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# Antiferromagnetic fluctuations and charge carrier localization in ferromagnetic bilayer manganites: electrical resistivity scales exponentially with short-range order controlled by temperature and magnetic field

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3 **Antiferromagnetic fluctuations and charge carrier**  
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6 **localization in ferromagnetic bilayer manganites: electrical**  
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9 **resistivity scales exponentially with short-range order**  
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12 **controlled by temperature and magnetic field**  
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45 **Abstract.** The compound  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ,  $x = 0.30 - 0.40$ , consists of bilayers of  
46 ferromagnetic metallic  $\text{MnO}_2$  sheets that are separated by insulating layers. The materials  
47 show colossal magnetoresistance – a reduction in resistivity of up to two orders of magnitude  
48 in a field of 7 T – at their three-dimensional ordering temperatures,  $T_C = 90 \text{ K} - 126 \text{ K}$ , and  
49 are the layered analogues of the widely studied pseudo-cubic perovskite manganites,  
50  $\text{R}_{1-x}\text{A}_x\text{MnO}_3$  (R = rare earth, A = Ca, Sr, Ba, Pb). Two distinct short-range orderings –  
51 antiferromagnetic fluctuations and correlated polarons, which are related to the magnetic and  
52 the lattice degrees of freedom respectively – have previously been discovered in  
53  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ,  $x = 0.40$ , and have each been qualitatively connected to the resistivity.  
54 Here, in a comprehensive study as a function of both temperature and magnetic field for the  
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3 different hole-concentrations per Mn site of  $x = 0.30$  and  $0.35$ , we show that  
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5 antiferromagnetic fluctuations also appear at temperatures just above  $T_C$ , and that the  
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7 intensities of both the antiferromagnetic fluctuations and polaron correlations closely track  
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9 the resistivity. In particular, for  $x = 0.35$  we show that there is a simple scaling relation  
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11 between the intensities of the antiferromagnetic fluctuations and the in-plane resistivity that  
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13 applies for the temperatures and magnetic fields used in the experiments. The results show  
14  
15 that antiferromagnetic fluctuations are a common feature of  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$  with  
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17 ferromagnetic bilayers, and that there is a close connection between the antiferromagnetic  
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19 fluctuations and polarons in these materials.  
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## 21 **1. Introduction**

### 22 23 1.1 Roger Cowley and magnetic phase transitions

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26 Throughout a wide-ranging career, a long-standing interest of Roger Cowley was phase  
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28 transitions in magnetic materials. From the very start of his career, he had made seminal  
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30 contributions in the field of structural phase transitions, for example testing the idea that a  
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32 soft phonon mode is responsible for the phase transition in a certain perovskite [1]. His  
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34 seminal work on magnetic phase transitions included a series of papers concerning the  
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36 percolation transition in Ising and Heisenberg insulators diluted with magnetic and non-  
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38 magnetic impurities, and the random field Ising model [2-6].

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40 He was a master of neutron scattering, which is the premier technique to probe the spatial and  
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42 temporal dynamics of magnetic systems at the scales set by the atomic spacing and the  
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44 magnetic interactions strengths. The scattering process itself directly yields the wave-vector  
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46 and frequency spectrum of the two-spin correlation function, barring simple and well-  
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48 understood constants and geometric terms, and so cuts straight to the underlying physics and  
49  
50 enables the most exacting quantitative tests of theories of order parameter fluctuations and  
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52 phase transitions.

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54 His classic experiments on soft modes and random field effects in diluted magnets were  
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56 performed on the reactor-based triple axis spectrometer (TAS), which with its flexible control  
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58 of resolution and more or less unrestricted access to the four dimensional (vector momentum  
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60 and energy) phase space relevant for many problems in condensed matter physics, permitted,  
during most of his lifetime, the most precise exploration of dynamics in the ordered state and

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3 of critical phenomena. However, he was quick to see the opportunities of time-of-flight  
4 methods at the pulsed source ISIS in the UK. Spectrometers at such sources require a very  
5 different approach to experiments: they have a large solid angle of detectors that map the  
6 wave vector and frequency dependence of the correlations in parallel, rather than point-by-  
7 point as on a TAS, and the required experimental skills have as much to do with the adroit  
8 use of software to explore the large data sets collected on the instruments as they do with  
9 mastery of the hardware. One of the earliest experiments that did much to establish the new  
10 time-of-flight approach to the exploration of dynamics in single crystals was Roger Cowley's  
11 influential work (with Alan Tennant and Stephen Nagler) that unambiguously showed the  
12 fractionalisation of spin excitations in the one-dimensional Heisenberg antiferromagnetic  
13 chain [7].  
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## 26 1.2 Bilayer manganites

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28 This article concerns the existence of antiferromagnetic correlations and polaron dynamics in  
29 the vicinity of the ferromagnetic phase transition in (poorly) metallic manganites. Two  
30 connections with ideas in the section above are as follows: the character of the magnetic  
31 dynamics changing through a phase transition, and also that the original discovery of an  
32 unexpected phenomenon – the appearance of *antiferromagnetic* fluctuations at a  
33 *ferromagnetic* transition – was serendipitous and only possible because of the parallel  
34 mapping of the dynamics in a large detector array that included regions of reciprocal space  
35 that were originally of no interest.  
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43 The starting point to understand the physics of the manganites is the venerable double  
44 exchange model [8]. Each Mn ion has a local magnetic moment with spin  $S=3/2$  arising from  
45 three electrons in the  $t_{2g}$   $d$ -orbitals, and a fraction  $(1-x)$  of the Mn ions have a fourth electron  
46 in a higher energy  $e_g$  orbital, whose spin is aligned parallel to the local moment by strong  
47 Hund's rule coupling  $J_H \sim 2\text{eV}$ . The essential physics is a competition between delocalisation  
48 of the  $e_g$  electrons, favouring a fully spin polarised ferromagnetic (FM) metal, and  
49 localisation, due to local lattice distortions around the Jahn-Teller active  $\text{Mn}^{3+}$  ions self-  
50 trapping the  $e_g$  electrons [9]. For sufficiently high hole concentration,  $x$ , the  $e_g$  electrons may  
51 form ordered lattices; the subsequent distortions of the  $\text{MnO}_6$  octahedral units which make up  
52 the perovskite structure can favour occupancy of one  $e_g$  orbital over others, which in turn can  
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3 control the magnetic exchange between Mn ions. It is the delicate balance between  
4 delocalisation and localisation, together with the coupling of the magnetic, lattice, charge and  
5 orbital degrees of freedom that results in the sensitivity of the transport properties to external  
6 stimuli. These manifest themselves through insulator-metal transitions induced by  
7 electromagnetic perturbations (including photons) and strain fields [10-13]. Theoretical and  
8 experimental work considers phase segregation in the manganites, at length scales from 1 nm  
9 to  $O(\mu\text{m})$  [14]. Transport measurements, neutron scattering and most spectacularly STM and  
10 AFM microscopy [15,16] reveal the coexistence of metallic and insulating phases for some  
11 manganites, where one phase shrinks or grows at the expense of others as temperature or  
12 magnetic field is altered.

