Neutron Scattering Investigation of Magnetic Bilayer Correlations in $La_{1.2}Sr_{1.8}Mn_2O_7$: Evidence of Canting above T_C

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Neutron scattering investigations of the paramagnetic correlations in the layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$, which exhibits colossal magnetoresistance above the Curie transition at $T_C = 112$ K, show that spins in neighboring layers within each bilayer are strongly canted at an average angle that is dependent on both the magnetic field and the temperature, as predicted by de Gennes. The in-plane correlation length does not diverge at T_C, although the magnetic Bragg intensity obeys critical scaling below T_C, with the same temperature dependence as the zero-field electrical conductance. [S0031-9007(98)07520-6]

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Naturally layered manganites have proved to be fruitful systems for understanding the mechanism of colossal magnetoresistance (CMR) and have become the focus of many recent investigations into this phenomenon [1–6]. The reduced dimensionality increases the magnitude of the CMR, although at the cost of reducing the ferromagnetic transition temperature to about 100 K [1]. However, the extended temperature range, over which ferromagnetic correlations are significant, and the strong anisotropy allow a detailed examination of the link between local spin correlations and the resulting magnetotransport.

The majority of experiments have been performed on the Ruddlesden-Popper phases with the general formula $(La_{1-x}Sr_xMnO_3)_nSrO$, which comprise n layers of corner-shared MnO_6 octahedra separated by (La, Sr)O blocking layers. In particular, the two-layer compounds have revealed a rich variety of properties which are strongly dependent on x [2]. Although most investigations of three-dimensional (3D) CMR compounds have concentrated on the possible role of electron-lattice interactions [7–9], of equal importance in the two-dimensional (2D) compounds has been the influence of antiferromagnetic interactions competing with the ferromagnetic double exchange. Perring *et al.* [3] have reported evidence of weak antiferromagnetic correlations within the planes above T_C that are fluctuating rapidly and are believed to coexist with the ferromagnetic correlations. On the other hand, Argyriou *et al.* [5] have inferred the existence of a canting of the ordered moments below T_C from the change in sign of Mn-O bond compressibilities at the transition. This aspect of the problem is only now receiving the theoretical attention it deserves, even though de Gennes first considered it nearly forty years ago [10–13].

The work reported here is part of a general study linking the magnetic and transport properties of naturally layered manganites directly to the underlying magnetic correlations measured by neutron diffraction and spectroscopy. We find evidence that, although the magnetic correlations are predominantly ferromagnetic within the two-dimensional planes, there is much weaker ferromagnetic correlation between spins in neighboring layers within each bilayer. This observation is consistent with a canting of the spins in neighboring layers with a cant angle that is dependent on both magnetic field and temperature, becoming smaller as the temperature approaches T_C. Our results imply that there is a delicate balance between competing double exchange and superexchange interactions in these compounds. In the critical regime below T_C, the link between magnetic ordering and electrical transport is strikingly evident, as the conductivity has approximately the same temperature dependence as the magnetic order parameter, with similar two-dimensional exponents.

An $x = 0.4$ single crystal, i.e., $La_{1.2}Sr_{1.8}Mn_2O_7$, which we will refer to as the 40% doped compound, weighing 150 mg was grown in a double mirror, floating zone image furnace. Details of sample preparation and characterization are given in Ref. [4]. Diffuse neutron scattering studies were performed on the single crystal diffractometer (SCD) at Los Alamos, followed by measurements using the triple-axis spectrometers BT2 and BT9 at Gaithersburg. For the measurements at BT9, we employed a superconducting solenoid to provide fields to 7 T applied in the ab plane. Using incident wave vectors of $\mathbf{k}_i = 2.57$ and 2.662 $Å^{-1}$ without energy analysis, we performed scans in the $(0k0)$ scattering plane, i.e., with the $[h00]$ and $[00l]$ reciprocal lattice vectors as orthogonal axes within the plane. The conductance was measured using a six-probe technique suitable for materials with highly anisotropic conductivities, such as the cuprate superconductors [14].

