Mn magnetic ordering in fully oxygenated $Lu_{1-x}Sc_xMnO_3$ (x=0, 0.5, and 1)

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The magnetic properties of fully oxygenated hexagonal $Lu_{1-x}Sc_xMnO_3$ (x=0, 0.5, and 1) have been investigated by means of neutron diffraction and ac magnetization measurements. All three compounds crystallized into a hexagonal symmetry of space-group $P6_3$cm. No structural changes were observed between 10 and 300 K. Anomaly of antiferromagnetic characters was observed at ~90, 95, and 126 K for the x=0, 0.5, and 1 compounds, respectively, in the temperature dependence of the ac magnetic susceptibility, signaling the ordering of the Mn spins. Both the ferromagnetic and antiferromagnetic components, associated with the Mn spins, were revealed in the low-temperature neutron magnetic diffraction patterns. The observed magnetic intensities are consistent with a magnetic structure that can be described by using the Kovalev Γ_5 irreducible representation, where the Mn moments lie in the basal MnO_2 planes and the couplings between the adjacent MnO_2 planes are ferromagnetic, with a saturated moment of $\langle\mu_z\rangle$=3.22(3)μ_B and 3.15(3)μ_B for the x=0 and 0.5 compounds, respectively. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1846372]

It is known that when smaller ions, such as Lu and Sc, are incorporated into the rare-earth lattice of the colossal magnetoresistance (CMR) perovskite-type manganites $RMnO_3(R$=rare-earth ions), the system crystallizes into a hexagonal structure, where the Mn atoms form a triangular lattice and each of the Mn atoms is surrounded by three in-plane and two apical oxygen ions. Antimagnetic and ferroelectric orders have been observed in this class of materials.[1,2] The magnetic properties of the systems arise from the $Mn^{3+}(3d^4)$ ions, with spin S=2, and they are ideal systems for the study of the triangular antiferromagnetic coupling.[3] Frequently, the Mn moments order antiferromagnetically and occur between 70 and 130 K.[4,5] In this paper, we report on the results of studies made on the magnetic properties of $Lu_{1-x}Sc_xMnO_3$.

Three polycrystalline samples of $Lu_{1-x}Sc_xMnO_3$ (x=0, 0.5, and 1) were prepared by employing the standard solid-state reaction techniques using a sintering temperature of 1100 °C for 48h. The resultant compounds were characterized by complete structural analyses using x-ray powder-diffraction measurements. The diffraction patterns were analyzed by using the general structure analysis system (GSAS) program, following the Rietveld method. The observed diffraction patterns for all three compounds can be described very well by the hexagonal $P6_3cm$ symmetry reported[1] for $LuMnO_3$. No unexpected peaks are present in the diffraction patterns for all three compounds, showing that they are single phase up to within the 4% x-ray resolution limitation. Careful analysis of the occupancy factors shows that the O

sites are fully occupied and the chemical compositions are consistent with the stoichiometric ones.

In searching for magnetic signals, ac magnetic susceptibility and neutron magnetic diffraction measurements were performed, employing standard setups. The temperature dependencies of the in-phase component of the susceptibility, $\chi'(T)$, for all three compounds are shown in Fig. 1. Whereas the effects of an applied dc magnetic field, H_a, on $\chi'(T)$ for the x=0.5 and 1 compounds are plotted in Figs. 2(a) and 2(b), respectively. The magnetic responses become stronger in compound with a higher Sc concentration, as can be seen in Fig. 1. Three anomalies, that response differently to an H_a, may be identified for each compound. Firstly, the anomaly marked as T_{m1} in Fig. 2 was essentially not affected by the
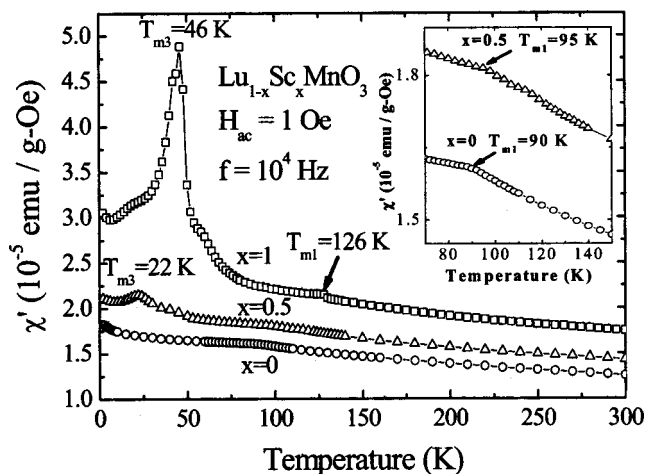

FIG. 1. The temperature dependencies of the in-phase components of the ac magnetic susceptibility for all three compounds.

