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Spin Excitations in [$La_{1-x}Ca_xMnO_3$] in the Mixed-Phase Region

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ABSTRACT

The magnetic excitations and the ferromagnetic order parameter have been studied by neutron scattering in a series of the manganese-based CMR perovskites [$La_{1-x}Ca_xMnO_3$] (x=0.46, 0.48, 0.50) near the metallic ferromagnetic to insulating antiferromagnetic phase. Well-defined ferromagnetic spin waves were detected for the x=0.46 and x=0.48 compositions. From the measurements of the order parameter, only the x=0.48 sample showed conclusive evidence of a coexistence of an antiferromagnetic phase with the ferromagnetic phase. For this compostion, hysteresis was observed in the spin wave intensity but not in the spin stiffness parameter. This effect indicates that the ferromagnetic exchange is not perturbed by the antiferromagnetic ordering. No measurable ferromagnetic magnetization was found in the x=0.50 sample; thus no spin waves could be detected. The results indicate that the onset of the antiferromagnetism upon hole doping for the series occurs in a narrow region of x below the x=0.50 phase boundary.

I. Introduction

Recently in the quest to understand colossal magnetoresistance (CMR) in manganites, the importance of the competition of coexisting phases has emerged.[1] One of the clearest examples of a manganite with mixed-phase character is $La_{1-x}Ca_xMnO_3$ with $x \approx 0.5$ which exhibits coexisting ferromagnetic (FM) charge-disordered and antiferromagnetic (AF) charge-ordered phases.[2] When cooled, $La_{0.5}Ca_{0.5}MnO_3$ becomes FM at T_C~225 K, and an AF phase then enters at T_N~155 K.[3] The FM-AF transition shows hysteresis indicating that it is of first order.[4] Additionally in the FM phase, AF incommensurate charge-ordered and FM charge-disordered microdomains have been found indicating electronic phase separation.[2] The x=0.5 composition is clearly an excellent example to use in examining the competing phases in manganites. However, in the effort to understand the progression of the magnetic states from the optimally doped $La_{0.67}Ca_{0.33}MnO_3$ to the x=0.5 composition upon increasing the hole density, studies of compositions near x=0.5 are useful.

Extensive study has been made in the region near x=0.5. Schiffer et. al.[4] found the coexistence of AF and FM phases at low temperatures in the composition x=0.48. Rhyne et. al.[5] found similar results for x=0.47. Huang et. al.[6] investigated the x=0.47, 0.50, and 0.53 compositions with neutron powder diffraction; they found that after the FM phase is reached upon cooling (T~265 K), a second crystallographic phase emerges at T~230 K for all three samples. This crystallographic phase then becomes AF at T~160 K. It was found that for x=0.47 60% of the sample was in the FM phase at 10 K which is consistent with Rhyne et. al.[5,6] These diffraction results showing coexisting FM and AF phases were the motivation for the present study of spin excitations in the mixed phase region near x=0.5. The study of spin excitations with neutrons gives a direct measure of the Fourier transformed exchange interaction. Also, neutrons detect incoherent quasistatic modes associated with spin diffusion or possibly with the formation of polarons. In the present article we studied the magnetic excitations and the ferromagnetic order parameter by neutron scattering for the compositions x=0.46, 0.48, and 0.50.

II. Experiments

Three polycrystalline samples of $La_{1-x}Ca_xMnO_3$ (x=0.46, 0.48, and 0.50) were used in the neutron elastic and inelastic scattering measurements. The measurements were taken at the University of Missouri Research Reactor using a triple axis spectrometer. For the inelastic experiments, the initial neutron energy was held constant at 14.6 meV. A focusing pyrolytic graphite monochromator was used with angular collimation 20'-10'-10'-20' before and after the monochromator and analyzer respectively. Because of the polycrystalline nature of the samples, inelastic measurements were restricted to the first Brillouin zone where the momentum transfer q of the excitation is uniquely defined. The spectrum of spin waves is assumed to be isotropic in q which is confirmed by the absence of width (above instrumental resolution) in the low T spin wave peaks. Due to energy and momentum conservation restrictions, as well as instrument considerations, q is limited to the range of approximately $0.04 \text{ Å}^{-1} < q < 0.10 \text{ Å}^{-1}$ for observing propagating modes.[7] Data taken at the lowest temperature (T~10 K) were subtracted from the higher temperature data in order to extract the magnetic inelastic scattering. This subtraction is justified because the spin wave energies lie outside the energy window of the spectrometer at low temperature. The only scattering observed at low temperature is spurious T-independent scattering due to background and parasitic scattering from the cryostat and sample holder.

For the elastic scattering experiments (measurement of the FM order parameter) an incident neutron energy of 14.8 meV was used with collimation 40'-40'-40'-0 and a pyrolytic graphite analyzer set for elastic scattering. Data taken at temperatures well above the magnetic transition temperature were used to subtract the nuclear peak from the lower temperature data.

