Pressure-Enhanced 3D Antiferromagnetic Correlations in $La_{1.4}Sr_{1.6}Mn_2O_7$

K. V. Kamenev,[1] G. J. McIntyre,[2] Z. Arnold,[3] J. Kamarád,[3] M. R. Lees,[4]
G. Balakrishnan,[4] E. M. L. Chung,[4] and D. McK. Paul[4]

[1]*Department of Physics and Astronomy, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom*
[2]*Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France*
[3]*Institute of Physics AS CR, Cukrovarnická 10, 162 53 Praha 6, Czech Republic*
[4]*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*

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Pressure effects on the stability of magnetic phases in $La_{1.4}Sr_{1.6}Mn_2O_7$ have been studied using magnetization measurements and neutron diffraction. At ambient conditions this material is a quasi-two-dimensional ferromagnet. On cooling it becomes ordered three dimensionally: at 90 K $La_{1.4}Sr_{1.6}Mn_2O_7$ it becomes an antiferromagnet, and at 65 K it undergoes a transition into a ferromagnetic phase. Using neutron diffraction techniques on a single crystal of $La_{1.4}Sr_{1.6}Mn_2O_7$ it has been shown that these two magnetic phases belong to a single structural phase and do not coexist at low temperatures. The application of pressure enhances the antiferromagnetic correlations between the Mn_2O_9 bilayers.

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Doped manganites with the Ruddlesden-Popper structure [1] have recently attracted considerable interest due to their "colossal" magnetoresistance (CMR) [2,3]. The general formula of the bilayered manganites is $R_{2-2x}A_{1+2x}Mn_2O_7$ (R is a rare-earth ion and A is a divalent cation) and the lattice consists of paired MnO_2 sheets (bilayers) separated by $(R, A)_2O_2$ layers. One of the first members of the layered manganite series, in which the CMR was discovered, was $La_{1.4}Sr_{1.6}Mn_2O_7$ [2]. This material shows a 1000-fold change in electrical resistivity at 50 kOe change from zero field at temperatures just above the three-dimensional (3D) ordering temperature of 90 K.

Despite the extensive structural, magnetic, and electronic studies of this compound in recent years, there is no single opinion among researchers on the magnetic and structural phase diagram of this material. However, all the studies agree that in $La_{1.4}Sr_{1.6}Mn_2O_7$ the pairing of the magnetic moments on the Mn sites within each bilayer is always parallel. As for the interbilayer coupling, two types of long-range 3D magnetic order have been reported for this material: tilted antiferromagnetic (3D-AF) and canted ferromagnetic (3D-FM). They are schematically presented in Fig. 1.

An initial study by Kimura *et al.* [2] reported that $La_{1.4}Sr_{1.6}Mn_2O_7$ undergoes a series of magnetic phase transitions. At temperatures below ~270 K the magnetic moments on the Mn sites are coupled ferromagnetically within each bilayer. The in-plane exchange is much stronger than the interbilayer exchange interaction and $La_{1.4}Sr_{1.6}Mn_2O_7$ is a quasi-two-dimensional ferromagnet (2D-FM). At about 100 K the interbilayer exchange becomes strong enough to support 3D coupling between the bilayers. Kimura *et al.* reported that this 3D phase is ferromagnetic (3D-FM) as shown in Fig. 1(a) [2]. This conclusion is supported by a neutron diffraction study performed by Louca *et al.,* who observed a phase transition from a paramagnetic state with short-range antiferromagnetic correlations to a 3D ferromagnetic phase at 116 K [4]. However, the neutron diffraction study of Perring *et al.* has shown that when the 3D ordering occurs the adjacent bilayers couple antiferromagnetically (3D-AF) as illustrated in Fig. 1(b) [5]. They observed the 3D-AF phase to appear at about 90 K and to remain stable down to liquid helium temperatures.

