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Two-Dimensional Ferromagnetic Correlations Above T_c in the Naturally Layered CMR Manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x = 0.3-0.4)

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DISCLAIMER

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Neutron diffuse scattering in the form of rod-like features are observed in single crystals of the layered CMR material $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.4,0.36), consistent with the presence of 2D ferromagnetic spin correlations. These diffuse features are observed over a wide temperature region, however, their coherence length does not appear to diverge at T_C, although there is evidence of the development of three-dimensional correlations around ferromagnetic reflections of the 3D-ordered magnetic structure close to T_C. Quasi-elastic neutron scattering on a ceramic sample of x=0.3 shows that the lifetime of these ferromagnetic correlations increases at $T \rightarrow T_C$. They exhibit a spin-diffusion constant above T_C of ~5 meV Å^2, much lower than that reported for $La_{2/3}Ca_{1/3}MnO_3$. We discuss the relationship of these magnetic correlations to models of the ferromagnetic transition in CMR compounds.

The close interplay among charge, spin, and lattice degrees of freedom in the colossal magnetoresistive (CMR) manganite oxides is widely believed to play an important role in the mechanism of transport in these itinerant ferromagnets. Among the current models of transport in the three-dimensional perovskite materials is that magnetic polarons—mobile lattice distortions carrying spin—are the fundamental charge-carrying entity, at least above the Curie temperature (T_C).[1, 2] Indeed, localized lattice distortions have been observed above and below T_C,[3, 4] in the (La,Ca)MnO_3 perovskite system. DeTeresa, *et al.* have extended this work by inferring that these lattice distortions carry spin (magnetic polarons) from recent in-field small angle neutron scattering (SANS) experiments on the perovskite $La_{2/3}Ca_{1/3}MnO_3$.[5]

While current attention is centered on perovskite manganites, the discovery of layered compounds $La_{2-2x}Sr_{1+2x}Mn_2O_7$ as another class of CMR oxides provides a rich opportunity to explore structure-property relationships on varying length and time scales in reduced dimensions. The material of interest, is comprised of perovskite bilayers of corner-linked MnO_6 octahedra forming infinite sheets. Bi-layers of (La,Sr)MnO_3 are separated along the *c*-axis by insulating (La,Sr)O layers. We have shown that although below T_C Mn-spins order ferromagnetically within the *ab*-plane[6] in a certain compositional range, a competition between super- and double-exchange may results to a canting of Mn-spins between adjacent ferromagnetic sheets, within the perovskite bi-layer.[7] There is evidence to show that this competition may be reflected within ferromagnetic correlations above T_C, as reported recently by Osborn *et al.*[8] Perring *et al.* also report that weak antiferromagnetic and ferromagnetic spin fluctuations coexist in these layered materials above T_C.[9] Clearly, understanding both long and short range magnetism —structure and dynamics— is an essential ingredient in developing a coherent picture of the physics of this class of transition metal oxides.

In this paper we report neutron scattering results from single crystals with x=0.4 and 0.36 that demonstrate that 2D ferromagnetic correlations exist in these layered CMR materials, as high as $2.8T_C$. Their size increases as $T \rightarrow T_C$ reaching a size of ~10 Å at T_C. The coherence length of these ferromagnetic correlations does not appear to diverge at T_C. Quasielastic neutron scattering from a polycrystalline x=0.3 sample, reproduce the single crystal results and find a spin diffusion constant of 5 meV $Å^2$, lower than that recently determined for the 3D perovskite materials.

Single crystals of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ were melt-grown in flowing 100% O_2 in a floating zone optical image furnace (NEC SC-M15HD). The crystals were characterized using Inductively Coupled Plasma spectroscopy (ICP), d.c. magnetization, and resistivity. Two single crystals were prepared and characterized by these methods; ICP measurement of their composition was determined to be consistent with a doping of x=0.40(1) ($La_{1.2}Sr_{1.8}Mn_2O_7$) and x=0.36(1) ($La_{1.28}Sr_{1.72}Mn_2O_7$). These sample exhibit transitions from a paramagnetic insulator (PI) to a ferromagnetic metal (FM) at 133 K for x=0.36 and 116K for x=0.4. Diffraction data were obtained as a function of temperature from these single crystals, using the neutron time-of-flight single crystal diffractometer (SCD) located at the Manual Lujan Jr., Neutron Scattering Center (MLNSC) at the Los Alamos National Laboratory. Quasi-elastic neutron scattering data were measured as a function of temperature from a polycrystalline sample with x=0.3 ($La_{1.4}Sr_{1.6}Mn_2O_7$) synthesized via standard ceramic techniques exhibiting coupled PI to FM transitions at 116K, using the time-of-flight chopper spectrometer PHAROS[10], also located at the MLNSC. Data were recorded using an incident energy of 12.1 meV, except for data measured at 115 K where an incident energy of 12.1 and 8.1 meV was used to extend the Q-range of the measurement. Neutron powder diffraction data were measured as a function of temperature from 20-300K, using the Special Environment Powder Diffractometer (SEPD)[11] at the Intense Pulsed Neutron Source at the Argonne National Laboratory.