21 Two discoveries salient to an understanding of the resistivity of the bilayer manganites  
22  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ,  $x = 0.30 - 0.40$  [17, 18] (figure 1(a)) are those of antiferromagnetic (AF)  
23 fluctuations [19] and polaron correlations [20]. Short-range, short-lived AF correlations were  
24 observed [19] in the case of  $x = 0.40$  to appear at  $(0.5,0,0)$  on warming through the three-  
25 dimensional ordering temperature  $T_C = 126\text{K}$  of this ferromagnet, decreasing in intensity with  
26 increasing temperature but surviving to at least  $2.2 T_C$ , and coexisting with the conventional  
27 FM critical scattering. The intensity of the scattering qualitatively follows that of the  
28 resistivity. The correlation length was found to be only  $\sim 2 a$ , where  $a$  is the distance between  
29 adjacent Mn sites within the bilayers, but with lifetimes considerably longer than the  
30 timescales defined both by characteristic phonon frequencies associated with the  $\text{MnO}_6$   
31 breathing and stretching modes, and by the hopping integral  $t \sim 0.3 \text{ eV}$  for movement of  
32 electrons between adjacent Mn ions. Within the spatial and temporal region defined by the  
33 correlation length and lifetime, the AF fluctuations break the long-range tetragonal  
34 symmetry, as they correspond to Mn moment reversal along only one of the in-plane Mn-Mn  
35 bonds (shown schematically in figure 1(b)). The significance of the long-lived AF  
36 fluctuations is that within the double-exchange model, adjacent Mn moments that are parallel  
37 provide a pathway for hopping of the  $e_g$  electrons, whereas antiparallel alignment blocks  
38 conduction. The latter follows from the penalty of the intrasite Hund's rule energy  
39 experienced by an  $e_g$  electron hopping to a  $\text{Mn}^{4+}$  site pointing in the opposite direction to the  
40 local  $t_{2g}$  moment. Soon after this discovery, diffuse x-ray scattering from a crystal of the same  
41 composition,  $x = 0.40$  [20], revealed the presence of local lattice distortions around the Mn  
42 sites. Just like the AF fluctuations, they only appear in the paramagnetic, insulating phase  
43 above  $T_C$ , and persist with decreasing intensity to at least  $2.6 T_C$ . The polarons exhibited

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3 short-range order with a characteristic wavevector  $(\pm\delta, 0, \pm 1)$  where  $\delta \approx 0.3$ , and the intensity  
4 of associated scattering followed a behaviour similar to that of the AF fluctuations as  
5 temperature was varied. Detailed investigations [21, 22] revealed the nature of the polaron  
6 correlations. The widths of the  $\text{MnO}_6$  octahedra in both sheets of a bilayer are modulated  
7 along one of the Mn-Mn directions in the plane of the bilayer, with wavevector  $(\delta, 0, 0)$ . The  
8 octahedra are tilted by rotation about the other in-plane Mn-Mn direction with the same  
9 period, but in anti-phase. At  $T = T_C + 13$  K, the correlation lengths are  $\approx 6 a$ ,  $\approx 4 a$  and  $\sim c/2$   
10 along the modulation wavevector, in the perpendicular in-plane direction, and perpendicular  
11 to the bilayers respectively. The same behaviour – correlated polarons with modulation  
12 vector  $(\approx 0.3, 0, 0)$  whose scattering intensity broadly follows the resistivity – was reported for  
13 higher hole concentrations  $x = 0.40 - 0.48$  [23]. Two unanswered questions are (i) are the AF  
14 fluctuations peculiar to the hole concentration  $x = 0.40$ , or do they exist for a range of  $x$ , and  
15 (ii) how are the two phenomena – AF fluctuations and correlated polarons – related. Here we  
16 answer both questions by showing comprehensive measurements of properties of both as a  
17 function of temperature and applied magnetic field for  $x = 0.30$  and  $0.35$ .  
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32  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$  crystals with  $x = 0.30$  and  $0.35$  were chosen for the study for the following  
33 reasons. First,  $x = 0.35$  has the same FM long-range order as  $x = 0.40$ , with very similar  
34  $T_C = 121$  K, and has the same qualitative behaviour of the in-plane,  $\rho_{ab}$ , and perpendicular  
35 resistivities,  $\rho_c$ . However, it lies well in the composition range  $\sim 0.32 - 0.40$  for which the  
36 ground state is FM, and away from the range  $x \sim 0.40 - 0.48$  for which the structure within the  
37 bilayers shows initially AF long-range ordering for  $T < T_N$  then AF canted order for  
38  $T < T_C < T_N$  [24, 25]. The instance of  $x = 0.35$  therefore provides an example free of  
39 complications arising from the proximity to phases with AF character in the ground state.  
40 Second,  $x = 0.30$  has qualitatively different  $\rho_{ab}$ , compared to  $x = 0.35$  and  $0.40$  (compare  
41 figures 2(b) and 3(b)). For both  $x = 0.30$  and  $0.35$ ,  $\rho_c$  peaks at the three-dimensional ordering  
42 temperatures and shows colossal negative magnetoresistance near these temperatures.  
43 However, whereas  $\rho_{ab}$  ( $x = 0.35$ ) has the same qualitative behaviour as  $\rho_c$  (albeit two orders  
44 of magnitude smaller, reflecting the insulating barriers in the layered structure),  $\rho_{ab}$  ( $x = 0.30$ )  
45 continues to increase to about 270 K. For  $x = 0.30$ , the magnetic structure within the bilayers  
46 is FM, just as for  $x = 0.35$  and  $0.40$ , but the bilayers are now coupled antiferromagnetically,  
47 with three-dimensional ordering temperature  $T_N = 90$  K. The case of  $x = 0.30$  provides a  
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3 qualitatively different material, as far as of resistivity and long-range magnetic ordering are  
4 concerned, for which to measure the development of the AF and polaron correlations.  
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## 10 **2. Methods**

