Neutron scattering investigation of the structure and spin dynamics in $La_{0.85}Sr_{0.15}MnO_3$

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We have performed diffraction and inelastic neutron scattering experiments on a $La_{0.85}Sr_{0.15}MnO_3$ single crystal. In the ferromagnetic phase of this system ($T_c=235$ K) the long wavelength dispersion relation along the (0,1,0) direction is well represented by $E=E_0+Dq^2$, but with the spin wave spectrum almost gapless ($E_0<0.1$ meV), and with $D_{T=0}=83.75\pm0.36$ meV Å^2. The spin-wave stiffness constant $D(T)$ exhibits a power law behavior as a function of temperature, and appears to collapse as $T\rightarrow T_c$. An orthorhombic–rhombohedral structural phase transition is observed at T_s = 360 K, and exhibits a hysteretic character suggesting a first-order transformation. Anomalies in magnetization measurements and Bragg peak intensities indicate the existence of a second phase transition at $T=200$ K. [S0021-8979(97)72608-2]

The discovery of the high temperature superconducting copper oxides has revived interest in the correlated dynamics of spins and charges near the Mott transition in neighboring 3*d* electron transition metal oxide systems such as hole-doped lanthanum manganites $La_{1-x}A_xMnO_3$ with the perovskite structure.[1,2] This renewed interest has been tremendously enhanced by the recent discovery of giant magnetoresistance phenomena in samples with Sr doping levels in the $0.2\leqslant x\leqslant 0.4$ regime,[3] and of collosal magnetoresistance anomalies in samples with Ca dopant densities around $x=1/3$.[4,5] The correlation between magnetism and conductivity in these systems has been extensively studied during the 1950s and 60s,[1] and the evolution of the magnetic properties with band filling was well explained by the double exchange hopping mechanism.[2] However, the anomalously large magnetoresistance effect, as well as the newly discovered lattice structure switching by an external magnetic field[6] or the field-induced insulator-metal transition,[7–9] cannot be explained within this model. These phenomena indicate that the lattice degrees of freedom must also be involved in the correlation between magnetism and conductivity in these systems. It was suggested that the understanding of these materials should include, in addition to the double exchange mechanism, strong electron correlations,[3] or a strong electron–phonon interaction.[10]

The existence of strong electron correlations is expected to affect the magnetic ordering and the magnetic excitation spectrum. The spin dynamics can provide crucial information for determining the itineracy of the system, as well as the importance of the electron correlations. Neutron scattering studies of the spin dynamics in the metallic ferromagnetic state of $La_{1-x}A_xMnO_3$ have been carried out in the optimally doped regime with $x\sim0.3$ for A=Pb,[12] Sr,[13,14] and Ca.[15] The results show essentially standard spin dynamics of a conventional metallic ferromagnet, except for the Ca-doped samples[15] which indicate a possible coexistence of spin-wave excitations and spin diffusion in the ferromagnetic phase. It is important to determine how the spin dynamics evolves with doping, particularly as the undoped antiferromagnetic insulating state is approached.[16,17] In the present publication we report diffraction and inelastic measurements of the spin dynamics in $La_{0.85}Sr_{0.15}MnO_3$.

The single crystal used in the present neutron scattering experiments was grown in Laboratoire de Chimie des Solides, Orsay, France, using the floating zone method. The crystal size is 5–6 mm in diameter and 3 cm in length. The sample was oriented such that the [010] and [101] axes of the orthorhombic Pbnm cell lie in the scattering plane. The neutron scattering measurements have been carried out on the BT2, BT4, and BT9 triple-axis spectrometers at the NIST research reactor. The (002) reflection of pyrolytic graphite (PG) was used as monochromator and analyzer, with PG or cold Be filters, for measuring the low-energy part of the spin-wave spectrum. A variety of collimator combinations was used as required by the measurements, ranging from as tight as 15′-12′-S-12′-40′ (in sequence from reactor to detector) to 60′-40′-S-40′-40′ The sample was placed in a helium-filled aluminum cell in a displex refrigerator. The sample temperature ranged from 10 to 300 K and was controlled to within 0.1°.