Single crystal time-of-flight neutron diffraction is ideally suited for the broad survey of reciprocal space for both Bragg reflections (long range structure) and also diffuse scattering which reflects structural features on a local scale. For both x=0.36 and x=0.4 single crystals, we observe a diffuse rod-like feature along c^* centered at (0,1,0) and (1,0,0). An example of these rod-like features is shown in Fig. 1, measured at 120 K from the x=0.36 crystal. The diffuse scattering is strongly temperature dependent, becoming more intense as $T \rightarrow T_C$, while below T_C it decreases, consistent with scattering from magnetic correlations. For the x=0.4 crystal we do observe rod like features for higher orders of h and k, ($(h,00)$ or $(0,k,0)$ with h or k as high as 7) where the magnetic form factor is expected to decrease substantially the magnetic scattering. These features have a smaller FWHM than the scattering at h=1, or k=1, suggesting that there is an additional nuclear component to the observed magnetic scattering. This nuclear scattering may arise from a low density of perovskite intergrowths in the crystal as proposed by Potter *et al.*[12] and also observed in high resolution electron microscopy.[13] For the x=0.36 crystal we did not observe any diffuse scattering at higher orders of h and k, suggesting a significantly lower concentration of intergrowths than the x=0.4 crystal.

Fig. 2 shows the variation of the intensity of the magnetic rod scattering in both x=0.36 and x=0.4 crystals as a function of temperature. These values were obtained by fitting data perpendicular to the rod, along the [010] direction, with a Lorentzian function and accounting for the nuclear scattering with a narrower Lorentzian with its width fixed at a value determined at 20 K. We find that the intensity of the magnetic diffuse scattering increases as $T \rightarrow T_C$ from above, while below T_C its intensity decreases, vanishing for $T < 0.5\ T_C$. That this scattering appears as a diffuse rod along c^* and with a finite width along $[h00]$ or $[0k0]$, clearly shows that the spin correlations are 2D. We find that these modulations are ferromagnetic but do not strictly obey a $\cos^2(\pi.\Delta z.l)$ dependence (where

Δz is the difference of the fractional z-coordinate between neighboring Mn-atoms); we have proposed a model were these modulations are described in terms of spin-canting in these ferromagnetic correlations resulting from a competition between super- and double-exchange which is reported elsewhere.[8] On fig. 2 we also show the variation of intensity of the (0,1,1) ferromagnetic reflection as a function of temperature. This demonstrates that peak in the intensity of the ferromagnetic 2D fluctuations is correlated with the onset of 3D magnetic ordering. The observed ferromagnetic reflections below T_C were consistent with ordered Mn-spins aligned ferromagnetically within the *ab*-plane as reported previously.[6]

The coherence length of the ferromagnetic correlations within the perovskite bi-layers, ξ_{2D}, are ~4-5 Å at 300 K, and increases up to ~ 10 Å at T_C. Surprisingly ξ_{2D} does not appear to diverge at T_C (see fig. 3). It is unclear where the critical region for these 2D ferromagnetic correlations lies, however, from a more detailed study on the same x=0.4 crystal we find that power law scaling of ξ_{2D} suggests a much lower critical temperature for these correlations than actually observed; a T_C^{2D}=98 K is obtained using a mean field exponent ν=0.5, or a T_C^{2D}=63K for a 2D-Ising exponent of ν=1.[8] Interestingly, measurement of the critical scattering close to the (004) ferromagnetic reflection, suggests that there is a build up of three-dimensional correlations below 120 K resulting in a coherence length that appears to diverges at T_C.[8] This data suggests that there may be a cross-over close to T_C from 2D to 3D critical scaling. However, we also note that in the same temperature region we have reported significant electron-phonon coupling in these materials.[6] As discussed below, these localized lattice distortions may contribute to the lack of divergence in the 2D coherence length. Theoretical considerations suggest that this coupling arises from local Jahn-Teller effects in these mixed valent materials.[1, 2]

To investigate the spin-dynamics of these 2D ferromagnetic correlations we have measured quasi-elastic neutron scattering from a large polycrystalline sample of x=0.3.

(The need for a large sample mass to yield sufficient signal-to-noise prohibited the use of a single crystal specimen for this experiment.) We have deliberately selected a Q,ω range to measure ferromagnetic scattering as l or Q→0 without the measurement being perturbed by spin waves and 3D spin correlations at lower Q. Fig. 4(a) and (b) show data measured at 128 and 30 K in Q,ω space, while panels (c) and (d) show the same data, integrated over the accessible Q-range, as a function of energy. On panels (c) and (d) we show a fit to the elastic incoherent peak using a Gaussian function with a fixed FWHM that reflects the resolution of the spectrometer (dashed line). At 30 K we find no significant deviations from the fit, as seen in Fig. 4(d). This contrasts with the scattering at higher temperatures, and especially close to T_C, where we find an additional broad Lorentzian component superimposed on the Gaussian elastic incoherent peak. This feature is clearly shown in fig. 4(a) and (c). The intensity of the Lorentzian component diverges as Q→0 , as expected for ferromagnetic correlations.