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13 Single crystals of  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ,  $x = 0.30$  and  $0.35$ , were grown using the floating zone  
14 method as described before [17]. The AF and polaron correlations as a function of both  
15 temperature and applied magnetic field were studied by neutron scattering from single crystal  
16 samples with mass 2.9g ( $x=0.35$ ) and 0.7g ( $x=0.30$ ). Intensity maps for the AF correlations  
17 were collected as a function of temperature and magnetic field using the HET spectrometer at  
18 the ISIS Neutron and Muon Source at the STFC Rutherford Appleton Laboratory, UK, with  
19 an incident neutron energy of 20 meV. This instrument had detector arrays that enabled  
20 intensity maps to be collected as a function of energy simultaneously along the  $(h, 0, 0)$  and  
21  $(h, h, 0)$  directions in the sheets of the bilayers, and which also allowed the AF fluctuations at  
22  $(0.5, 0)$  to be isolated from scattering due to non-magnetic and sample environment  
23 scattering, as explained below. We collected data at three temperatures 6 K, 126 K and 300 K  
24 using the MAPS spectrometer at ISIS with an incident energy of 65 meV to give detailed  
25 intensity maps as a function of energy in the  $(h, k, 0)$  plane. The diffuse scattering arising  
26 from polaron correlations were measured on the PRISMA instrument at ISIS, operating in  
27 white beam (Laue) diffraction mode.  
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## 43 **3. Results**

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45 Figures 1(c-f) show representative maps gathered in zero applied magnetic field from the  
46 single crystal with  $x = 0.35$ . In addition, figure 1(g) shows an overview of the energy-  
47 integrated magnetic scattering in the  $(h,k,0)$  plane at 126K, just above  $T_C \equiv 121$  K, collected  
48 on the MAPS instrument. At integer  $h$  and  $k$  there is the ferromagnetic critical scattering that  
49 is expected for a ferromagnet, but at the AF wavevector  $(0.5, 0, 0)$  and symmetry related  
50 positions there is additional diffuse intensity. The magnetic origin is confirmed by the fact  
51 that the intensity at  $(0.5, 1, 0)$  and symmetry related positions, which arises at the same  
52 position in the Brillouin zone as  $(0.5, 0, 0)$ , is weaker, whereas scattering from lattice  
53 fluctuations would be more intense. Figures 1(c) and 1(d) show spectra of the AF fluctuations  
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3 as a function of excitation energy,  $\varepsilon$ , and momentum along the  $(h, 0, 0)$  direction in the plane  
4 of the bilayers i.e. along one of the Mn-Mn bond directions. Figure 1(c) shows that the AF  
5 scattering at  $(0.5, 0, 0)$  is centred at  $\varepsilon = 0$ , and so does not arise from a propagating mode, but  
6 is also diffuse in energy and therefore has a finite lifetime. (The intensity centred at  $\varepsilon = 0$ ,  
7 increasing as  $h$  approaches unity is due to FM fluctuations with maximum at  $(1, 0, 0)$ ).  
8 Warming to 275 K (figure 1(d)) broadens the scattering in both  $h$  and  $\varepsilon$ , that is, it reduces the  
9 correlation length and time, but the correlations remain clearly visible. Maps of intensity as a  
10 function of energy and momentum along  $(h, h, 0)$  were gathered in parallel, and show little  
11 momentum dependence, except for that arising from the FM fluctuations, as is evident from  
12 figure 1(g). In particular, there is no AF scattering at  $(0.5, 0.5, 0)$ . These data were  
13 subsequently subtracted as estimates of the non-magnetic scattering that arises from the  
14 sample and cryostat. Figures 1(e) and 1(f) show the energy-integrated scattering at similar  
15 temperatures arising from the structural distortions produced by the polarons. The strain field  
16 from individual polarons is responsible for the scattering centred at the  $(2, 0, 0)$  Bragg position  
17 (Huang scattering), whereas the polaron correlations produce the peaks at  $(2+\delta, 0, \pm 1)$ ,  
18  $\delta = 0.275$ , an incommensurability reduced from  $\delta = 0.30$  for  $x = 0.4$  [20]. Just as for the AF  
19 fluctuations, warming to 250 K broadens and reduces the intensity of the peaks. (Note that  
20 symmetry equivalent scattering at  $(2-\delta, 0, \pm 1)$  is largely obscured by scattering from the  
21 polycrystalline material of the sample holder and cryostat.) Qualitatively identical intensity  
22 maps of scattering from both AF and polaron correlations were gathered from the single  
23 crystal with  $x = 0.30$ , except that the onset of scattering is at  $T_N = 90\text{K}$ , and there is a further  
24 reduction of the incommensurate wavevector to  $\delta = 0.25$ . Figure 4 shows data as a function of  
25  $\delta h$  along  $(2+\delta h, 0, 1)$  for both  $x = 0.35$  and  $x = 0.30$  just above the respective ordering  
26 temperatures that show the reduction in  $\delta$  on reducing  $x$ . The data for both hole  
27 concentrations are strongly reminiscent of those for  $x = 0.40$  for the AF fluctuations [19] and  
28 polarons [20].