$La_{0.85}Sr_{0.15}MnO_3$ was previously reported[11] to be an insulating ferromagnet below $T_c=235$ K, although some comments are necessary on this point. Above T_c the resistivity of this system increases with decreasing temperature, but shows an abrupt drop at T_c, and a fairly sharp upturn at a lower temperature around 200 K. From the point of view of the resistivity behavior, the phase for 200 K$\leqslant T\leqslant T_c$ can be identified as a metallic phase. Using neutron diffraction on $La_{1-x}Sr_xMnO_3$, Kawano *et al.*[18] have established that samples with $x=0.10$, and 0.125 show two transitions, marking the onset of ferromagnetic long-range ordering at T_c, and

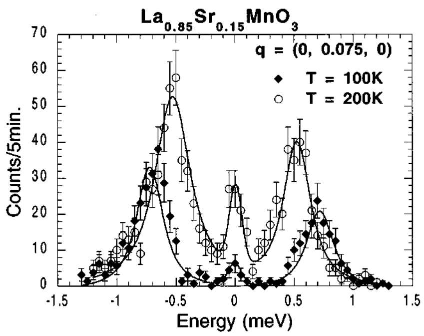

FIG. 1. Magnetic inelastic spectrum collected at 100 and 200 K for a reduced wave vector $q=0.075$ in the (0,1,0) direction, showing the softening of the spin-wave energy with increasing temperature. The spin waves are observed in energy gain ($E<0$) and energy loss ($E>0$). The elastic peak originates from nuclear incoherent scattering plus a contribution from magnetic diffuse scattering.

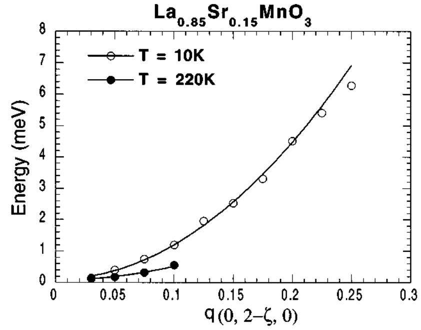

FIG. 2. Spin-wave dispersion along (0,1,0) at 10 K (open circles) and 220 K (closed circles). Solid lines are fits to $E=E_0+Dq^2$, where E_0 is the spin-wave energy gap, and D is the spin-wave stiffness coefficient.

of antiferromagnetic ordering at $T_{CA} \leqslant T_c$. Correlating the temperature dependence of the resistivity with their results, these authors have suggested that samples with $0.10 \leqslant x \leqslant 0.16$ have an intermediate ferromagnetic metallic phase for $T_{CA} \leqslant T \leqslant T_c$, and a low-temperature canted antiferromagnetic insulating phase for $T \leqslant T_{CA}$, T_{CA} coinciding with the temperature of resistivity upturn for those samples that exhibit such an anomaly. A search for a low-temperature canted antiferromagnetic phase in the $x=0.15$ system is now in progress. We observe anomalies in the Bragg peak intensities consistent with this interpretation.

The crystal structure of $La_{0.85}Sr_{0.15}MnO_3$ at room temperature is orthorhombic (Pbnm) with $a=5.512$ Å, $b=5.548$ Å, and $c=7.779$ Å. This system undergoes a structural phase transition at $T_s=360$ K to a rhombohedral phase ($R3c$). This transition exhibits a hysteretic character suggesting a first-order transformation.

We have measured the spin-wave excitations in the ferromagnetic state to determine how this material compares to other related ferromagnets. Figure 1 shows typical magnetic inelastic spectra collected at 100 and 200 K, and reduced wave vector $q=0.075$ away from the (020) reciprocal point. We can see that the spectrum is dominated at both temperatures by spin waves observed in energy gain ($E<0$) and energy loss ($E>0$). The central peak originates from weak temperature-independent nuclear incoherent scattering plus a contribution from magnetic diffuse scattering. The data in Fig. 1 show an increase in the intensity of the central peak at 200 K compared to 100 K, with no detectable broadening of the width. The study of the q and temperature dependence of the central peak needs to be pursued in order to determine the origin of this effect, and in particular whether there is coexistence of spin-wave excitations and quasielastic scattering associated with spin diffusion below T_c, as has been reported for $La_{0.67}Ca_{0.33}MnO_3$ (Ref. 15). Similar data were obtained at a series of wave vectors, and Fig. 2 shows the measured spin-wave dispersion relation along the (0,1,0) direction at two different temperatures. We see that in the long wavelength regime, the dispersion relation is well fit by $E=E_0+Dq^2$, where E_0 is the spin-wave energy gap, and D is the spin-wave stiffness coefficient, directly related to the exchange interactions. The fitted values of D are 83.75 ± 0.36 meV Å^2 and 33.6 ± 0.8 meV Å^2 at 10 and 220 K, respectively. The low temperature value of the spin stiffness constant gives a ratio of $D/kT_c \sim 4.1$ Å^2, which is a reasonable value for an insulating ferromagnet. The fitted values of E_0 are 0.10 ± 0.004 meV and 0.07 ± 0.003 meV for 10 and 220 K, respectively, and were too small to be measured directly in energy scans at $Q=(020)$ with the best resolution available. The energy gap E_0 is a measure of the energetic cost to perform a uniform rotation of all the spins from the easy spin direction into a ''hard'' direction. Therefore, the very small value of E_0 in the present system indicates that we are dealing with a ''soft'' ferromagnet.[19] Negligible values of the spin-wave energy gap have also been reported for the metallic ferromagnets $La_{0.67}Sr_{0.33}MnO_3$ (Ref. 14) and $La_{0.67}Ca_{0.33}MnO_3$ (Ref. 15). A low-temperature spin energy gap of 0.75 meV was reported for $La_{0.70}Sr_{0.30}MnO_3$,[13] but this value came from an extrapolation of higher q data, and not from direct measurements near $q=0$.