The SCD measurements, illustrated in Fig. 1, show that the scattering above T_C consists of rods parallel to the c axis, i.e., parallel to $[00l]$, at all integer h including $h = 0$. The rods are strongly temperature dependent, becoming narrower as $T \rightarrow T_C$, consistent with magnetic scattering

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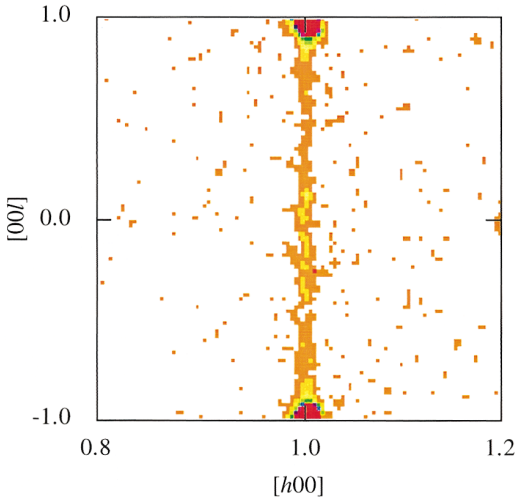

FIG. 1(color). Diffuse neutron scattering above T_C (at 130 K) in the $(0k0)$ plane showing the rod of magnetic scattering along the $[h0l]$ direction.

from predominantly ferromagnetic correlations which have much longer correlation lengths within the MnO_2 planes than perpendicular to them. Below T_C, the scattering results from inelastic spin-wave excitations and so becomes weaker with decreasing temperature. A much weaker additional component to the diffuse scattering, which we attribute to a low density of multilayer intergrowths, as identified by Potter *et al.* [15], has been excluded from our analysis and will be discussed in a later publication.

In the triple-axis experiments, scans were performed both parallel and perpendicular to the rods at $(00l)$ and $(10l)$. The magnetic neutron scattering cross section is proportional to

$$S(\mathbf{Q}) = \sum_{\alpha\beta} S^{\alpha\beta}(\mathbf{Q}) = \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \langle S_\alpha(\mathbf{Q}) S_\beta(-\mathbf{Q}) \rangle \quad (1)$$

with

$$S_\alpha(\mathbf{Q}) = \frac{1}{\sqrt{N}} \sum_{i=1,N} S_{\alpha,i} \exp(i\mathbf{Q} \cdot \mathbf{r}_i),$$

where $\mathbf{Q}$ is the wave-vector transfer, and $S_{\alpha,i}$ and $\mathbf{r}_i$ are the magnetic moments and atomic coordinates, respectively, of the Mn ions ($\alpha, \beta = x, y, z$; the z direction is parallel to the crystal c axis). $S(\mathbf{Q})$ is sensitive only to magnetic fluctuations perpendicular to $\mathbf{Q}$, so scans along $\mathbf{Q} = [00l]$ will measure in-plane correlations, $S^{xx}(\mathbf{Q}) + S^{yy}(\mathbf{Q})$, while scans along $[h0l]$ will be dominated by $S^{yy}(\mathbf{Q}) + S^{zz}(\mathbf{Q})$, for small values of l. By combining the results of scans along $[0.05\,0\,l]$ and $[0.95\,0\,l]$, we have been able to separate $S^{xx,yy}(\mathbf{Q})$ from $S^{zz}(\mathbf{Q})$.

If the only significant correlations are between neighboring Mn spins within a bilayer, i.e., at $\mathbf{r}_i = \pm z\mathbf{c}$, then the rod scattering will be modulated as a function of l such that

$$S(\mathbf{Q}) = S^2[\tfrac{1}{2}(1 + \hat{Q}_z^2)\langle\cos^2\gamma\rangle(1 + R\langle\cos\theta\rangle\cos 4\pi z l) + (1 - \hat{Q}_z^2)\langle\sin^2\gamma\rangle], \quad (2)$$

where θ is the in-plane angle between spins in neighboring layers within the bilayer, γ is the angle of the spin with respect to the planes, and $R = \langle\cos\gamma\rangle^2/\langle\cos^2\gamma\rangle$, assuming that the z-axis spin components are uncorrelated $(8/\pi^2 \le R \le 1)$. Since $S(\mathbf{Q})$ is determined by instantaneous $(t = 0)$ spin correlations, the angular brackets represent ensemble averages over the crystal. In the 40% compound, $z = 0.0964$ so that a ferromagnetic modulation would peak at $l = 0$ and fall to zero at $l = 2.59$.