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50 Quantitative analysis of the intensities is presented in figures 2 and 3. First, let us consider the  
51 AF fluctuations. Figure 2(c) shows the integrated intensity for  $x = 0.35$ . With no applied  
52 magnetic field, the intensity increases sharply on warming to a maximum at  $T_C$  (as revealed  
53 by a comparison with the  $(004)$  Bragg peak intensity, which is proportional to the square of  
54 the magnetic order parameter, shown in figure 2(a)), and falls only slowly as the temperature  
55 is raised further. We confirmed that the AF fluctuations are independent of thermal history  
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3 i.e. whether they were collected on warming or cooling through the transition temperature.  
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5 The intensity tracks that of  $\log(\rho_{ab})$  and  $\log(\rho_c)$ . This behaviour is similar to that reported in  
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7 our earlier work for  $x = 0.40$  [19]. What is additionally revealed is that the AF fluctuations  
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9 are suppressed in an applied magnetic field of 7 T for temperatures below  $\sim 200$  K, again  
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11 mimicking the behaviour of  $\log(\rho_{ab})$  and  $\log(\rho_c)$ . The same is true for the scans as a function  
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13 of applied field just above  $T_C$  (figures 2(e) and 2(f)). The direct relationship between the  
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15 intensity of the AF fluctuations and  $\log(\rho_{ab})$  is made clear in figure 5, where the temperature  
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17 and magnetic field dependent AF intensity data of figures 2(c) and 2(f) are plotted as a  
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19 function of  $\log(\rho_{ab})$ . Figure 5 shows that there is strong correlation between the intensity of  
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21 the AF fluctuations and the in-plane resistivity that applies irrespective of the temperature or  
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23 magnetic field. Similar data is presented for  $x = 0.30$  in figures 3(b) and 3(c). As for  $x=0.35$ ,  
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25 the AF fluctuations are independent of warming or cooling through  $T_N$ . Two important points  
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27 emerge from the data for  $x = 0.30$ . Firstly, the AF intensity reaches its maximum close to  
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29  $T_N = 90$  K, which is substantially less than the temperature of the peak intensity for  $x = 0.35$ ,  
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31 which is close to  $T_C = 121$  K. The fact that the peak intensity coincides with the three-  
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33 dimensional ordering temperature for  $x = 0.30, 0.35$  as well as for 0.40 [19] demonstrates that  
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35 the phenomenon of AF fluctuations is an intrinsic property of the bilayer manganites, and  
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37 does not originate from an extrinsic impurity phase. Secondly, the intensity tracks  $\rho_c$ , not  $\rho_{ab}$ .  
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39 Note that the AF fluctuations described here are short-range correlations within the bilayers  
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41 and are unrelated to the critical scattering that is expected near  $T_N$  associated with the three-  
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43 dimensional long-range antiferromagnetic order from the antiferromagnetic stacking of the  
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45 (ferromagnetic) bilayers. That critical scattering is expected at wave vectors  $(h, k, l)$  near  
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47 integer  $h$  and  $k$  for odd-integer  $l$ . The AF fluctuations investigated here are centred on  $(0.5, 0,$   
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49  $0)$ ; nor do their correlation lengths and lifetimes diverge at  $T_N$ , as is described below.

46 The correlation lengths,  $\xi = 1/\kappa$ , and the inverse lifetimes,  $\gamma = 1/\tau$ , of the fluctuations as a  
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48 function of temperature in zero applied field for both  $x=0.30$  and  $x=0.35$  are shown in  
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50 figures 6(c) and 6(d). They were obtained from fits to sections parallel to the  $(h, 0, 0)$  and  $\varepsilon$   
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52 axes from the momentum and energy intensity maps, of which figures 6(a) and 6(b) are  
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54 examples taken from the maps in figures 1(c) and 1(d). The momentum and energy  
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56 dependence of the AF fluctuations was modelled by the following function:  
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$$A |F(|\mathbf{Q}|)|^2 \frac{\exp\left(-\left(q_{ip}/\kappa\right)^2 \ln 2\right)}{\kappa^2} \frac{\varepsilon}{1 - \exp(-\varepsilon/k_B T)} \frac{\gamma/\pi}{\varepsilon^2 + \gamma^2} \cos^2(Q_z a/2)$$

where  $\kappa$ ,  $\gamma$  and the overall scale factor,  $A$ , were treated as free parameters to be obtained from simultaneous least-squares fitting of the model to the pair of sections for each temperature. In the model,  $\mathbf{Q}$  is the momentum with  $Q_z$  the component (in  $\text{\AA}^{-1}$ ) along the direction perpendicular to the plane of the bilayers,  $q_{ip}$  is the in-plane momentum (in  $\text{\AA}^{-1}$ ) with respect to the origin of the AF fluctuations at  $(0.5,0,0)$ ,  $a = 3.87 \text{\AA}$  is the Mn-Mn distance within a bilayer,  $|F(|\mathbf{Q}|)|^2$  is the magnetic form factor for  $\text{Mn}^{3+}$ , and  $1/(1 - \exp(-\varepsilon/k_B T))$  is the detailed balance factor. The more conventional Lorentzian form for momentum correlations,  $1/(\kappa^2 + q_{ip}^2)$ , has been replaced by a Gaussian with the same height and half-width half-maximum to make the determination of  $\kappa$  less sensitive to details of the tails of the momentum correlation function. The non-linear tail from the FM fluctuations centred on  $(1,0,0)$  was accounted for by a Gaussian function in momentum. The cosine-squared modulation of intensity perpendicular to the bilayers arises from FM correlation of the moments along Mn-Mn bonds connecting the two sheets of the bilayer. This variation with  $Q_z$  was measured for both  $x = 0.30$  and  $0.35$ , and together with the absence of magnetic scattering at  $(0.5,0.5,0)$  confirms that the instantaneous ordering wavevector in the AF correlated regions is the same as that found for  $x = 0.40$  [19] and shown in figure 1(b). For both  $x = 0.30$  and  $0.35$ ,  $\xi$  and  $\gamma$  are almost identical, as is shown in figures 6(c) and 6(d), varying according to temperature between 1 - 2 Mn-Mn distances and 0.5 - 4 meV ( $\equiv \tau \sim 1 - 0.1$  ps), values very similar to those for  $x = 0.40$ . Both  $\xi$  and  $\gamma$  show no evidence of divergence near the critical temperature, but instead vary slowly and monotonically on warming through  $T_N$  ( $x = 0.30$ ) or  $T_C$  ( $x = 0.35$ ). This result, in conjunction with the temperature dependence of the intensity of the AF scattering, implies that near the critical temperature the volume fraction of AF correlated regions is changing, but that the size and longevity of the regions themselves does not change.

We turn now to the polaron correlations. Figures 2(d) and 3(d) show the temperature variation of the scattering intensity for  $x = 0.30$  and  $x = 0.35$  respectively. With no applied magnetic field, the intensity appears rapidly on warming through the critical temperature, with the peak close to  $T_N$  ( $x = 0.30$ ) or  $T_C$  ( $x = 0.35$ ), and decreasing slowly as the temperature is raised further. This behaviour is qualitatively the same as that of the AF

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3 fluctuations. The intensity is similarly suppressed by the application of a 7 T magnetic field  
4 (also figures 2(d) and 3(d)). In the case of  $x = 0.35$ , we also performed a scan as a function of  
5 applied field at  $135 \text{ K} = T_C + 14 \text{ K}$ , which, just like the AF intensity, tracks the field  
6 dependence of  $\rho_{ab}$  (figures 2(e) and 2(g)) [26].  
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#### 10 11 12 13 14 **4. Discussion**