Both quantitatively and qualitatively this ceramic x=0.3 sample behaves similarly to the single crystals discussed above. A broad Lorentzian component is observed as high as $2.8T_C$ (fig. 5(b)), while with decreasing temperature and approaching T_C, the intensity of the quasi-elastic scattering increases and reaches a maximum at T_C. Below T_C the quasi-elastic scattering decreases linearly with temperature suggesting that it may result from soft c-axis spin wave scattering.[14] The peak in the quasi-elastic scattering at T_C strongly correlates with a sharp decrease in the resistivity of the sample, and the development of three dimensional ordering of Mn-spins determined from neutron powder diffraction, as shown in Fig. 5(a). These observations resemble those reported from inelastic scattering experiments on three dimensional perovskite materials.[15] The spatial extent of the ferromagnetic correlations—computed from the Q-dependence of the Lorentzian signal—yields an overall ξ of ~5 Å (~1.30a), increasing to ~12 Å at T_C (~3.1a), similar to that found for the single crystal samples above (see fig. 5(c)).

The lifetime of these ferromagnetic correlations, obtained from the width of the quasielastic scattering integrated over the accessible Q-range of the measurement, increases $T \rightarrow T_C$, reaching a values of 1.1(1) $x10^{-11}$ sec at T_C . Interestingly like the correlation length, the lifetime does not diverge suggesting that even close to T_C, there are 2D ferromagnetic spins that are rapidly fluctuating. (see fig. 5(c)). Lynn *et al.*[15] have suggested that the magnetic transition in CMR perovskites is unusual as the spin waves stiffness constant D does not collapse close to T_C. Instead they describe the magnetic transition in the perovskite $La_{2/3}Ca_{1/3}MnO_3$ in terms of spin-diffusion due to slow polaronic hoping of e_g carriers with a spin diffusion constant, Λ, of 30 meV $Å^2$, a quantity that is analogous to the spin-stiffness constant for an magnetically ordered system. From the Q-dependence of the Lorentzian width we estimate a spin-diffusion constant $\Lambda \sim 5$ meV $Å^2$ at 115 K for our sample (see fig. 6), a value substantially lower than the perovskite material (30 meV $Å^2$). Presumably, this reduced Λ is a consequence of the low-dimensionality of these naturally layered manganites.

The results presented here clearly demonstrate that in these naturally layered materials 2D ferromagnetic correlations exist at temperatures as high as ~ 2.8 T_C. As $T \rightarrow T_C$, their size and lifetime increases, however these quantities do not appear to diverge at T_C. Clearly there is a need to reconcile the behavior of these ferromagnetic correlations with the 3D ferromagnetic transition at T_C, where critical behavior and a divergent coherence length is observed about magnetic reflections. The data does support a model where the 3D magnetic transition interrupts 2D fluctuations that would otherwise order over a long range at a lower T_C (see also ref. [8]). That the measured T_C occurs at a higher temperature that than the estimate of T_C^{2D} suggests that at a critical size of ξ_{2D}, Mn-spins in adjacent perovskite bi-layers may start ordering ferromagnetically in three dimensions. This will implies a cross-over to 3D critical scaling close to T_C. Indeed the underlying

physics of these 2D ferromagnetic correlations may be competing antiferromagnetic super-exchange and ferromagnetic double-exchange; in a previous paper we have reported that this competition may result in a canted Type-A ferromagnetic structure in x=0.4 below T_C[7] As pointed out by Osborn *et al.* these ferromagnetic correlations may arise from the same competition above TC.[8]

Alternatively the observation of a non-divergent ferromagnetic correlations over a wide temperature region, may lend support to the small polaron model put forward to explain CMR in the manganite perovskites.[1, 2] Röder *et al.*[1] have calculated the magnetic behavior of localized phenomena such as Jahn-Teller polarons associated with localized e_g carriers and argue that the magnetic transition in the CMR manganites is accompanied by a crossover of length scales from a quasi-self-trapped small polaron to a large polaronic state below T_C. At T_C their calculation predicts a magnetic coherence length of ~3-4 Mn sites or ~12-16 Å. As magnetic polarons have a finite size, their coherence length is not necessarily expected to diverge as in a 2nd order magnetic transition. That is, the coherence length of the 2D magnetic correlations may be constrained by the lattice degrees of freedom(localized Jahn-Teller effects), which are in turn influenced by the electronic state. Our values of ξ_{2D} are in reasonable agreement with the prediction of Röder *et al.* and the size measurements of magneto elastic polarons by DeTeresa *et al.* in $La_{2/3}Ca_{1/3}MnO_3$[5] , while the lower value of Λ observed here, may reflect polaronic mobility in reduced dimensions compared to the 3D octahedral network of perovskite materials. However, since the degree of electron-phonon coupling (via the Jahn-Teller effect) and T_C are closely coupled in the CMR materials,[1, 2, 16] the difference between the two possible explanations put forward here may be subtle.

