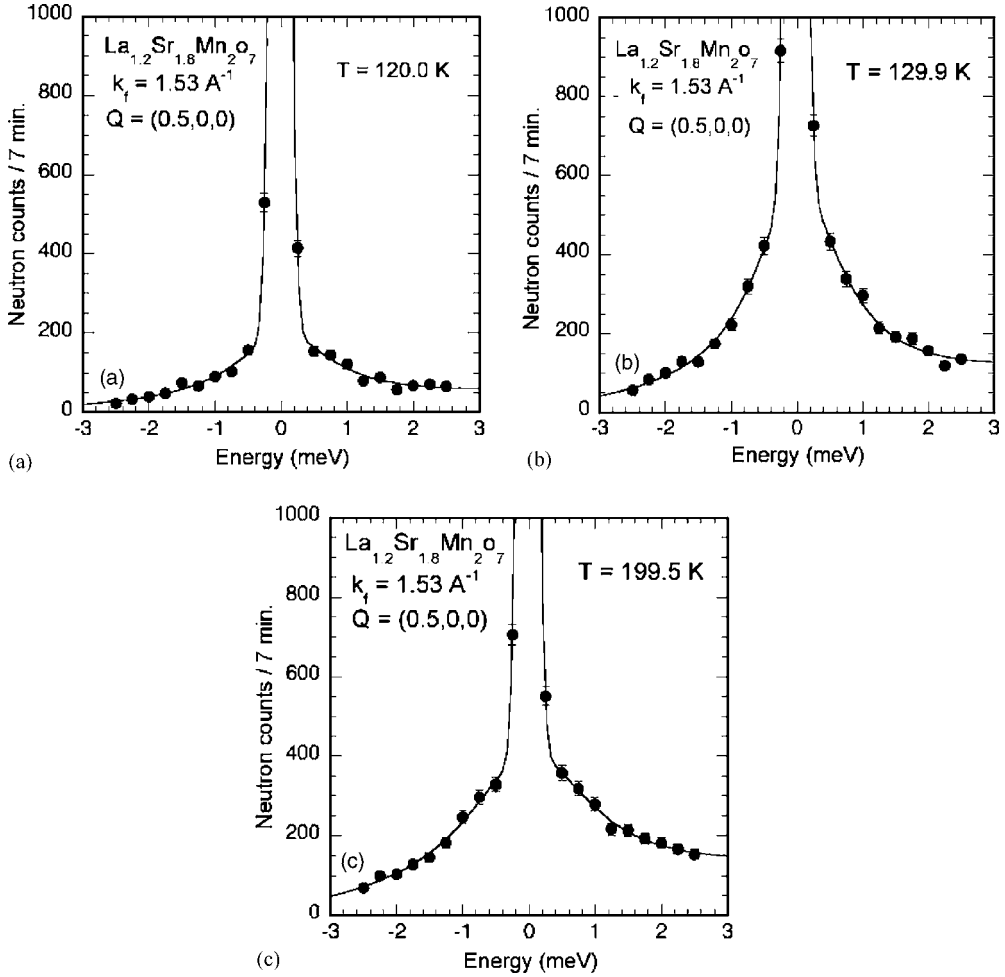

FIG. 4. Constant-Q scans of the antiferromagnetic fluctuations in $La_{1.2}Sr_{1.8}Mn_2O_7$ at $Q=(0.5,0,0)$ at (a) $T=120$ K, (b) $T=129.9$ K, and (c) $T=199.5$ K. The continuous curves are the least-squares fit of the data with a Lorentzian function for the quasielastic scattering plus a Gaussian function for the incoherent elastic scattering.

crystal was [010] and the magnetic field was applied parallel to this direction. Figure 6 shows the diffuse scattering in the (*hol*) at $H=0$ and 6.5 T at $T=145$ K. The relatively weaker diffuse intensity due to antiferromagnetic correlations is clearly seen in between the modulated strong intensity due to ferromagnetic correlations at $H=0$. Also seen is the diffuse scattering due to around the 200 Bragg position which also shows peaks at $(2\pm0.3, 0, \pm1)$. This diffuse scattering arises from lattice distortion or polarons and the satellite peaks are due to short-range correlations between the polarons. At $H=6.5$ T, intensity due to AF and polaron correlations disappear completely. We determined the integrated intensity of the broad peak at $Q=(0.5,0,0)$ arising due to AF correlations at $T=130$ K. We measured the intensity in both increasing and decreasing field up to 6 T but detected no appreciable hysteresis. Figure 7 shows the scattered neutron intensity due to the AF correlations at $Q=(0.5,0,0)$ as a function of the increasing magnetic field applied parallel to [010] along with the magnetic field dependence of the resistivity in the *a*-*b* plane measured by Moritomo *et al.*[1] The AF correlations and resistivity have a very similar magnetic field dependence suggesting that the AF correlations may be related to the CMR effect. The resistivity is expected to be related to antiferromagnetic fluctuations which imply that adjacent Mn moments are antiparallel. The antiparallel arrangement of spins reduces hopping of the electrons and therefore increases resistivity. The application of magnetic field along the *b* axis reduces the AF correlations and also causes the reduction in resistivity. The AF and polaron correlations have very similar field dependence. Also the temperature dependence of these two correlations are very similar. It is thus possible that both are a consequence of some more general phenomenon that has not yet been identified.