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16 Our results can be summarised as follows: (i) short-range ( $\sim 2 a$ ), short-lived ( $\gamma \sim 0.5 - 4$   
17 meV) AF correlations are a common feature in the bilayer manganites  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ,  
18  $x = 0.30 - 0.40$ , which appear on warming above the three-dimensional magnetic ordering  
19 temperature; (ii) the intensity of the correlations tracks the resistivity both as a function of  
20 temperature and applied magnetic field; (iii) on cooling through  $T_N$  or  $T_C$  the population of  
21 AF correlated regions collapses, but the nature of the regions, as characterised by their extent  
22 and lifetime, does not change; (iv) correlated polarons appear above  $T_N$  ( $x = 0.30$ ) or  $T_C$   
23 ( $x = 0.35$ ), whose temperature and magnetic field dependent scattering intensity likewise  
24 tracks that of the resistivity. The association of both phenomena to the resistivity suggests a  
25 close relation which proceeds via Anderson localisation, as described in our original paper  
26 [19].  
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36 One possibility is that the AF fluctuations (AFF) follow from the atomic arrangements  
37 associated with the polaron correlations (PC). Both break the tetragonal symmetry by  
38 selecting one of the in-plane Mn-Mn directions, the former selecting the direction for AF  
39 correlations of Mn moments, and the latter selecting the direction for modulated elongation of  
40 the Mn-Mn octahedra [21]. However, the wavevectors are different, at 0.5 (AFF) and  
41  $\delta = 0.25 - 0.30$  (PC), but these are not serious discrepancies given that the correlation  
42 lengths,  $< 2 a$  for the AFF, and  $\approx 5-6 a$  for the polarons, are of the same order as the  
43 periodicities implied by the wavevectors at which the fluctuations are peaked. Weak  
44 modulation of the FM bonds along  $(h, 0, 0)$  from modulation of the occupancy of the  $3x^2-r^2$   
45 orbital [21, 22] would result in ferrimagnetic correlations. Alternatively, sufficiently large  
46 modulation of the charge ordering allows for AF interactions along  $(h, 0, 0)$  between Mn sites  
47 that bracket the valence maxima in the charge modulation (due to superexchange between the  
48  $t_{2g}$  electrons), and/or AF interactions along  $(0, k, 0)$  at the valence minima (from application  
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3 of the Goodenough-Kanamori rules for the sign of magnetic exchange integrals in charge-  
4 ordered transition metal oxides [27, 28]).

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7 In the above we have presupposed that the charge and lattice distortions are static and thereby  
8 set the stage for the AF fluctuations. This is actually erroneous because the timescales for the  
9 AF and correlated polaron fluctuation are comparable: the lifetimes of the AF fluctuations at  
10  $T_N$  ( $x = 0.30$ ) or  $T_C$  ( $x = 0.35$ ) are  $\tau \approx 2$  ps and  $\approx 1$  ps respectively ( $\equiv \gamma \approx 0.6 - 1.0$  meV),  
11 while the characteristic timescale quoted for the polaron correlations for  $x = 0.40$  is  $\sim 1$  ps  
12 [20]. The consequence is that the dynamic objects responsible for both the AFF and PC's  
13 must be thought of as either the same bubbles or co-existing bubbles nucleating, decaying  
14 and moving in the MnO planes which are interleaved with the chemically disordered  
15 (La,Sr)O planes. The underlying Born-Oppenheimer approximation notwithstanding, the  
16 previous paragraph provides a starting point for a description where the largest lattice  
17 distortions coincide with antiferromagnetism, resulting in single bubbles.

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20 An alternative possibility to that of the AF fluctuations occurring within regions of correlated  
21 polarons is that they are separate phenomena – for example the AF correlations could be  
22 found at the boundaries between nanodomains of correlated polarons with average size  
23  $\xi \sim 6a$ . Nanoscale inhomogeneity in the manganites is a common phenomenon both  
24 experimentally and theoretically [14]. The coexistence of AF and FM fluctuations above  $T_C$   
25 for  $x = 0.40$  has already been explained as arising from different but adjacent nanovolumes  
26 defined by the static (on the scale of the underlying hopping matrix elements) disorder  
27 potential [19] (see also [29, 30]). In cuprates, phenomena belonging to different co-existing  
28 nearly macroscopic sub-volumes have been observed, for example spatial exclusivity  
29 between polarons and oxygen ordering in oxygen over-doped  $\text{La}_2\text{CuO}_{4+y}$  [31].

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32 There is little qualitative difference in the AF fluctuations and polaron correlations measured  
33 for the three compositions  $x = 0.40, 0.35$  and  $0.30$ . On the other hand, the  $x = 0.30$  material  
34 stands out, as do the superconducting cuprates, in displaying metallic (i.e. resistivity  
35 decreasing with  $T$ ) transport within the bilayers above the ordering temperature even while  
36 the interlayer transport is that of an insulator [18]. The analogy with the cuprates is complete  
37 also below the ordering temperature in the sense that the  $x = 0.30$  manganite becomes (except  
38 at the lowest fields and temperatures) a three-dimensional metal and the cuprates become  
39 three-dimensional superconductors. From scanning tunnelling microscopy and infrared  
40 spectroscopy for  $x = 0.30$ , the out-of-plane resistivity as a function of temperature was  
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3 explained by confinement of mobile polarons within the two-dimensional bilayer sheets, with  
4 hopping between the bilayers requiring their costly deconstruction and reconstruction [32]. In  
5 the language of the localisation problem, the slow fluctuations (seen by magnetic and non-  
6 magnetic neutron scattering as in this paper) in the potential sensed by the polarons formed  
7 around the holes are relatively small on the scale of their effective in-plane hopping  $t_{ab}^{eff}$  and  
8 large on the scale of the interbilayer  $t_c^{eff}$ . Thus, in the high temperature phase, the relation  
9 between the scattering data and electrical transport suggested by strong localisation will  
10 obtain for  $\rho_c$  but not  $\rho_{ab}$ . As the Fermi level and effective hopping terms are changed, for  
11 example by increasing the composition  $x$  from 0.30, both  $t_{ab}^{eff}$  and  $t_c^{eff}$  can become  
12 sufficiently small to confine the motion of the holes in *all three* dimensions, implying that  
13  $\rho_{ab}$  as well as  $\rho_c$  will track the measured scattering intensities in similar ways. Of course,  
14 ferromagnetic ordering, induced by cooling and/or magnetic fields, will - on account of the  
15 double exchange mechanism - enhance the effective hopping so as to defeat Anderson  
16 localization in all three dimensions, leaving only relatively subtle interlayer tunnelling and  
17 weak localization effects to dominate at low temperatures and fields.  
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### 33 **5. Conclusion**