In conclusion, we have demonstrated the existence of 2D ferromagnetic correlations in layered CMR materials over a wide temperature range, with a coherence length ξ_{2D} and lifetime that do not diverge at T_C. These 2D ferromagnetic correlations accompany the

ferromagnetic transition at T_C, which appears to exhibit critical scattering and a divergent coherence length. Quasi-elastic neutron scattering shows these ferromagnetic correlations still fluctuate rapidly close to T_C, while the spin diffusion constant is much lower than the perovskite materials. Importantly, the naturally layered manganites provide a unique opportunity to examine in detail the mechanism of this crossover between 2D and 3D magnetism.

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References

[1]H. Röder, J. Zang and A. R. Bishop, Phys. Rev. Lett. **76**, 1356 (1996).

[2]A. J. Millis, P. B. Littlewood and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).

[3]S. J. L. Billinge, R. G. Difranscesco, G. H. Kwei, J. J. Neumier and J. D. Thompson, Phys. Rev. Lett. **77**, 515 (1996).

[4]P. G. Radaelli, D. E. Cox, M. Marezio, S.-W. Cheong, P. E. Schiffer and A. P. Ramirez, Phys. Rev. Lett. **75**, 4488 (1995).

[5]J. M. Deteresa, M. R. Ibarra, P. A. Algarabeli, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. Delmoral and Z. Arnold, Nature **386**, 256 (1997).

[6]J. F. Mitchell, D. N. Argyriou, J. D. Jorgensen, D. G. Hinks, C. D. Potter and S. D. Bader, Phys. Rev. B **55**, 63 (1996).

[7]D. N. Argyriou, J. F. Mitchell, J. B. Goodenough, O. Chmaissem, S. Short and J. D. Jorgensen, Phys. Rev. Lett. **78**, 1568 (1997).

[8]R. Osborn, S. Rozenkrantz, D. N. Argyriou, L. Vasiliu-Doloc, J. W. Lynn, S. K. Sinha, J. F. Mitchell, K. E. Grey and S. D. Bader, Phys. Rev. Lett. **Submitted**, (1997).

[9]T. G. Perring, G. Aeppli, Y. Moritomo and Y. Tokura, Phys. Rev. Lett. **78**, 3197 (1997).

[10]R. A. Robinson, M. Nutter, R. L. Ricketts, E. Larson, J. P. Sandoval, P. Lysaght and B. J. Olivier, *International Conference on Neutron Scattering XII, Rutherford Appleton Laboratory, 1994* (Rutherford Appleton Laboratory, RAL 94-025, p. 44.

[11]J. D. Jorgensen, J. J. Faber, J. M. Carpenter, R. K. Crawford, J. R. Haumann, R. L. Hitterman, R. Kleb, G. E. Ostrowski, F. J. Rotella and T. G. Worton, J.Appl.Crystallogr. **22**, 321 (1989).

[12]C. D. Potter, S. D. Bader, J. F. Mitchell and D. N. Argyriou, Phys. Rev. B (in press) (1997).

[13]D. Miller. private communication (1997).

[14]K. Hirakawa, H. Yoshizawa and K. Ubukoshi, J.Phys.Soc.Japan **51**, 2151 (1982).

[15]J. W. Lynn, R. W. Erwin, J. A. Borchers, Q. Huang, A. Santoro, J.-L. Peng and Z. Y. Li, Phys. Rev. Lett. **76**, 4046 (1996).

[16]G.-M. Zhao, K. Conder, H. Keller and K. A. Müller, Nature **381**, 676 (1996).

Figures Captions

Fig. 1: Time-of-flight neutron diffraction data measured from a single crystal of $La_{1.28}Sr_{1.72}Mn_2O_7$ at 120 K. The observed scattering is shown as a section through reciprocal space (a) perpendicular to [100] and (b) perpendicular to [001]. The small peak just below the (011) reflection corresponds to a much smaller second crystal in the sample with a relative intensity of the main (011) reflection of 1/5000.

Fig 2: Temperature dependence of diffuse scattering intensity at (0,1,0) and the intensity of the ferromagnetic (0,1,1) measured from single crystals of x=0.4 and 0.36. The intensity of the (0,1,1) reflection has been normalized to its intensity measured at 300 K.

Fig 3: The planar coherence length ξ_{2D} as a function of temperature.