Short-range spin correlations within the plane produce a Lorentzian broadening of the rods with the half-width equal to the inverse correlation length. This is seen in Fig. 2(a), which shows a scan perpendicular to the $[10l]$ rod at $l = 1.833$, from which we can estimate the ferromagnetic in-plane correlation length to be 9.7 Å at

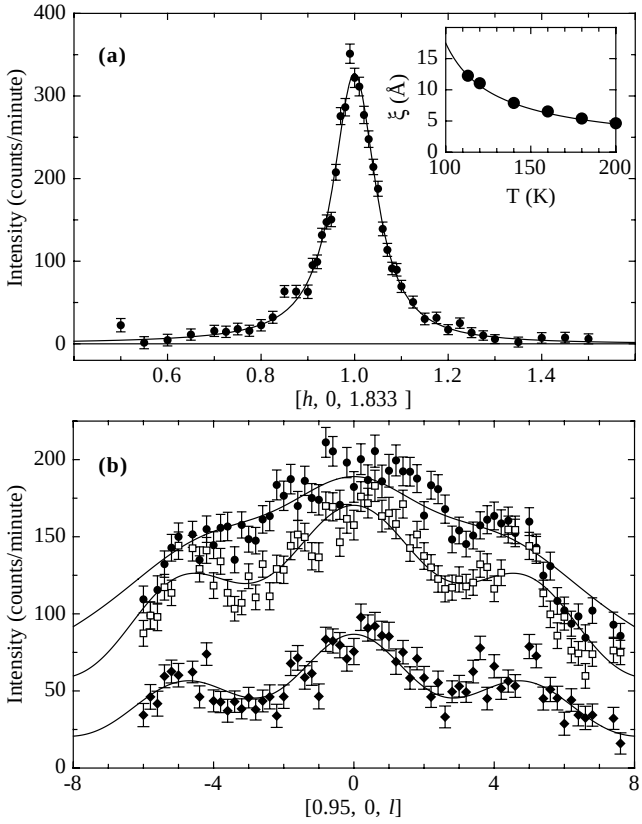

FIG. 2. (a) Diffuse neutron scattering at 125 K along the $\mathbf{Q} = [h\,0\,1.833]$ direction. The solid line is a fit to a Lorentzian line shape convolved with the instrumental resolution. The half-width $\kappa = 0.102$ Å^{-1} is the inverse correlation length within the two-dimensional planes. The inset shows the correlation length ξ vs temperature with a fit to a power law with $T_C^{2D} = 75 \pm 11$ K and exponent $\nu = 0.84 \pm 0.15$. (b) Diffuse scattering at 125 K along the $\mathbf{Q} = [0.95\,0\,l]$ direction with an applied field of 0 T (filled circles), 1 T (open squares), and 2 T (filled diamonds). The solid lines are fits to Eq. (2) with $\theta = 86.6°$, 74.1°, and 53°, respectively.

125 K. In order to optimize the energy integration of the scans, the scattered wave vector $\mathbf{k}_f$ was aligned parallel to the rods. The inset to Fig. 2(a) shows that the correlation length ξ does not diverge at T_C, reaching only a value of 12.1 Å. A power-law fit to the data gives an exponent of $\nu = 0.84 \pm 0.15$ and a divergence at $T_C^{2D} = 75 \pm 11$ K, where T_C^{2D} represents the predicted value of T_C in the absence of the additional interactions which drive the three-dimensional transition.

The most striking observation is that the modulation along the rod, shown in Fig. 2(b), is very weak even close to T_C, indicating that $\langle \cos\theta \rangle \ll 1$. From fits to Eq. (2), we have determined that $\langle \cos\theta \rangle \approx 0.06$ at 125 K in zero field, whereas, if the ferromagnetic correlations between the spins at $\pm z\mathbf{c}$ were as strong as those within the plane, then $\langle \cos\theta \rangle$ would be approximately 0.67. Since we measure only the average value of $\cos\theta$, and not its distribution, there are three reasonable interpretations of this observation.

The first is that the average value of θ is zero, but that the correlations between the neighboring planes within the bilayer (intrabilayer correlations) are much weaker than those within the plane (intraplanar correlations). This interpretation would require the intrabilayer coupling to be more than an order of magnitude weaker than the intraplanar coupling. Since the nearest-neighbor Mn-Mn distance between these planes is the same as within the planes, such a large anisotropy in the exchange interactions appears unlikely, but cannot be ruled out *a priori*.