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35 We have shown that the appearance of short-range, short-lived, AF fluctuations on warming  
36 into the paramagnetic phase is a common feature of the bilayered manganites  
37  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ,  $x = 0.30 - 0.40$ . The dependency of the intensity of the AF fluctuations on  
38 both temperature and applied magnetic field closely follows that of  $\rho_{ab}$  and  $\rho_c$  for  $x = 0.35$ ,  
39 and  $\rho_c$  for  $x = 0.30$ . The intensity of the polaron correlations that appear on warming into the  
40 paramagnetic phase also tracks the temperature and magnetic field dependent resistivity. The  
41 possible relationship of the AF and polaron correlations, implied by their association with the  
42 resistivity, is discussed. The observed interplay of static chemical disorder, lattice dynamics  
43 and spin fluctuations presents the type of puzzle which we would have very much enjoyed to  
44 present to Roger Cowley, and which we now offer in his memory.  
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## Figure Captions

Figure 1. Crystal structure of  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ , and scattering intensity maps of the AF fluctuations and polaron correlations for  $x = 0.35$ , at temperatures just above  $T_C \equiv 121$  K, and close to room temperature. (a)  $\text{MnO}_6$  octahedra are shown in orange; the green circles correspond to La and Sr. (b) The local, instantaneous, arrangement of magnetic moments in the antiferromagnetically correlated regions in a bilayer. Note that the data determine the antiferromagnetic ordering wave vector, but not the direction of the magnetic moments; they are drawn in-plane here but could equally be perpendicular to the plane of the bilayers as was drawn in figure 1(c) of [19]. (c) The spectrum of the magnetic fluctuations as a function of energy,  $\varepsilon$ , and momentum along  $(h, 0, 0)$  at 125K and (d) 275K, showing the short-range, short-lived AF fluctuations centred at  $h = 0.5$  and zero energy. The spectra were determined by taking the difference between the measured intensity maps along the  $(h, 0, 0)$  and  $(h, h, 0)$  directions, collected in parallel in different detector banks of the HET spectrometer. Except close to (000), the intensity along  $(h, h, 0)$  is almost independent of momentum, and arises from non-magnetic scattering by the sample and container. (e) Energy-integrated scattering (the spectrum of the moderator used peaks at  $\approx 10$  meV) taken on the PRISMA diffractometer as a function of momentum in the  $(h, 0, l)$  plane for 135K and (f) 250K, determined by taking the difference between the measured intensities at those temperatures and that at 10K ( $\ll T_C$ ), the lowest temperature measured. The scattering from polaron correlations is centred at  $(\sim 2.3, 0, \pm 1)$ , and the Huang scattering is centred around (200). The arcs of intensity centred on (000) arise from powder diffraction from the aluminium sample holder and heat shields on the cryogenic equipment. The incomplete subtraction of the arcs is due to changes in the Debye-Waller thermal factor, as is that at the (200) and (202) Bragg positions. (g) Map of scattering intensity in the  $(h, k, 0)$  plane integrated over the energy range  $-5 \leq \varepsilon \leq 5$  meV for  $T = 126$ K. The non-magnetic scattering and background has been removed by subtracting data collected at 6K ( $\ll T_C$ ).

Figure 2. Summary of magnetic and polaron scattering intensities, and resistivity, for  $x = 0.35$ : (a) Magnetic order parameter squared for  $x = 0.35$  as determined by the (004) Bragg peak intensity. The almost constant value at  $T > \sim 120$ K arises from the structural (i.e. non-magnetic) Bragg peak. (b) In-plane and out-of-plane resistivities,  $\rho_{ab}$  and  $\rho_c$ , at 0 T and 7 T.