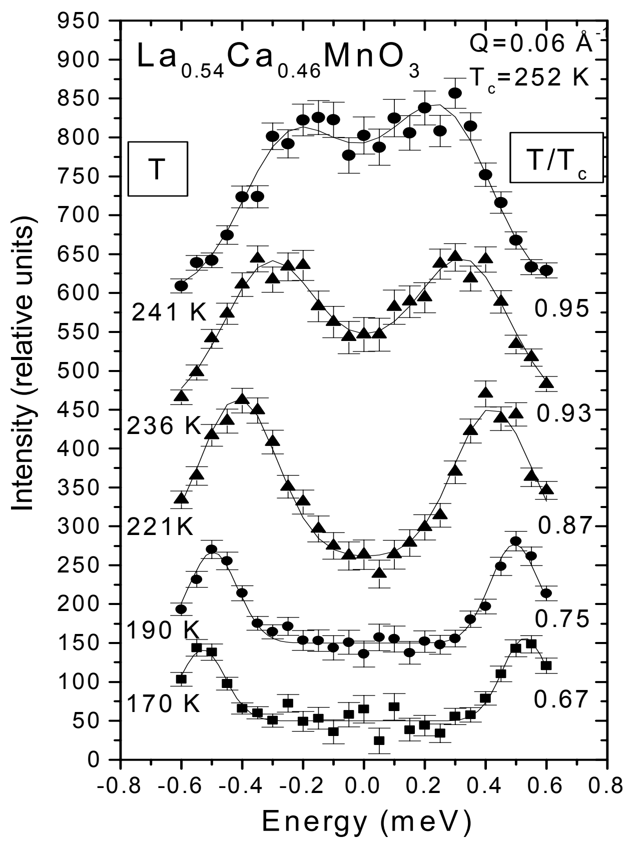

Figure 1 - Constant Q = 0.06 Å^{-1} inelastic scattering intensity versus neutron energy transfer for temperatures below T_c = 252 K for $La_{0.54}Ca_{0.46}MnO_3$. The plots are displaced along the y-axis for clarity. Spin wave creation (E>0) and annihilation (E<0) processes are shown.

III. Results

Figure 1 shows the spin wave peaks observed for $La_{0.54}Ca_{0.46}MnO_3$ for constant q=0.06 Å^{-1}. The peaks at E>0 (E<0) indicate spin wave creation (annihilation). Several temperatures are shown for this particular constant q scan. The peaks begin to merge together as T_c is approached due to the fact that it takes less energy for the neutrons to excite/absorb a spin wave mode as T increases. The spin waves show conventional behavior as they follow the dispersion relation

$$E = \Delta + Dq^2 \qquad (1)$$

where Δ is the q = 0 Å^{-1} energy gap and D is the temperature dependent spin stiffness parameter. The energy gap in this case was due mostly to the vertical divergence of the instrument. A central quasi-elastic mode was observed at T > 230 K (0.91 T_c). In $La_{0.7}Ca_{0.3}MnO_3$ this central component has been proposed to be the spin component of polarons[8]. Figure 2 shows the spin stiffness parameter versus the temperature. The extrapolated value for D(T=0 K) was near 140 meV-Å^2 which is consistent with the x=0.375 and lower x compositions.[7] No hysteresis was observed in D or in the ferromagnetic Mn order parameter (inset to Figure 2). The T_c obtained from the order parameter is 252 K. The solid line in the spin wave data is the $T^{5/2}$ (Dyson) dependence at low T and a power law at higher T. The values of the power law exponents are consistent with a second order magnetic phase transition.

Figure 3 shows a constant q=0.06 Å^{-1} scan of the spin wave peaks for $La_{0.52}Ca_{0.48}MnO_3$. The excitations exhibited conventional spin wave dispersion. However, the spin wave amplitudes below T≈200 K were markedly lower for data taken with increasing temperature than those taken with decreasing temperature. The spin stiffness parameter (shown in Figure 4) with D(T=0 K) ≈140 meV-Å^2 showed no hysteresis effects. The ferromagnetic order parameter (inset to Figure 4),

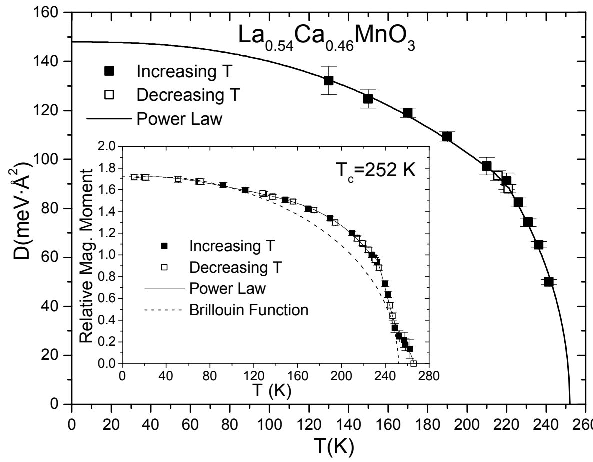

Figure 2 - Spin wave stiffness D versus temperature and the temperature dependence of the ferromagnetic order parameter (figure inset) for $La_{0.54}Ca_{0.46}MnO_3$. No temperature hysteresis was observed. For comparison the mean field Brillouin curve for the magnetization is shown.