The second is that there is an inhomogeneous distribution of ferromagnetic and antiferromagnetic regions of nearly equal volume. Some theoretical models predict such a phase separation into hole-rich and hole-poor domains with a concomitant change in the strength of the double exchange mechanism [13]. These models have been developed for the 3D perovskites and so the restrictions imposed by the two dimensionality of the layered compounds have not yet been addressed. We do not believe that it can explain the present results, because the intraplanar correlations are always strongly ferromagnetic with no evidence of a distribution of in-plane correlation lengths in scans measured along the rod.

The third interpretation is that there is a canting of the spins in neighboring planes; i.e., the average value of θ is nonzero. Measurements of spin-wave energies in $LaMnO_3$ [16,17] have provided evidence, in a related structure, of competing ferromagnetic and antiferromagnetic exchange interactions of the usual Heisenberg form. However, nearest-neighbor Heisenberg exchange, whose energy is proportional to $S^2 \cos\theta$, will produce only collinear ferromagnetic or antiferromagnetic ordering, except when strong magnetocrystalline anisotropy tilts the spins away from symmetry directions. In $La_{1.2}Sr_{1.8}Mn_2O_7$, there is no buckling of the MnO_2 planes to induce such tilts [4]. On the other hand, the energy of double-exchange interactions for a pair of spins depends on $\cos\theta/2$ [18], making noncollinear spin correlations, i.e., with a minimum free energy at $\theta \neq 0$ or π in zero field, a possibility when ferromagnetic double exchange and antiferromagnetic superexchange are competing, as first pointed out by de Gennes [10]. The observed modulation gives an average cant angle of 86.6° ± 1.5° at 125 K in zero field, which suggests that the competing interactions are of the same order of magnitude in this compound.

Important evidence favoring the canting model is provided by a comparison of neutron data with the field dependent magnetization data of Potter *et al.* [15] (see Fig. 3). At 126 K, they observed an initial linear dependence in M vs H with an increase in slope at a field of about 0.4 T. Our model provides a natural explanation of this anomaly; this low-field slope corresponds to the region in which the canted spins rotate into the direction of the field, and the upturn in the magnetization marks the field required to start reducing the cant angle. In order to confirm this, we measured the rod modulation with a magnetic field applied vertically, i.e., parallel to $[0k0]$. As expected, the modulation becomes stronger with field [see Fig. 2(b)], corresponding to a reduction of the cant angle at 125 K to 74.1° ± 2.1° at $H = 1$ T and 53° ± 6° at $H = 2$ T (the decrease of the scattering intensity occurs because the spin fluctuations have been reduced by the growth of 3D magnetic order). However, there is negligible change in the cant angle up to $H = 0.5$ T, in agreement with our interpretation of the magnetization anomalies.

We still need to understand why the intraplanar interactions are more strongly ferromagnetic than the intrabilayer interactions. In the double exchange mechanism, the mobile electrons lower their kinetic energy by polarizing the localized Mn spins, so the free energy gain from delocalizing the electrons would be greater within the planes, where a large number of spins can participate in the ferromagnetic cluster, than between the neighboring planes, where only two sites are involved. The competing superexchange therefore has a relatively stronger influence on the correlations along the c axis. Our results demonstrate the

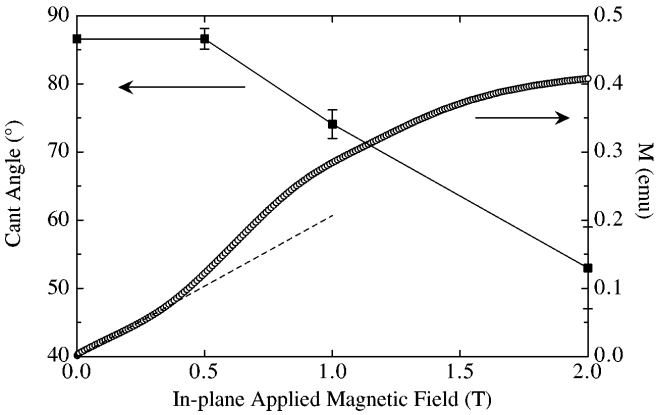

FIG. 3. Bilayer cant angle vs in-plane applied magnetic field (solid squares) determined from fits to the data in Fig. 2(b). The results are compared to magnetization data (circles) taken from Potter *et al.* [15]. The dashed line is a linear extrapolation of the low-field magnetization.