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3 (c) Magnetic scattering centred on the AF reciprocal lattice position as a function of  
4 temperature, obtained by integrating the measured energy-momentum intensity maps over  
5  $0.35 \leq h \leq 0.65$  and  $-15 \leq \epsilon \leq 15$ , and subtracting the lowest temperature at which data were  
6 gathered, which arises solely from non-magnetic scattering from the sample and cryogenic  
7 equipment. (d) Intensity of the energy-integrated scattering from polaron correlations around  
8  $(2+\delta, 0, \pm 1)$ ,  $\delta = 0.275$ , as a function of temperature, obtained by taking the section  
9  $2.15 \leq h \leq 2.40$  from the intensity maps in the  $(h, 0, l)$  plane, fitting the resulting function of  
10  $l$  to a pair of peaks centred at  $l \approx \pm 1$  on a linear background, and adding the two peak areas.  
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12 (e)  $\rho_{ab}$  and  $\rho_c$ , (f) magnetic scattering and (g) scattering from polaron correlations, as a  
13 function of applied magnetic field.  
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25 Figure 3. Summary of magnetic and polaron scattering intensities, and resistivity, for  
26  $x = 0.30$ : (a) Magnetic order parameter squared for  $x = 0.30$  as determined by the (005)  
27 magnetic Bragg peak intensity. The unusual shape is due to the fact that the spins rotate from  
28 perpendicular to the plane of the bilayers for  $T \ll T_N$  to lying within the bilayers as  $T$   
29 approaches  $T_N$  [33] (b) In-plane and out-of-plane resistivities,  $\rho_{ab}$  and  $\rho_c$ , at 0 T and 7 T. (c)  
30 Magnetic scattering centred on the AF scattering position as a function of temperature,  
31 obtained by the same procedure as for  $x = 0.35$  described in the caption for figure 2(c). (d)  
32 Intensity of the energy-integrated scattering from polaron correlations around  $(2+\delta, 0, \pm 1)$ ,  
33  $\delta = 0.25$ , as a function of temperature, obtained by the same procedure as for  $x = 0.35$   
34 described in the caption for figure 2(d), except that  $2.12 \leq h \leq 2.37$ .  
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46 Figure 4. Cuts as a function  $\delta h$  in  $(2+\delta h, 0, 1)$  through the polaron correlation peaks at  
47  $(2+\delta, 0, 1)$  to determine the incommensurate ordering wavevector,  $\delta$ , (a) for  $x = 0.35$   
48 ( $T = 135$  K), showing  $\delta = 0.275$ , and (b) for  $x = 0.30$  ( $T = 100$  K), showing  $\delta = 0.25$ .  
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55 Figure 5. Intensity of the AF fluctuations as a function of  $\log(\rho_{ab})$ . The 0T data, 7T and field-  
56 scan data taken at 127K, taken from figure 2(c) and figure 2(f), are indicated by the blue, red  
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3 and yellow symbols respectively. The line is the result of a linear regression to the data  
4 points.  
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10 Figure 6. (a) Sections from the intensity maps gathered for  $x = 0.35$  in figure 1(c) and  
11 figure 1(d) as a function of  $\varepsilon$  integrated over  $0.35 \leq h \leq 0.65$ , and (b) as a function of  $h$   
12 integrated over  $-5 \leq \varepsilon \leq 5$ . The lines show the result of fits to the model described in the text.  
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14 (c) Correlation length  $\xi$ , and (d) inverse lifetime  $\gamma \equiv 1/\tau$  for  $x = 0.35$  (circles, blue) and  
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16  $x = 0.30$  (triangles, red). Error bars are smaller than the symbols except where shown.  
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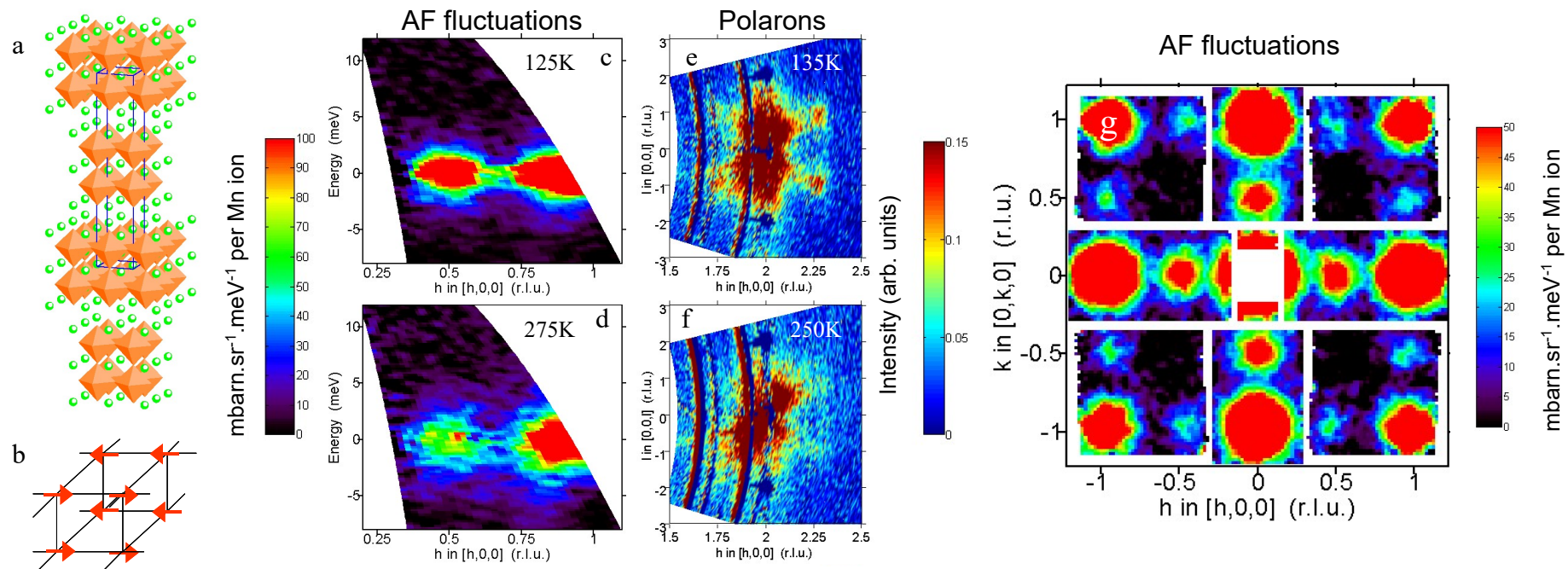


Figure 1 (Perring et. al.)

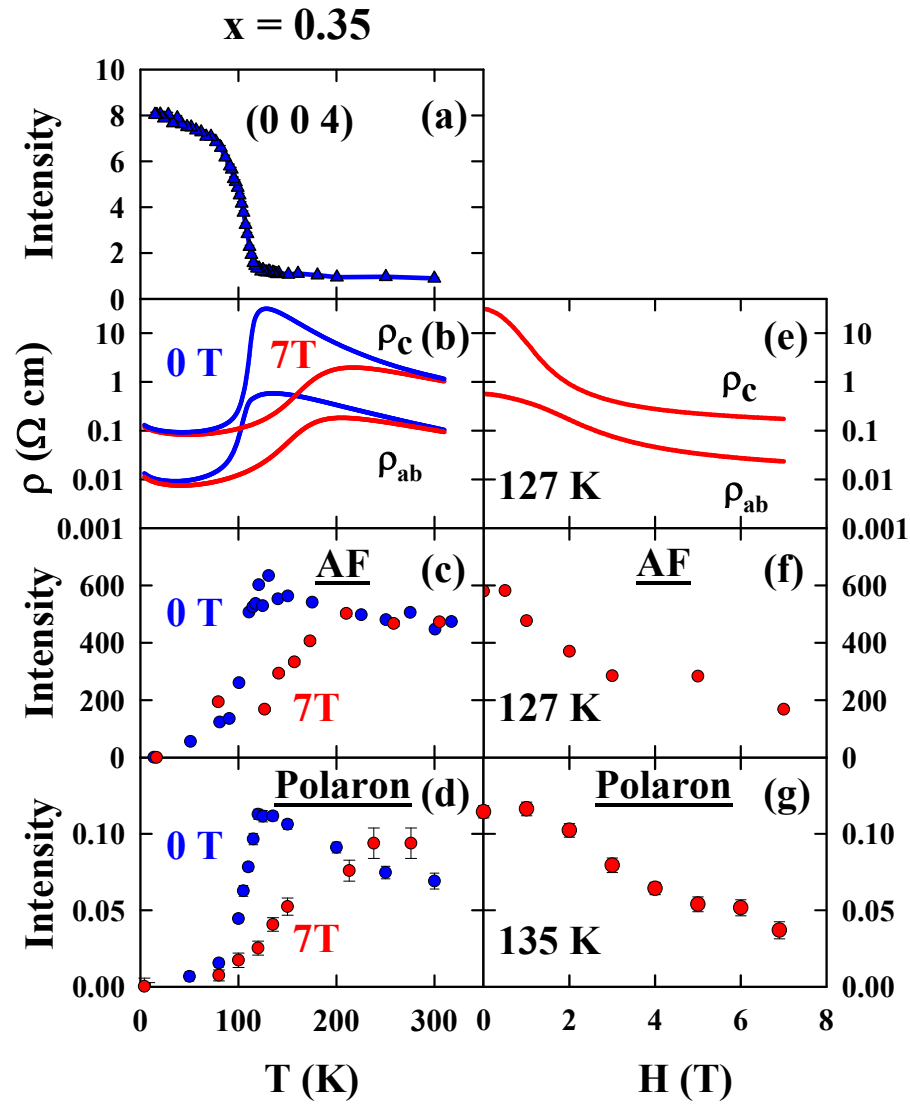


Figure 2 (Perring et. al.)