Another powder diffraction study performed by Argyriou *et al.* [6] has shown that $La_{1.4}Sr_{1.6}Mn_2O_7$ undergoes two phase transitions at low temperatures. The transition to the 3D-AF phase occurs at about 100 K. This phase

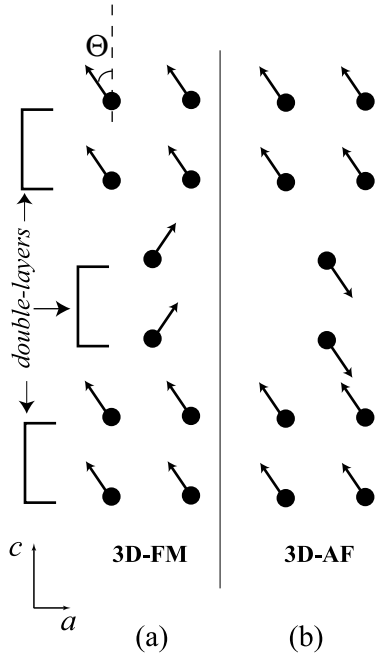

FIG. 1. Schematic diagram of the two types of long-range order observed in $La_{1.4}Sr_{1.6}Mn_2O_7$: (a) 3D-FM and (b) 3D-AF. Adjacent bilayers are displaced by $b/2$ in the tetragonal $I4/mmm$ space group, in addition to the $a/2$ shown.

is stable down to 5 K. The phase transition to the 3D-FM state occurs at about 75 K and corresponds to the development of a ferromagnetic component along the fourfold c axis. Below 75 K the 3D-AF and 3D-FM phases coexist. The authors explain such a coexistence by ascribing the two magnetic phases to two $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.3 \leq x \leq 0.32$) structural phases with slightly different lattice parameters.

Both of the 3D magnetic phases were found in $La_{1.4}Sr_{1.6}Mn_2O_7$ by Kubota *et al.* in a neutron powder diffraction experiment [7]. However, no coexistence of 3D-AF and 3D-FM was observed. They observed the 3D-AF phase to exist in a narrow temperature interval from 100 to 70 K. At 70 K the magnetic phase changed to the 3D-FM phase with magnetic moments aligned close to the c axis. Although no extra structural phase in the studied sample was reported, Kubota *et al.* concluded that there exists a boundary in the composition-temperature diagram at $x = 0.30-0.32$, and that a more detailed study with a good-quality single crystal was needed in order to clarify the magnetic structure for $La_{1.4}Sr_{1.6}Mn_2O_7$ [7]. In this Letter we present the results of such a single-crystal neutron-diffraction experiment together with dc magnetization measurements, both under pressure.

Single crystals of $La_{1.4}Sr_{1.6}Mn_2O_7$ were grown by the floating-zone method. A miniature hydrostatic pressure cell made of nonmagnetic CuBe alloy was used for magnetization measurements in a SQUID magnetometer (Quantum Design Ltd.). The magnetization has been measured under pressures up to 7 kbar at temperatures from 5 to 300 K. The neutron diffraction studies were performed on the single-crystal diffractometer D10 at the Institut Laue-Langevin. Ambient pressure measurements were conducted in a four-circle helium-flow cryostat. For high-pressure studies we used a standard ILL "Orange" cryostat and a pressure cell with gaseous helium as the pressure-transmitting medium.

The temperature dependence of the magnetization measured along the fourfold axis at pressures of 0, 3.7, and 7.0 kbar is shown in Fig. 2. At ambient pressure we observed an increase in magnetization starting at about 100 K. The phase transition is smeared over a temperature range between 80 and 110 K. However, the observed behavior is similar to the phase transition reported by Kimura *et al.* [2] and we have assumed that this is the phase transition from the 2D-FM to the 3D-FM phase. Surprisingly, under an applied pressure of 3.7 kbar the transition becomes visibly broader, and for 7.0 kbar it splits into two transitions with a clear break in the slope of the magnetization curve at $T = 100$ K. It is, however, difficult to draw a conclusion from these magnetization measurements alone about the nature of the observed pressure effect on the magnetic properties of $La_{1.4}Sr_{1.6}Mn_2O_7$.