In the present paper we focus mainly on the AF spin correlations. However, it is to be noted that $La_{1.2}Sr_{1.8}Mn_2O_7$ is a ferromagnet and the paramagnetic scattering consists mainly of the modulated rodlike strong quasielastic scattering due to ferromagnetic spin correlations. The quasielastic scattered neutron intensity due to the AF correlations is only about 10% that of the ferromagnetic correlations.[2] The quasielstic scattering due to the ferromagnetic spin correlations has already been reported by us[5,19,20] and is also shown in Fig. 6. Figure 2 shows the evolution of ferromagnetic spin correlations together with the AF correlations.

The double-exchange physics implies a ferromagnetic interaction between core spins, mediated by itinerant e_g electrons. But there exists the possibility of an antiferromagnetic

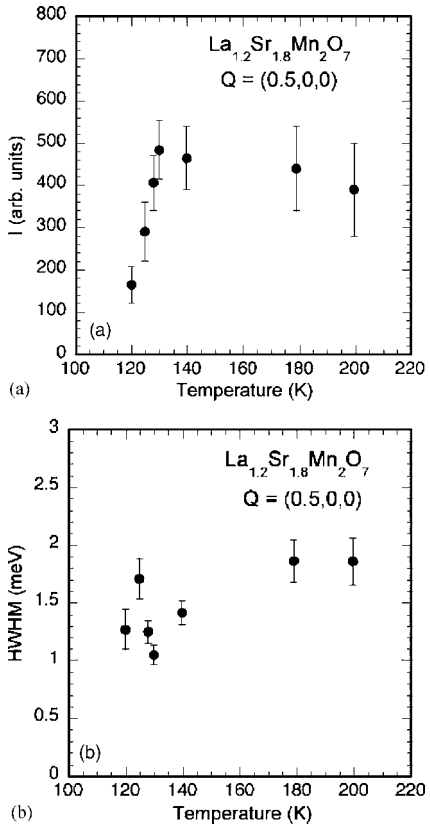

FIG. 5. Temperature variation of (a) the intensity and (b) the HWHM of the AF scattering.

core-spin interaction arising from virtual processes involving the t_{2g} levels. This has already been pointed out by several authors.[21–24] It is known that the change in doping causes the stabilization and/or the coexistence of the AF phase along with the ferromagnetic phase in bilayer manganites. Okamoto *et al.*[26] explained this behavior in terms of the occupation of the $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ orbitals. This interaction, if appreciable, would compete with the double-exchange. The possible importance of antiferromagnetic interactions in the bilayer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ has been discussed before[11,25] but the issue is still controversial. Perring *et al.*[11] suggested, from their neutron scattering data, the presence of antiferromagnetic regions in the material at temperatures close to T_C, whereas Millis[25] argued that the observation of the antiferromagnetic correlations can be more naturally interpreted as implying a ferromagnetically correlated state with a spatially modulated magnetic moment, arising perhaps from charge-stripe correlations. The spatially modulated moment can arise in the paramagnetic state because the sites with holes have a spin $S=3/2$ whereas the sites without holes have spins $S=2$. This can explain as well the insulating behavior of the paramagnetic state. The charge-stripe correlations can account for the spin correlations observed at $Q=(0.5,0,0)$. When the system becomes metallic below T_C, the stripes disappear as does the peak at $Q=(0.5,0,0)$. In this viewpoint, the spin correlations observed at $Q=(0.5,0,0)$ are actually the ferromagnetic correlations filtered by the factor relating to the charge correlations. However, the present data do not distinguish between the two alternative models for AF correlations described above.