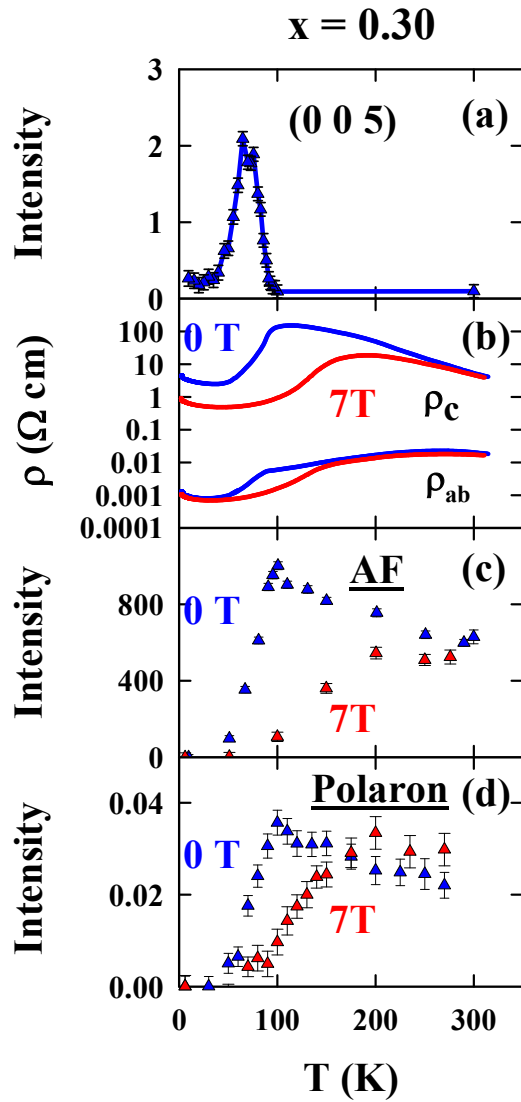


Figure 3 (Perring et. al.)

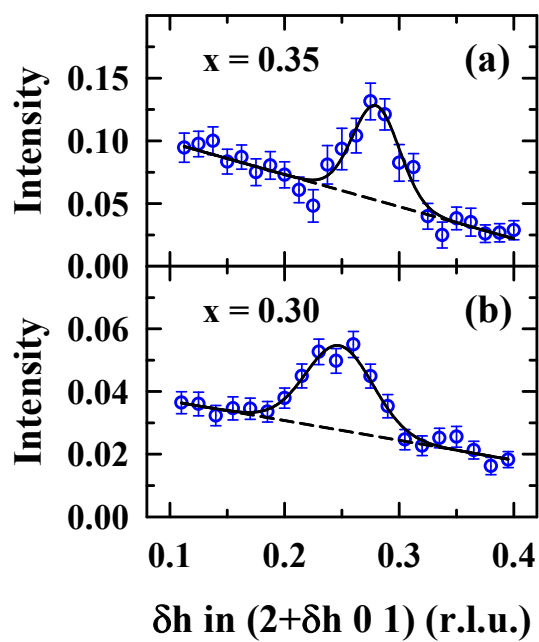


Figure 4 (Perring et. al.)

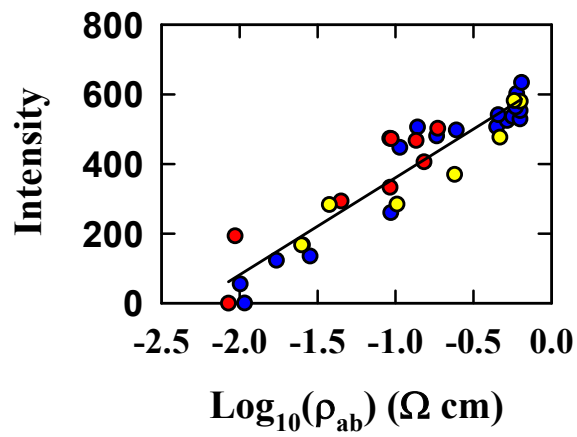


Figure 5 (Perring et. al.)

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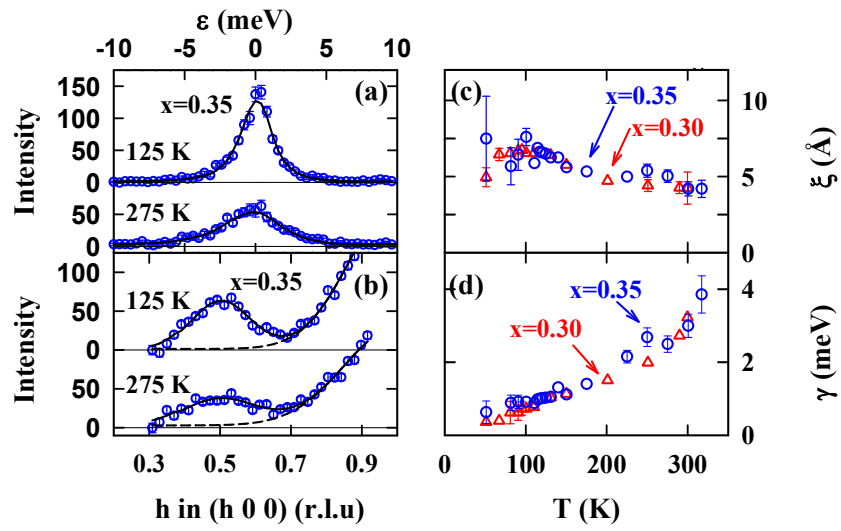


Figure 6 (Perring et. al.)