Fig. 4: Inelastic neutron data in Q,ω space measured at 128 K (a) and 30 K (b) using an incident neutron energy of 12.1 meV. The same data measured at 128 K (c) and 30 K (d) plotted as a function of energy integrated over the accessible Q-range of this measurement. See text for details.

Fig. 5: (a) Temperature dependent resistivity and magnetization (determined from full profile Rietveld refinement of neutron powder data) from the polycrystalline sample $La_{1.4}Sr_{1.6}Mn_2O_7$, (b) integrated intensity of the quasi-elastic Lorentzian component, and (c) coherence length as a function of reduced temperature T/T_C. In (c) the dashed lines are a fit to a power law function. Magnetic reflections from the x=0.3 sample were consistent with a ferromagnetic alignment of Mn-spins in the *a-b* plane.[6]

Fig. 6: The Q-dependence of the Lorentzian quasielastic width (Γ) at 115 K measured from a ceramic sample of $La_{1.4}Sr_{1.6}Mn_2O_7$. The dashed line represent a fit to $\Gamma=\Lambda Q^2$, while the solid line represents the behavior observed in $La_{2/3}Ca_{1/3}MnO_3$ reported by Lynn *et al.*[15]

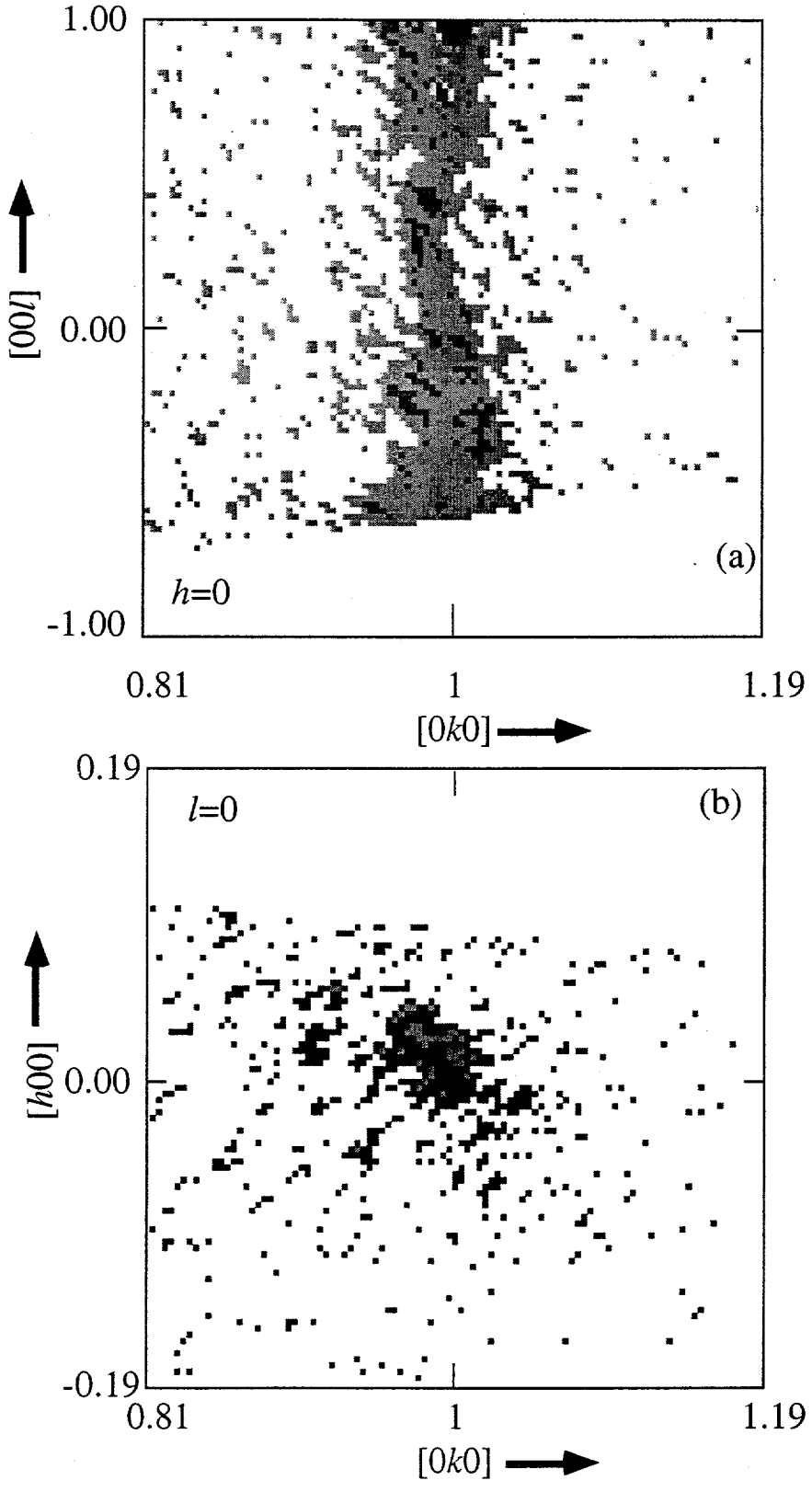
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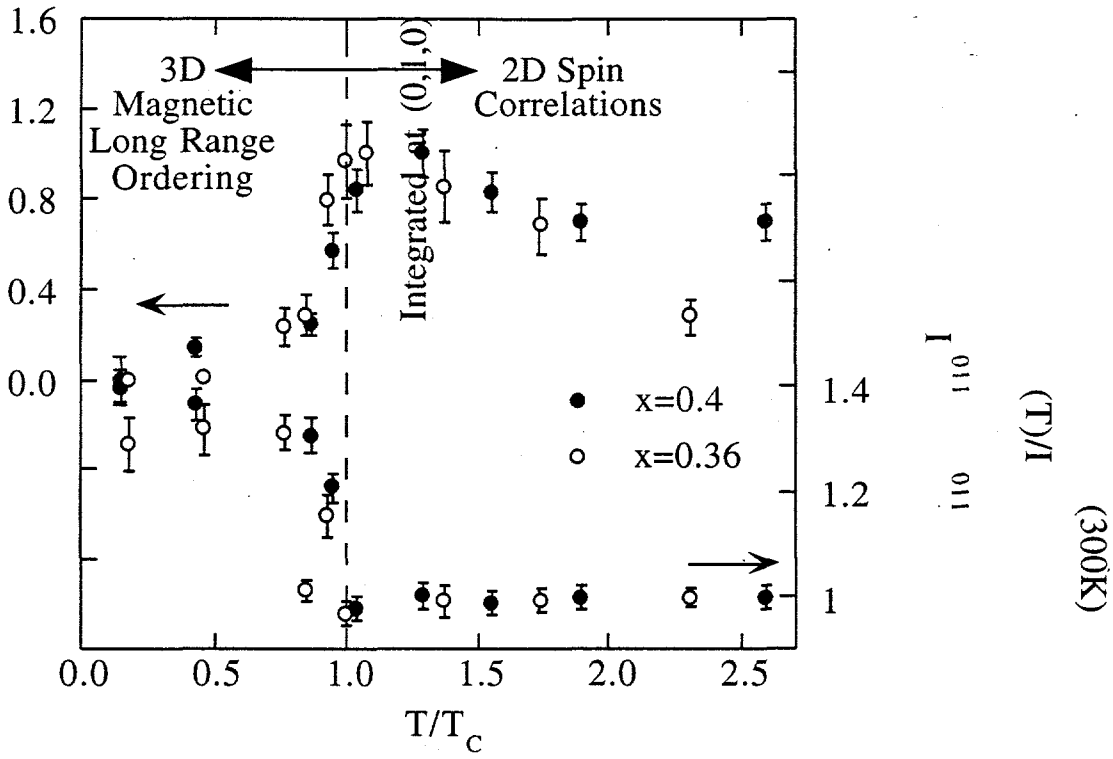
Fig. 1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Magnetic
Long Range
Ordering
2D Spin
Correlations
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1.2
0.8
0.4
0.0
1.4
1.2
1
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T/T_C
I_011 (T)/I_011 (300K)