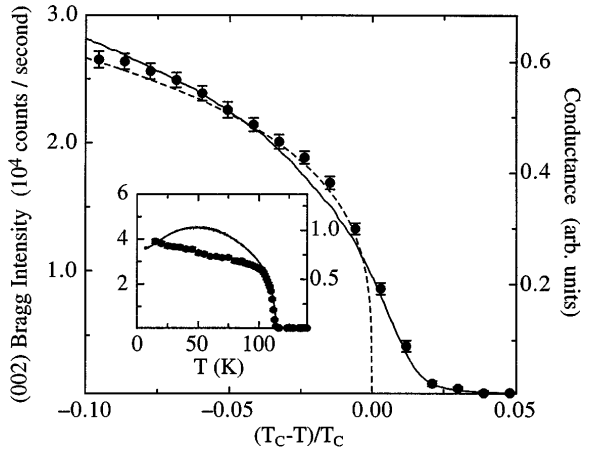

FIG. 4. Intensity of (002) Bragg peak vs reduced temperature $(T - T_C)/T_C$. The dashed line is a power-law fit from 100 to 111 K with $T_C = 111.7 \pm 0.2$ K and $\beta = 0.13 \pm 0.01$. The solid line is the in-plane electrical conductance measured on a sample of the same composition. The inset shows the same measurements over an expanded temperature range.

limitations of neglecting the many-body nature of the double exchange model.

Recently, Perring *et al.* reported the observation of 2D quasielastic scattering along rods at $h = 0.5$ in addition to those at integers h and k [3]. Their data imply the existence of short-lived antiferromagnetic fluctuations *within* the planes, whereas the results reported here imply the existence of competing interactions *between* the planes in each bilayer. We have confirmed the existence of an antiferromagnetic rod in our own crystal, but find that its energy-integrated intensity is only 2% of the intensity of the ferromagnetic rod. We do not believe that such a small volume fraction can have a significant impact on the bulk properties of this compound, although it supports the conclusion that ferromagnetic and antiferromagnetic interactions are finely balanced in this compound.

Below T_C, we observe scaling of the magnetic order parameter. Scans through the (002) Bragg peak, which has extremely weak nuclear intensity, show that the intensity, which is proportional to M^2, scales as $t^{2\beta}$, where $t = (T - T_C)/T_C$, from 100 to 111 K, with $T_C = 111.7 \pm 0.2$ K and $\beta = 0.13 \pm 0.01$. The small value for β indicates that the fluctuations below T_C are still strongly two dimensional (e.g., $\beta = 0.125$ in the 2D Ising model). Figure 4 shows that there is a strong tail that extends to $\sim$3% above the scaling value of T_C, which could result from inhomogeneous broadening of the transition. Superimposed on the neutron data in Fig. 4 are in-plane conductance results on a single crystal (grown in the same way as the neutron sample) which has $T_C = 113.3$ K and $\beta = 0.17 \pm 0.01$ determined between 90 and 110 K. When scaled to the slightly different T_C values, the coincidence of the two sets of data is manifest. This shows that, in the critical regime, the electrical conductance has the same temperature dependence as the squared zero-field magnetization. Although correlations between the magnetization and conductivity are central to the observation of CMR [19,20], we are not aware of other observations in which the conductivity has been shown to have the same scaling behavior as the magnetic order parameter in zero field. If this connection is universal, it will constrain theoretical approaches to the spontaneous magnetic state below T_C.

In conclusion, we have observed evidence that Mn spins in neighboring layers within each bilayer of the naturally layered CMR manganite $La_{1.2}Sr_{1.8}Mn_2O_7$ are strongly canted above T_C at an angle that is both temperature and field dependent. It is possible to identify this canting because of the reduced dimensionality of the magnetic correlations, so if it also occurs in the regular perovskites, it would be more difficult to observe. The lack of divergence of the 2D correlation length at T_C may be evidence that the phase transition is weakly first order or that the ordering is unconventional [8,21], but further measurements of the 3D correlations are necessary before conclusions can be drawn. The direct link between magnetic order and electronic transport is clearly seen in the 2D critical scaling below T_C.

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