To clarify the nature of these transitions we have studied the magnetic phase diagram using neutron diffraction. At ambient conditions $La_{1.4}Sr_{1.6}Mn_2O_7$ behaves as a two-

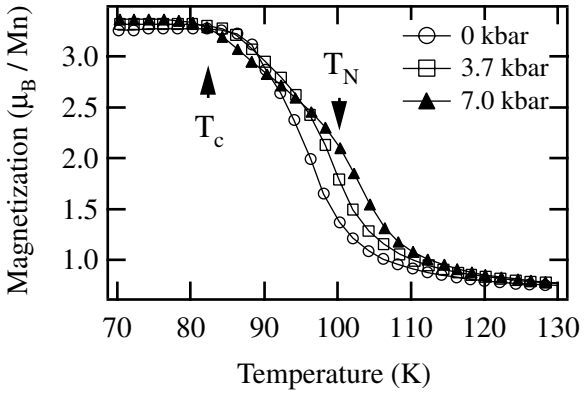

FIG. 2. Temperature dependence of the dc magnetization of $La_{1.4}Sr_{1.6}Mn_2O_7$ measured along the c axis with increasing temperature in 100 Oe at different pressures.

dimensional magnet. Recent inelastic neutron-scattering experiments have revealed that the coupling between the magnetic moments in the bilayers is ferromagnetic [8]. In an elastic neutron-scattering experiment such a short-range order would be seen as a rod-shaped diffuse scattering parallel to the $\overline{c}^*$ axis. We performed Q scans along the $[01l]$ rod at several temperatures and observed maxima at $l = 0$, 5, and 10, which indeed indicates the presence of 2D-FM correlations in the bilayers. We observed 2D-FM correlations over the studied temperature range at ambient pressure. Even at low temperatures they are not completely suppressed by the 3D long-range order, and they are still present at the highest available temperature of 340 K, which is nearly four times the 3D ordering temperature.

The refinement of the neutron diffraction data has confirmed that the structure is tetragonal with space group $I4/mmm$ and lattice parameters $a = 3.851(4)$ Å and $c = 20.243(9)$ Å at ambient conditions. The symmetry remains unchanged throughout the studied pressure and temperature regions.

The temperature dependence of some magnetic reflections characteristic of the possible magnetic structures found in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series [7] during heating runs at various pressures is presented in Fig. 3. At about 90 K we observed nonzero intensity in the (111), (001), (003), and (005) reflections. The (005) reflection is shown in Fig. 3(a); the (001) and (003) reflections have a similar temperature dependence. The (005) reflection arises from ferromagnetic coupling of the magnetic moments in each bilayer, while the (001) and (003) reflections correspond to antiferromagnetic coupling between the adjacent bilayers. The (111) reflection represents a combination of these two interactions. Therefore, the magnetic order corresponds to the 3D-AF arrangement of magnetic moments shown in Fig. 1(b). As the temperature is lowered from $T_N = 90$ K to 75 K, the intensity of the reflections increases continuously, implying strengthening of the long-range 3D coupling between adjacent bilayers. Refinement of the

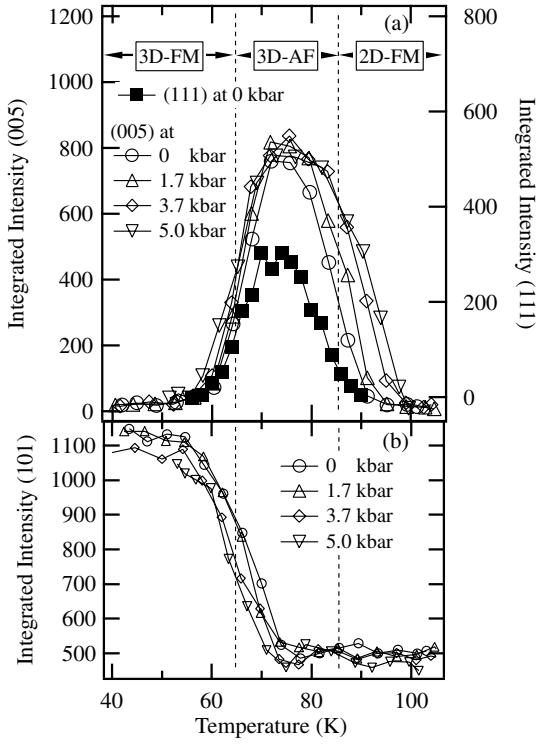

FIG. 3. Temperature dependence of the integrated intensities of (005) (a) and (101) (b) and reflections (heating) of $La_{1.4}Sr_{1.6}Mn_2O_7$ at pressures of 0, 1.7, 3.7, and 5.0 kbar. The dashed lines indicate the phase boundaries at 0 kbar. The integrated intensity of (111) peak at ambient pressure is shown in (a).

magnetic structure against extensive diffraction data collected at 75 K showed that the ordered magnetic moment is $2.8\mu_B$ per Mn site and that the moments are tilted at about 60° to the c axis.

