Magnetic, structural, and spin dynamical properties of $La_{1-x}Ca_xMnO_3$

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Neutron scattering has been used to study the magnetic order, spin dynamics, and structural properties of $La_{1-x}Ca_xMnO_3$ in the ferromagnetic regime ($0<x<\frac{1}{2}$). For $x=\frac{1}{3}$($T_C=250$ K) where the magnetoresistance effects are largest the system behaves as an ideal isotropic ferromagnet at low T, with a gapless (<0.04 meV) dispersion relation $E=Dq^2$ and $D_{T=0}\approx 155$ meV Å^2. However, an anomalous diffusive component develops above ~200 K and dominates the fluctuation spectrum as $T\rightarrow T_C$. A magnetic field strongly reduces this quasielastic scattering, shifting the spectral weight into the spin wave component of the fluctuation spectrum. © *1997 American Institute of Physics.* [S0021-8979(97)72508-8]

The magnetic properties of the doped $LaMnO_3$ class of materials have been under very active investigation recently because of the recent discovery[1] of a dramatic increase in the conductivity when the spins order ferromagnetically, either by lowering the temperature or applying a magnetic field. This large variation in the carrier mobility originates from a metal–insulator transition that is closely associated with the magnetic ordering. We have been carrying out diffraction and inelastic studies on the calcium-doped $La_{1-x}Ca_xMnO_3$ materials.[2] We find that the undoped material is antiferromagnetic, but can be converted to a ferromagnet under appropriate oxygen heat treatments.[3] At larger x the system is always a ferromagnet, and for the $x=\frac{1}{3}$ doping where the magnetoresistance anomalies are largest[1] we found that the magnetic system behaves as an ideal isotropic ferromagnet at low T.[4] The magnetic excitations are conventional spin waves, with a dispersion relation $E=\Delta+D(T)q^2$, where Δ represents the spin wave energy gap and the spin stiffness coefficient $D(T)$ is directly related to the exchange interactions. For $x=\frac{1}{3}$ the spin wave gap Δ was too small (<0.04 meV) to be determined, which demonstrates that it is a ''soft'' ferromagnet, comparable to very soft amorphous ferromagnets.[5] We have extended the measurements of the spin wave spectrum to lower temperatures, and the measured spin stiffness constant $D(0)$ is 155 meV Å^2. At elevated temperatures, however, a quasielastic component to the fluctuation spectrum develops for the $x=\frac{1}{3}$ doping, and becomes the dominant spectral weight as $T\rightarrow T_C$. This behavior is in stark contrast both to the conventional behavior observed for isotropic ferromagnets and to the Ca-doped materials away from $x=\frac{1}{3}$. The width of this scattering is proportional to q^2, indicating that it represents spin diffusion. The correlation length, on the other hand, is anomalously small (~10 Å) and only weakly temperature dependent.[6] These results suggest that this quasielastic component is associated with the localization of electrons on the Mn^{3+}/Mn^{4+} lattice, and may be related to the formation of spin polarons in the system. It is this spin diffusion that drives the ferromagnetic phase transition rather than the thermal population of conventional spin waves. Here we report on the field dependence of both the quasielastic and inelastic scattering.

The inelastic experiments were carried out at the NIST research reactor. Because the long wavelength spin dynamics turn out to be approximately isotropic, inelastic measurements on polycrystalline samples may be made in the forward scattering direction [i.e., around the (000) reciprocal lattice point] without loss in generality.[5] All the inelastic measurements reported here were taken on the BT-9 triple-axis spectrometer, with pyrolytic graphite monochromator, analyzer, and filter. The incident energy was chosen to be 13.7 meV, and horizontal collimations of 12′-11′-12′-16′ full width at half-maximum were used. The field-dependent measurements were taken in a horizontal field superconducting magnet, equipped with sapphire windows to suppress the small angle background scattering.