For a conventional ferromagnet that exhibits a second-order phase transition, we expect the intensity of the spin-wave scattering at each q to increase rapidly upon raising the temperature towards T_c, both because of the increase in the thermal population according to the Bose factor, and because of the renormalization (softening) of the spin-wave energy. The energy scans in Fig. 1 show that the spin waves do soften with increasing temperature, while gaining in intensity. Figure 3(a) plots the temperature dependence of the spin stiffness coefficient $D(T)$, which exhibits a power law behavior and appears to collapse as $T \rightarrow T_c$. The integrated intensity of the (020) Bragg reflection as a function of temperature near T_c is shown in Fig. 3(b) for comparison. This reflection has a weak nuclear structure factor, and therefore has a small intensity in the paramagnetic phase. Below T_c, magnetic scattering due to the ferromagnetism of spins aligning on the manganese atoms will produce a magnetic structure factor and will result in an increase of the intensity. The data in Fig. 3(b) are the same on warming and on cooling, with no visible hysteresis. It is thus very likely that this ferromagnet exhibits a second-order phase transition. Nevertheless, these data cannot be used to extract a critical magnetic exponent β, since we see anomalies in the intensity below

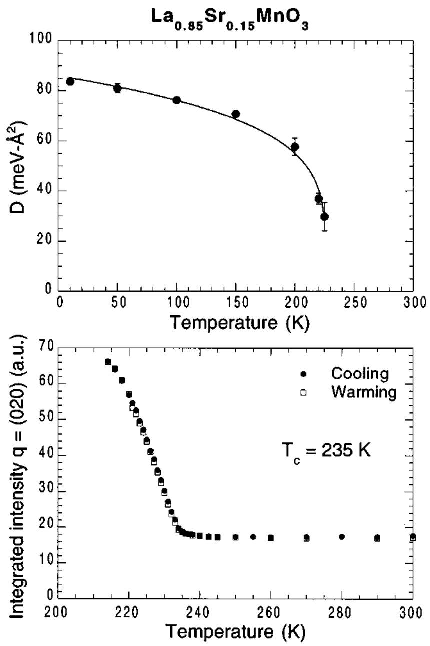

FIG. 3. (a) Spin-wave stiffness coefficient D in $E=E_0+Dq^2$ as a function of temperature. D appears to vanish at the ferromagnetic transition temperature, as expected for a conventional ferromagnet. The solid curve is a fit to a power law. (b) Temperature dependence of the integrated intensity of the (020) Bragg peak. There is a nuclear contribution to this peak, and the additional temperature-dependent intensity originates from the onset of the ferromagnetic order at T_c=235 K. The data are the same on warming and on cooling, with no apparent hysteresis.

210 K, that indicate another phase transition occurring at $T\sim200$ K, of structural and/or magnetic nature. In this case, the two order parameters would be coupled, and would make it very difficult to separate them individually. Further analysis is needed before proposing a possible interpretation.

Although the long wavelength limit of the spin-wave dispersion relation along the (0,1,0) direction is quadratic in q, with a negligible spin-wave energy gap, as expected for an isotropic ferromagnet, ongoing studies of the spin-wave dispersion along different high-symmetry directions seem to indicate anisotropy in the exchange interactions, with an interplane coupling smaller than the in-plane coupling. Preliminary measurements of the spin-wave dispersion relation throughout the Brillouin zone also have been carried out and further work is in progress.

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