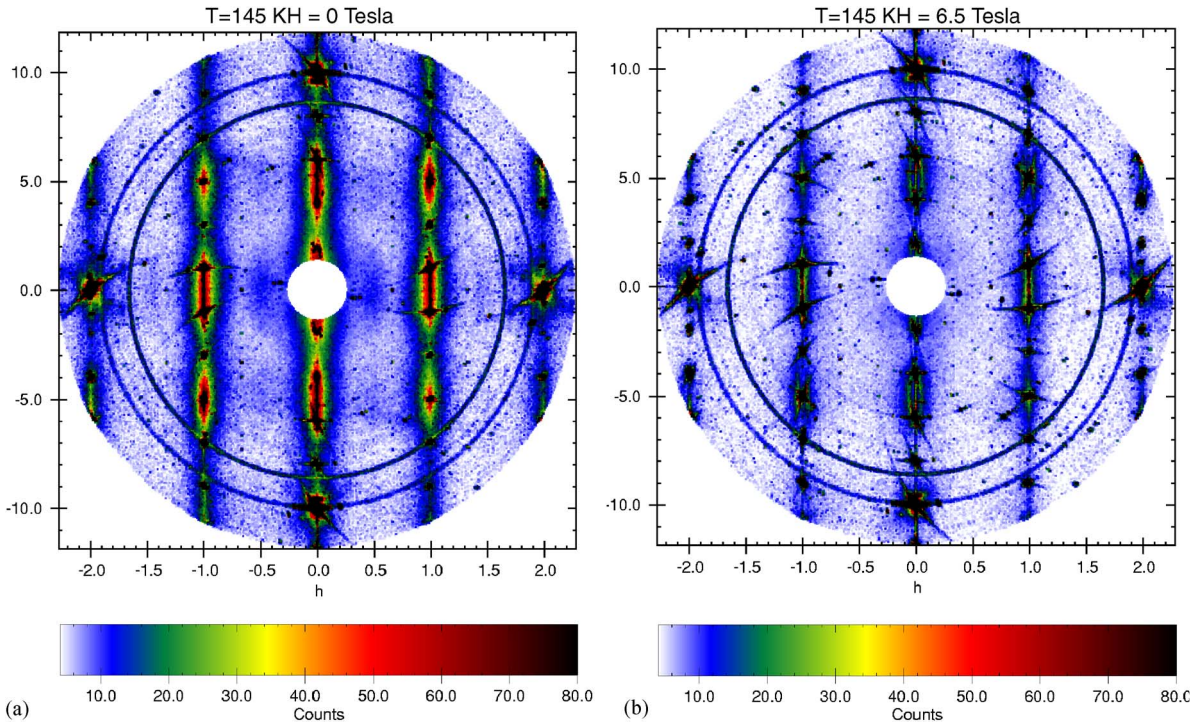

FIG. 6. (Color online) (a) Diffuse magnetic scattering from $La_{1.2}Sr_{1.8}Mn_2O_7$ in the reciprocal $(hk0)$ layer at $T=144$ K with zero applied magnetic field. Only half of the reciprocal layer has actually been measured; the other half has been generated by symmetry. (b) Diffuse magnetic scattering from $La_{1.2}Sr_{1.8}Mn_2O_7$ in the reciprocal $(hk0)$ layer at $T=145$ K under an applied magnetic field of 6.5 T.

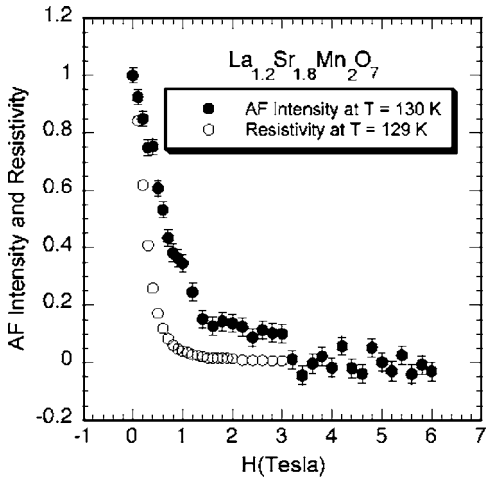

FIG. 7. Magnetic field variation of the neutron intensity due to antiferromagnetic correlations at $Q=(0.5,0,0)$ compared with field variation of resistivity measured by Moritomo *et al.* (Ref. 1). Both data are normalized to unity for $H=0$.

The implication of the AF spin correlations in the physics of colossal magnetoresistive manganites is an interesting topic for further investigations. The present experimental finding strongly suggests that the AF spin correlations are connected with the CMR effect. The temperature and field dependence of polaron and charge correlations have already been reported by Vasiliu-Doloc *et al.*[27] These seem to be connected with the CMR effect. Also the AF correlations observed in the present investigation may be connected with the bilayer correlations investigated by Osborn *et al.*[28] It is not apparent how these different correlations are interconnected and also connected with the CMR effect. Further experiments which measure the field and temperature dependence of all these correlations along with the simultaneous resistivity measurements on the same single crystal are warranted.

In conclusion, we have investigated the temperature and energy dependence of the antiferromagnetic fluctuations in $La_{1.2}Sr_{1.8}Mn_2O_7$ at $Q=(0.5,0,0)$. The AF correlations arise at about 10 K below the ferromagnetic transition temperature and persist at least up to 200 K. We have also given a simple explanation for its origin. We have determined the field dependence of the AF correlations and have found that it is very similar to the field dependence of resistivity suggesting that the AF correlations may be relevant to the CMR effect. The antiferromagnetic correlations must therefore be considered along with the polaron correlations in order to explain the CMR effect.

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