The use of polycrystalline samples has the distinct advantage that powder diffraction profile refinements may be performed to establish the oxygen content and provide detailed crystallographic parameters for the same sample. These measurements were performed on the BT-1 high resolution diffractometer, where a vertical field superconducting magnet was employed for the field-dependent measurements. For the $x=\frac{1}{3}$($T_c=250$ K) material of central interest the crystal structure is orthorhombic (*Pnma* space group) over the full range of temperatures and fields explored here. The lattice parameters are observed to decrease with decreasing temperature, but exhibit a strong anomaly associated with the ferromagnetic ordering. At fixed temperature, on the other hand, we find that the lattice parameters also decrease substantially with increasing magnetic field. Thus there is a substantial lattice contraction of the system associated with the development of a bulk magnetic moment, regardless of whether the ferromagnetism develops due to the temperature decreasing or is induced by the application of a magnetic field. In Fig. 1(a) we plot the measured (Bragg peak) magnetization as a function of temperature, and we see that it is rather typical of the magnetization curve for a ferromagnet,

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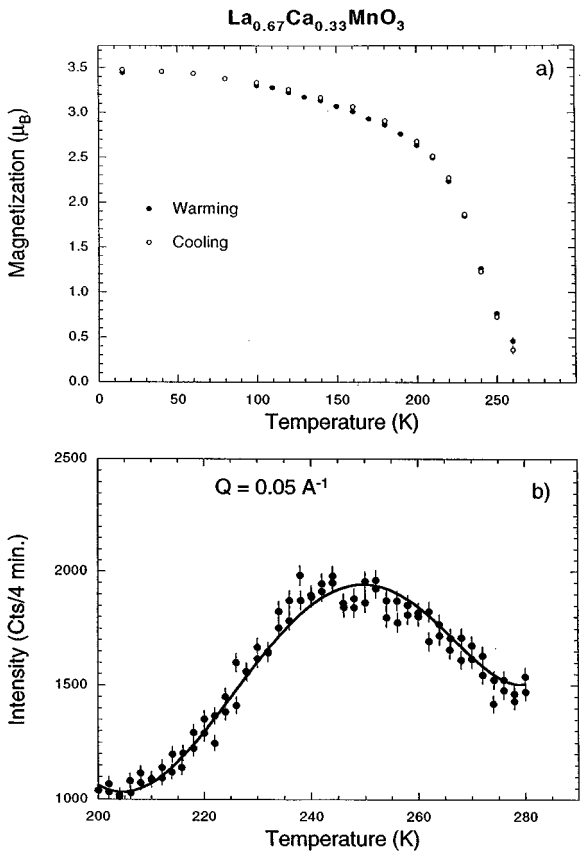

FIG. 1. (a) Magnetization versus temperature obtained from the intensity of the ferromagnetic Bragg peak. (b) Intensity of the critical scattering at 0.05 $Å^{-1}$, showing that the scattering peaks at T_C in the usual manner. The solid curve is a guide to the eye.

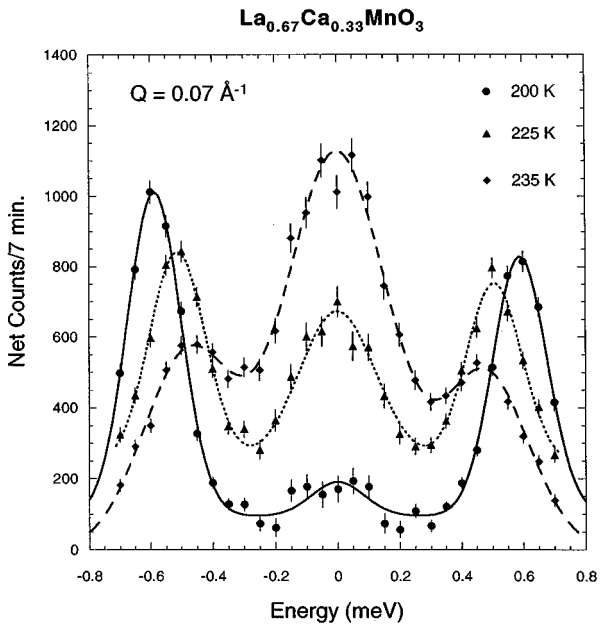

FIG. 2. Magnetic inelastic scattering below T_C for $x=\frac{1}{3}$ at a wave vector of 0.07 $Å^{-1}$. At 200 K the spectrum is dominated by the spin waves in energy gain ($E<0$) and energy loss ($E>0$), while as $T\rightarrow T_C$ a quasielastic component develops and dominates the fluctuation spectrum.

with $T_C \approx 250$ K.[7] The temperature dependence of the critical scattering is shown in Fig. 1(b), where we see a maximum in the vicinity of the ferromagnetic transition as expected. Similar results have been recently presented for $La_{0.7}Sr_{0.3}MnO_3$.[8]