Below 75 K the intensity of the 3D-AF peaks starts to decrease [Fig. 3(a)]. At the same time we observe an increase in the intensity of the (101), (103), and (105) nuclear reflections. The (101) reflection is shown in Fig. 3(b); the (103) and (105) reflections have a similar temperature dependence. The extra intensity corresponds to the magnetic scattering due to ordered magnetic moment along the c axis. The absence of (002), (004), and (006) reflections allowed us to exclude the possibility of existence of the ferromagnetic phase with a component of the total magnetic moment in the ab plane. Therefore, we can conclude that below $T_c = 75$ K we observe a phase transition into the 3D-FM phase shown schematically in Fig. 1(a). The 3D-AF to 3D-FM transition is complete by 50 K. The (111) peak also disappears, signaling the removal of the AF ordering along the c axis. In earlier powder diffraction studies this peak was found to exist down to lower temperatures [6]. We emphasize that the correspondence between the disappearance of the 3D-AF phase and the appearance of the 3D-FM phase indicates that these magnetic phases belong to a single structural phase in the $La_{1.4}Sr_{1.6}Mn_2O_7$ crystal. We observed no additional peaks that might be attributed to another phase in our limited but nonetheless large survey of reciprocal space with the position-sensitive detector.

The refinement against extensive diffraction data collected at 7 K shows that the total ordered magnetic moment is $3.4\mu_B$ per Mn site and that the moments are canted at 8° to the c axis [Θ angle, Fig. 1(a)]. The observed moment is in good agreement with the calculated value of $3.7\mu_B$ per Mn site for this composition.

After we had established the sequence of the magnetic phase transitions at ambient pressure, we transferred the sample into a high-pressure cell and studied the phase diagram during the cooling and heating runs at pressures of 0, 1.7, 3.7, and 5.0 kbar. We chose the (005) [Fig. 3(a)] and (101) [Fig. 3(b)] as the strongest characteristic reflections for monitoring the magnetic phase transitions. We have defined the temperatures T_N and T_c of the 2D-FM to 3D-AF and the 3D-AF to 3D-FM transitions, respectively, by the midpoint of the slope in the temperature dependencies of the integrated intensities. The results of the temperature variations at various pressures are summarized in the pressure-temperature (P-T) phase diagram presented in Fig. 4. A linear fit of the data in Fig. 4 gave the following values for the slopes of the transition temperatures T_N and T_c: $dT_N/dP = 2.1$ K/kbar and $dT_c/dP = -0.4$ K/kbar. Thus, increasing applied pressure makes the 3D-AF phase more stable with respect to the other two magnetic phases found in $La_{1.4}Sr_{1.6}Mn_2O_7$. This has also been observed in the magnetization measurements (Fig. 2).

Applied pressure of up to 7 kbar has little effect on the low-temperature 3D-FM order. Refinement against extensive neutron diffraction data collected in a zero magnetic field at $T = 7$ K and $P = 5$ kbar has shown that the total ordered magnetic moment is unchanged: $3.4\mu_B$ per Mn

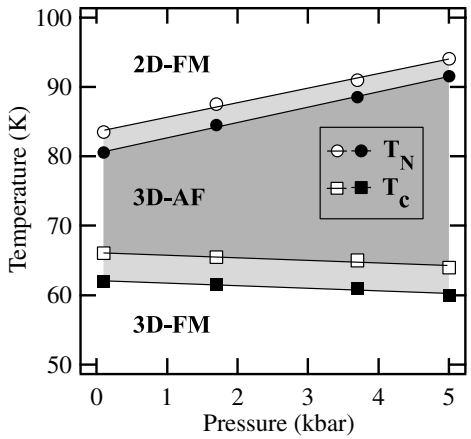

FIG. 4. Magnetic pressure-temperature phase diagram of $La_{1.4}Sr_{1.6}Mn_2O_7$. Open symbols correspond to the phase transitions detected during the heating runs while filled symbols mark the phase transitions observed on cooling. Light-shaded areas between filled and opened symbols represent the regions of temperature hysteresis.

site. The moments are canted at an angle Θ of about 11° [Fig. 1(a)], i.e., at a slightly larger angle than at the same temperature at ambient pressure. Magnetization measurements in the field of 100 Oe showed no change in the value of the magnetization below T_c for pressures up to 7 kbar (Fig. 2).