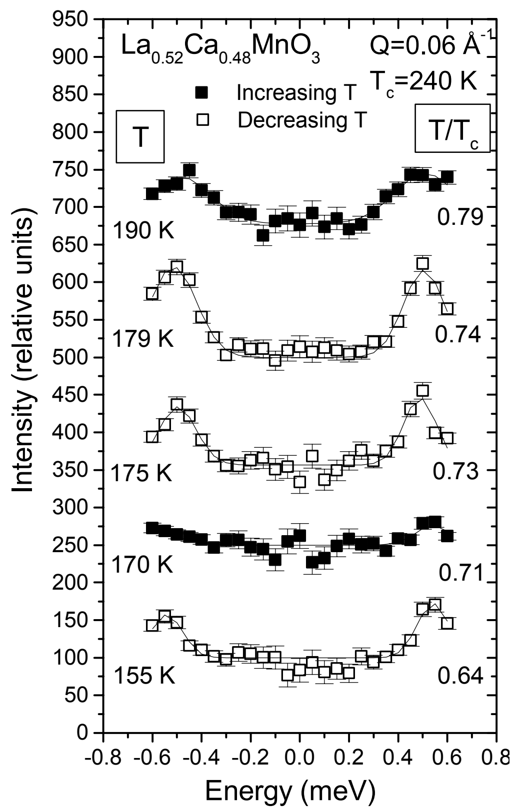

Figure 3 Constant Q = 0.06 Å^{-1} inelastic scattering intensity versus neutron energy transfer for temperatures below T_c = 240 K for $La_{0.52}Ca_{0.48}MnO_3$. The solid (open) symbols indicate increasing (decreasing) temperature. The spin wave intensity is less for increasing temperature than it is for decreasing temperature in the range 160 K – 190 K.

on the other hand, showed strong hysteresis effects between 160 K and 190 K with a Curie temperature of 240 K. On cooling, the magnetization follows a mean field T-dependence down to T ≈ 160 K. It then falls sharply and remains constant to low temperature reflecting the increase in AF order. Comparison of the low-T value of the measured magnetization to the extrapolation of the high-T mean field curve indicates that about 50% of the spins are ordered antiferromagnetically. The hysteresis in the spin wave intensity reflects different FM and AF domain populations on warming and cooling. The fact that the spin wave stiffness parameter D (which is directly related to the FM exchange interaction) shows a similar T-dependence to the x=0.46 system and no hysteresis indicates that the FM exchange is not perturbed by the AF ordering.

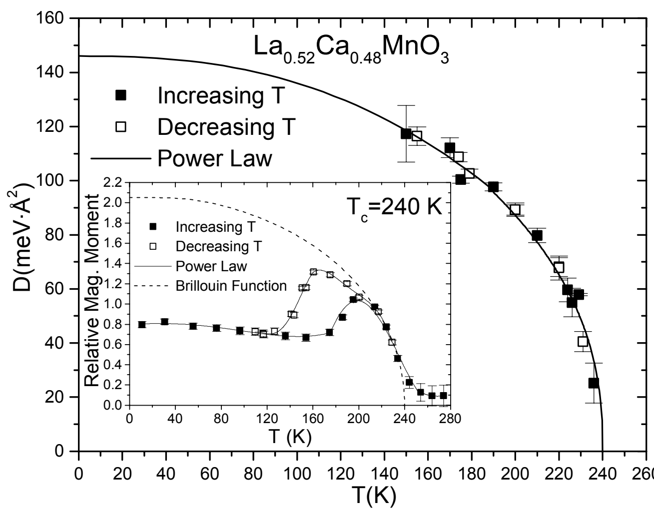

Figure 4 Spin wave stiffness D versus temperature and the temperature dependence of the ferromagnetic order parameter (figure inset) for $La_{0.52}Ca_{0.48}MnO_3$. Strong temperature hysteresis was observed in the order parameter. However, no hysteresis was observed in the spin wave stiffness parameter D. Solid (open) symbols indicate increasing (decreasing) temperature.

A central quasi-elastic peak appeared in the $La_{0.52}Ca_{0.48}MnO_3$ spin wave data at T>225 K (0.94 T_c). It did not appear to have any hysteresis effects.

For the x=0.5 composition, no FM scattering intensity could be detected at the nuclear peak positions. Therefore, no FM excitations could be observed. This implies that the mixed phase regime observed for x < 0.5 does not extend symmetrically above this metal-insulator boundary.

The results obtained for the x=0.46, 0.48, and 0.50 compositions of $La_{1-x}Ca_xMnO_3$ indicate that the transition from FM to AF upon hole doping occurs in a narrow region of x. The hysteresis present in the x=0.48 spin wave intensity and its absence in the T-dependence of the spin wave stiffness indicates that the FM and AF competing phases act independently.

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