Fig. 2

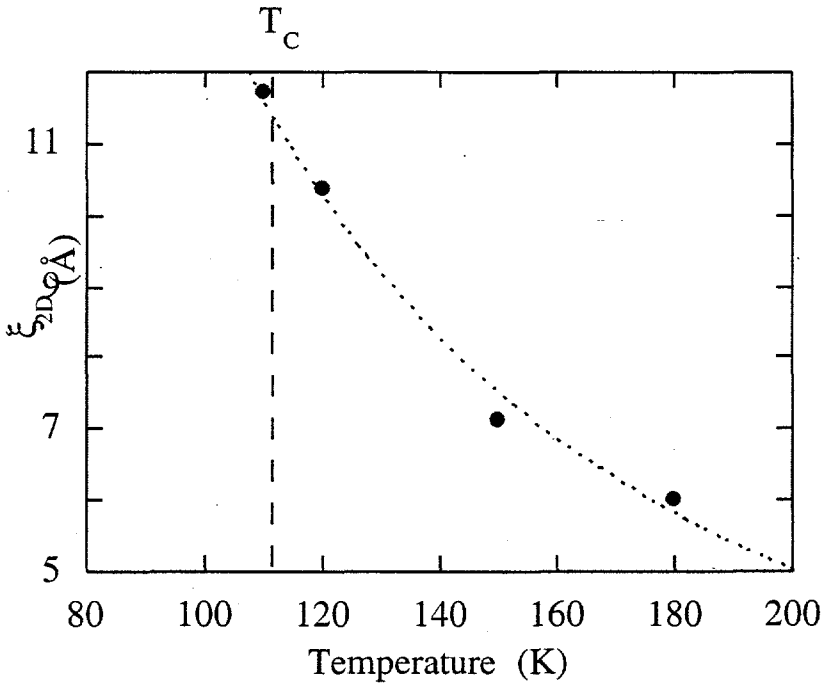

Fig. 3

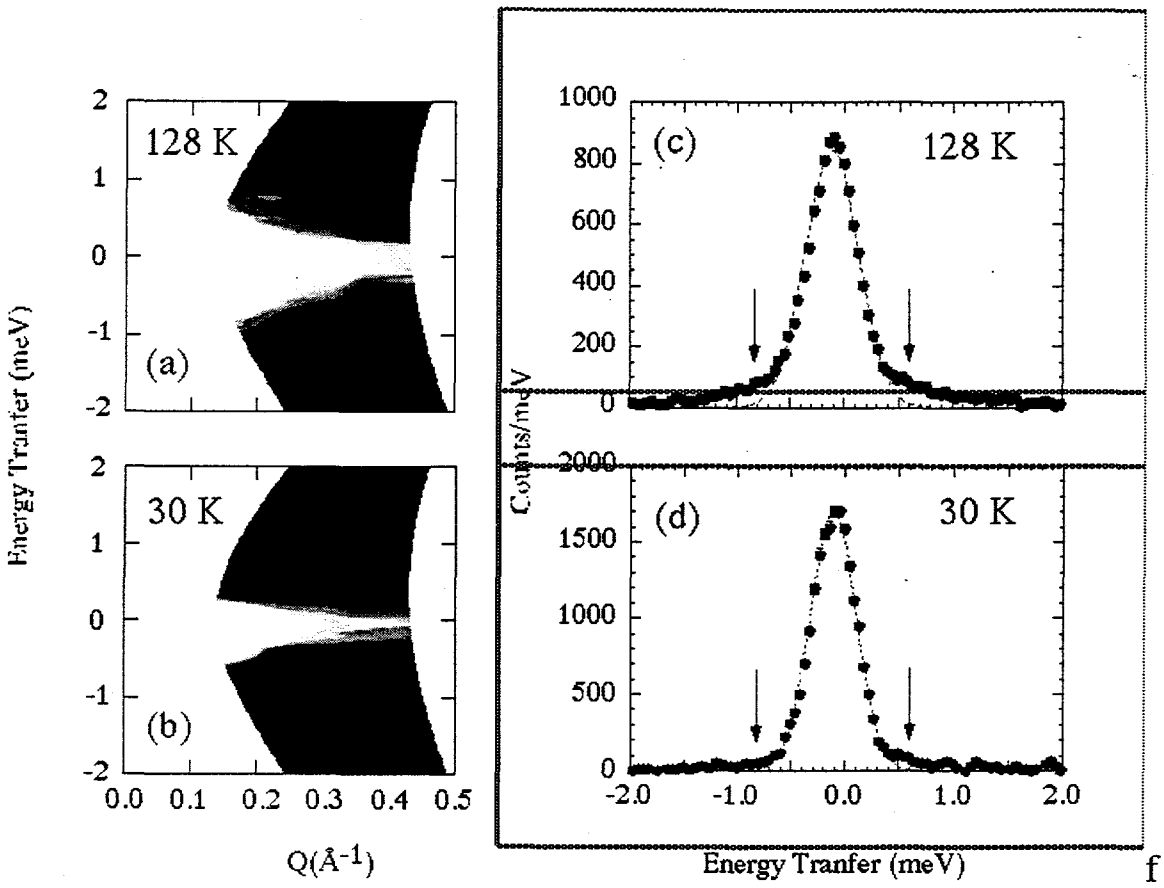
128 K
(a)
30 K
(b)
Energy Tranfer (meV)
Q(Å-1)
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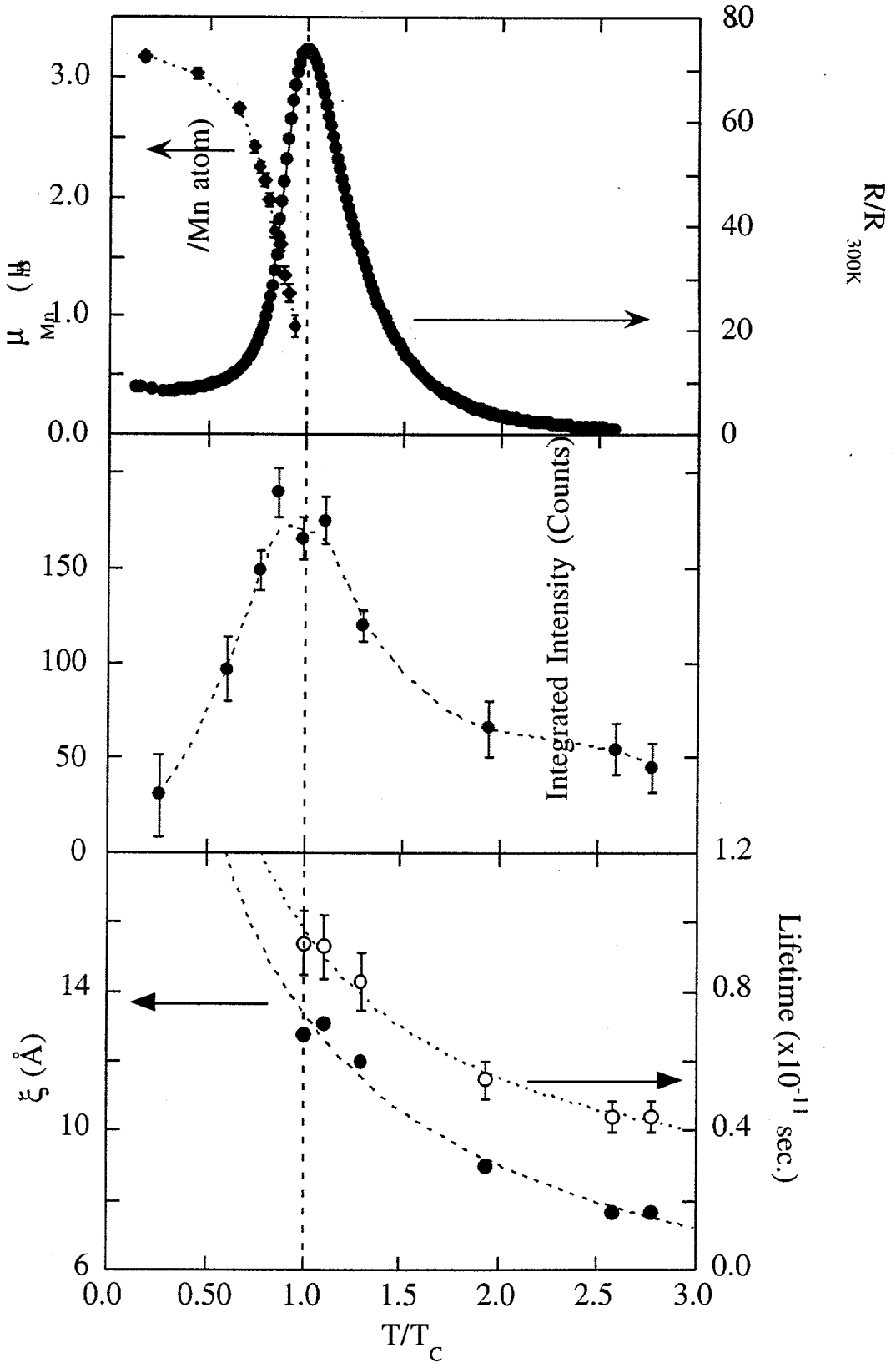
Fig. 5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0
R/R 300K
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Integrated Intensity (Counts)