Let us now compare the pressure-induced changes in the magnetic properties of $La_{1.4}Sr_{1.6}Mn_2O_7$ with the effect on the behavior of the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series of chemical pressure, introduced by Sr doping. We will contrast the P-T phase diagram (Fig. 4) with the magnetic x-T phase diagram for the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series [7]. Increasing the Sr content from $x = 0.30$ leads to the disappearance of the 2D-FM to 3D-AF transition at $x \approx 0.31$ [7]. To explain this change in magnetic properties induced by Sr doping, we need to link the charge distribution and spin dynamics of the localized magnetic moments on the Mn sites. Within the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series the concentration of electrons increases with increasing x. The doped electrons occupy the e_g orbitals of the manganese ions, since the lower energy t_{2g} triplet is already half filled. It has been found that due to the Jahn-Teller distortion of MnO_6 octahedra the e_g level splits into two orbital states: $3d_{x^2-y^2}$ (in the ab plane) and $3d_{3z^2-r^2}$ (along the c axis). For the lightly doped members of the series ($x \approx 0.3$) the electrons prefer to occupy $3d_{x^2-y^2}$ states, while for higher levels of Sr doping they tend to occupy the $3d_{3z^2-r^2}$ state [9]. Comparing this difference in the occupation of the e_g level with the magnetic properties of the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ series [7,9,10], we can conclude that the decrease in x leads to the transfer of electrons from the $3d_{3z^2-r^2}$ to the $3d_{x^2-y^2}$ orbitals, accompanied by a shortening of the apical Mn-O bond [11]. This in return enhances the 3D-AF coupling.

A similar scenario is valid when external pressure is applied. Ishihara *et al.* have recently performed numerical calculations [12], which show that externally applied pressure controls the dimensionality of the spin and charge dynamics through changes of the orbital states. It has been shown that, by compressing the apical Mn-O bonds, applied pressure brings the bilayers closer to each other, and stabilizes the in-plane orbital through electron transfer from $3d_{3z^2-r^2}$ to $3d_{x^2-y^2}$ [9,12]. The higher occupancy of the $3d_{x^2-y^2}$ level favors the 3D-AF type of interbilayer coupling (Fig. 1b).

This is what we observe in $La_{1.4}Sr_{1.6}Mn_2O_7$. The effect of pressure is twofold. First, it brings the bilayers closer together due to the large compressibility of the interbilayer spacing in comparison to the low compressibility of the bilayers themselves. Second, applied pressure enhances the Jahn-Teller distortion of the MnO_6 octahedra, which is caused by the greater compressibility of the apical Mn-O bonds. Both of these effects promote 3D-AF coupling between adjacent bilayers.

In conclusion, we have studied the effect of external pressure on the magnetic properties of $La_{1.4}Sr_{1.6}Mn_2O_7$ using magnetization and neutron diffraction measurements. At ambient conditions, this material is a quasi-two-dimensional ferromagnet (2D-FM). The range of existence of the 2D-FM phase extends to the highest studied temperature of 340 K. At temperatures below 90 K, $La_{1.4}Sr_{1.6}Mn_2O_7$ undergoes two magnetic phase transitions: first to an antiferromagnetic (3D-AF) and then to a ferromagnetic (3D-FM) state. Our observations show that the 3D-AF and 3D-FM phases actually belong to the same structure and do not occur as a result of any structural phase segregation, as has been reported elsewhere. We suggest that the earlier observations of coexistence and phase segregation are due simply to very small compositional variations around a steep boundary in the composition-temperature phase diagram. We have also found that applied pressure induces the electron transfer from the out-of-plane to the in-plane orbital in Mn, which enhances the 3D-AF order and enlarges the area occupied by the 3D-AF phase on the pressure-temperature diagram.

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