In the long wavelength (hydrodynamic) regime, the magnetic excitations are conventional spin waves at low temperatures, with a quadratic dispersion relation $E=D(T)q^2$. Figure 2 shows a typical magnetic inelastic spectrum for a wave vector $q=0.07$ $Å^{-1}$. A flat background of nine counts plus an elastic incoherent nuclear peak of 647 counts, measured at 14 K, have been subtracted from these data. We see that at 200 K the spectrum is dominated by spin waves observed in energy gain ($E<0$) and energy loss ($E>0$). The solid curve is the result of a least-squares fit of the spin wave cross section, plus a spin-diffusion central component as described below, convoluted with the instrumental resolution. As we raise the temperature towards T_c we see two changes in the spectrum. One is that the spin wave energies renormalize to lower energies and broaden, as indicated in Fig. 2 for the data at 225 and 235 K. This is the expected behavior for a conventional ferromagnet. However, they do not collapse as $T\rightarrow T_C$, with $D(T_C)$ only about half of its low temperature value,[4] even though the overall behavior is quite typical of a conventional isotropic ferromagnet.

The second anomalous feature revealed in Fig. 2 is the dramatic development of a central component to the spectrum $T\rightarrow T_C$. The intrinsic shape of the scattering is Lorentzian in energy, and the width of this quasielastic component varies as q^2, revealing that this scattering is associated with spin diffusion in the system. This component develops rapidly as the transition temperature is approached, and dominates the fluctuation spectrum as $T\rightarrow T_C$. Note, however, that the overall intensity of scattering maximizes at T_C in the usual way [Fig. 1(b)]. Thus the development of this central component to the fluctuation spectrum occurs at the expense of the spin wave scattering.[4]

We now turn to the field dependence of the scattering. Figure 3 shows the inelastic spectrum at a wave vector of 0.09 $Å^{-1}$ and 240 K. At this larger Q (compared to Fig. 2) we see that in zero field the spin waves are cleanly separated from the quasielastic peak. With the application of a field parallel to the incident wave vector we see essentially no change in the spectrum until we approach the tesla field range. At $H=2$ T the spin waves have shifted substantially to larger energy and sharpened. More interestingly, the spin wave intensity has *increased*, even though the thermal population factor should reduce the spin wave intensity because of the increase in the spin wave energy. For 4 T the shift in the spin waves is large enough that they are almost out of the measurement range, while at 6 T they have completely shifted out. Associated with this increase in the spin wave scattering we see that the intensity of the central component steadily decreases with increasing field.

Figure 4 shows data at $Q=0.09$ $Å^{-1}$ for a temperature of 250 K, the ferromagnetic transition temperature determined in Fig. 1(a). The quasielastic scattering dominates, but broad spin waves are present as well. Applying a magnetic field has the same qualitative effect as for a temperature of 240 K. At 2 T the intensity of the central component decreases while

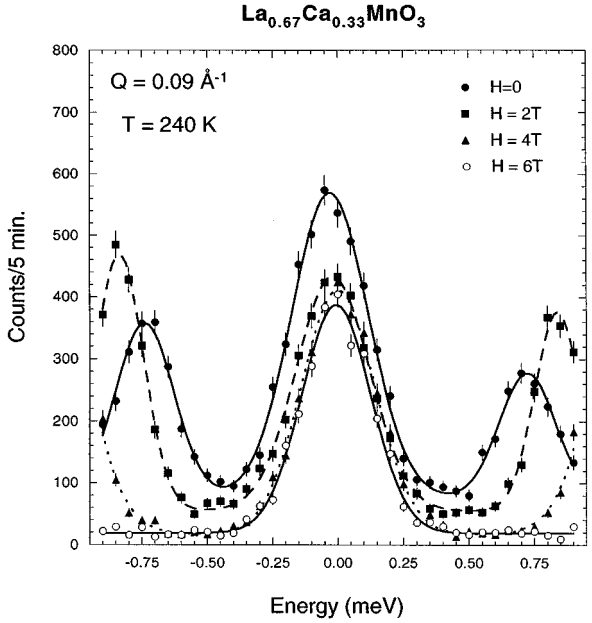

FIG. 3. Observed inelastic spectrum at 240 K and $Q=0.09$ Å^{-1} as a function of applied field. The spin waves increase in energy and sharpen with increasing field, but also increase in intensity as well. The quasielastic scattering, on the other hand, decreases with increasing field. Thus the strength of the spectrum shifts from the central component into the spin wave component as the field is increased. The curves are fits to the data.