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0.4
0.0
Lifetime (x10^-11 sec.)
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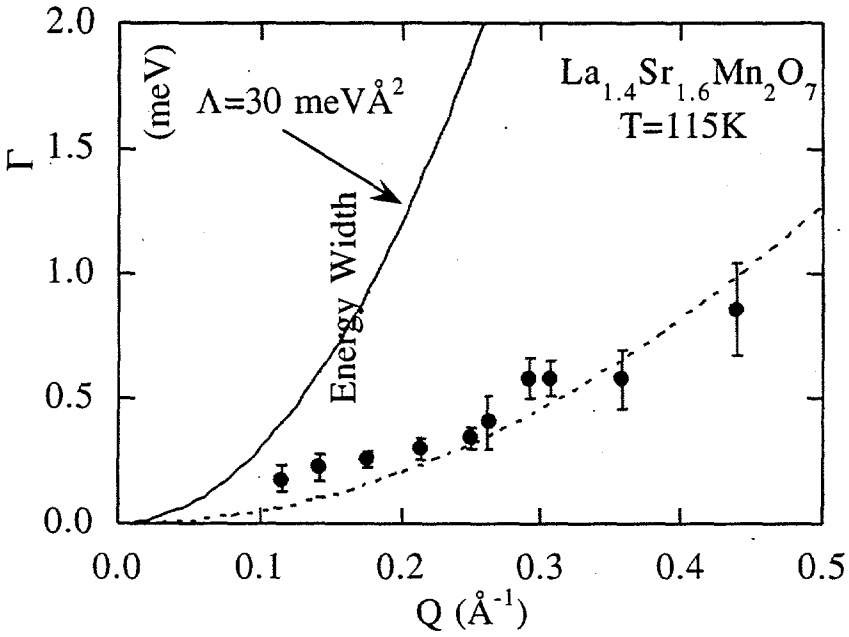
T/T_C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Γ (meV)
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T=115K
0.0
0.1
0.2
0.3
0.4
0.5
Q (Å⁻¹)

Fig. 6