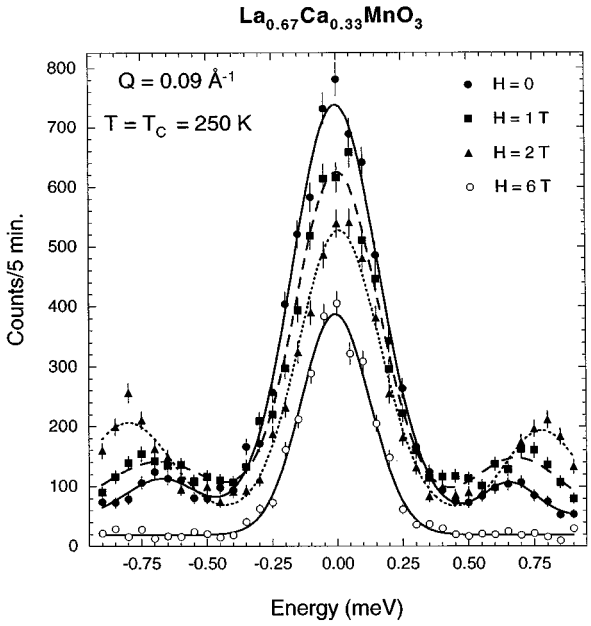

FIG. 4. Observed inelastic spectrum at 250 K (T_C) and $Q=0.09$ Å^{-1} as a function of applied field. At this temperature there are still spin waves present, but the spectrum is dominated by the quasielastic scattering. With increasing field the spin waves increase in energy while increasing in intensity, and sharpen, while the quasielastic response decreases.

the spin waves increase energy, increase intensity, and sharpen. Applying a field of 6 T again moves the spin waves out of the accessible energy range.

Finally, we remark that there are orientation factors in the neutron cross section, so that some of the intensity changes are due to the fact that the spins rotate to align with the field. For conventional spin wave (inelastic) scattering the intensity should be proportional to $1+(\hat{Q}\cdot\hat{M})^2$, where the hats denote unit vectors, while for longitudinal fluctuations the intensity scattering should follow $1-(\hat{Q}\cdot\hat{M})^2$.[9] For randomly oriented spins in zero field the factor $(\hat{Q}\cdot\hat{M})^2$ should average to $\frac{1}{3}$. For the data shown in Figs. 3 and 4, the field was applied along the incident wave vector, so that at the elastic position Q is approximately perpendicular to M. In this situation any reorientation should increase the quasielastic scattering, while we observe a strong decrease. This demonstrates that this scattering is not simply associated with longitudinal (S^zS^z) fluctuations. At the spin wave position, on the other hand, Q makes a rather large angle with M, and any increase in the spin wave intensity due to the orientation factor is too small to explain the observed increase. Moreover, we have also taken data with the field applied perpendicular to the incident beam, and have found the same qualitative behavior of both the quasielastic and spin wave components. The field-dependent inelastic scattering measurements demonstrate conclusively that the spectral weight associated with the central component of the fluctuation spectrum shifts into the spin wave component with increasing field. Thus just as for the lattice parameters, increasing field has the same effect as decreasing temperature, and the field regime of a few tesla is the same as that associated with the colossal magnetoresistance effects.[1]

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[6] R. W. Erwin, J. W. Lynn, J. A. Borchers, J. L. Peng, and R. L. Greene, in these proceedings.

[7] For the present data no significant difference was found on warming and cooling, and therefore our earlier report of significant irreversibility probably was due to extrinsic factors rather than an intrinsic effect.

[8] M. C. Martin, G. Shirane, Y. Endoh, K. Hirota, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, 14285 (1996).

[9] The quasielastic scattering found in ordinary ferromagnets originates from the S^zS^z (longitudinal) fluctuation spectrum rather than from the (transverse) scattering associated with the spin wave operators S^+,S^- while our field-dependent inelastic scattering results for $La_{0.67}Ca_{0.33}MnO_3$ show that the quasielastic scattering has both transverse as well as longitudinal character. For a recent discussion of this point see J. W. Lynn, N. Rosov, M. Acet, and H. Bach, J. Appl. Phys. **75**, 6069 (1994).