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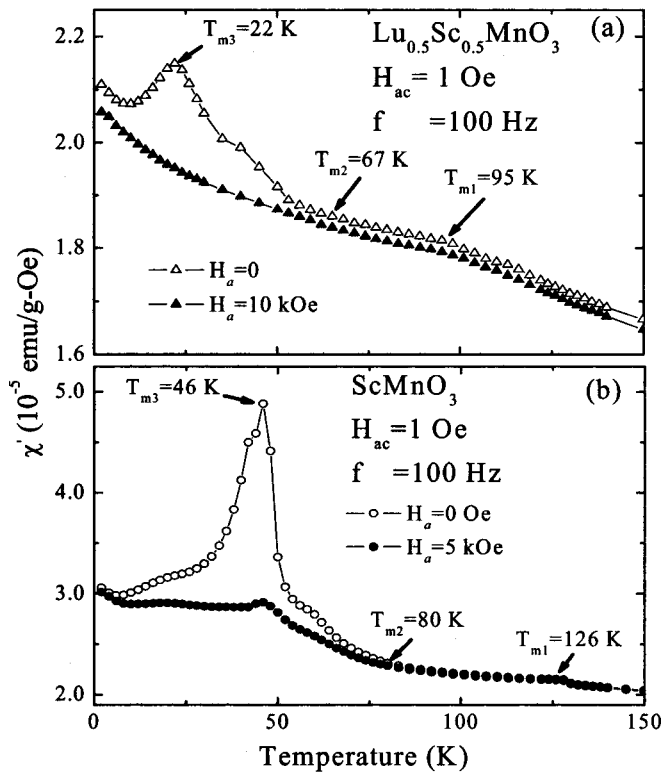
FIG. 2. Effects of an applied magnetic field on $\chi'(T)$ for the (a) $x=0.5$ and (b) $x=1$ compounds. It appears that the magnetic responses marked as T_{m3} are largely suppressed by the applied field.

FIG. 3. The magnetic diffraction pattern of the (a) $x=0$ compound obtained at 1.6 K and (b) $x=0.5$ compound obtained at 10 K.

H_a, which is associated with the ordering of the Mn moments and appears at a higher temperature in a system of higher Sc concentration (see the inset to Fig. 1). It appears that the magnetic couplings between the Mn ions, which are believed to be mediated through the O ions located between them, are stronger in the Sc compound than in the Lu compound. This characteristic is understandable, since the Mn–O–Mn bond lengths in the Sc compound are noticeably shorter than that in the Lu compound. Note that the ionic radius of Sc(~ 0.73 Å) is much smaller than that of Lu (~ 0.85 Å). Secondly, the anomaly marked as T_{m2}, which is not seen in the Sc-free compound, is seen to be noticeably affected by the H_a. Neutron-diffraction measurements (see below) show that it is associated with the reorientation of the Mn spin arrangement. Thirdly, although the anomaly marked as T_{m3} is the main feature perceivable in the H_a-free $\chi'(T)$ plot, it, however, is strongly suppressed by the H_a and appears at a higher temperature in a system of higher Sc concentration. The origin of the anomaly is not clear to us at the present time and may be associated with the fluctuations of the Mn spins. Note that the magnetic interaction in ScMnO$_3$ has been suggested to be dominated by the Dzyaloshinsky[6] and Moruya[7] interaction, which is anisotropic in nature and influenced by an H_a may be anticipated.

The neutron magnetic diffraction measurements were carried out at the NIST Center for Neutron Research using the BT-7 triple-axis spectrometer and employing a standard setup for magnetic diffraction. The magnetic diffraction patterns obtained for the $x=0$ compound at 1.6 K and for the $x=0.5$ compound at 10 K are plotted in Figs. 3(a) and 3(b),
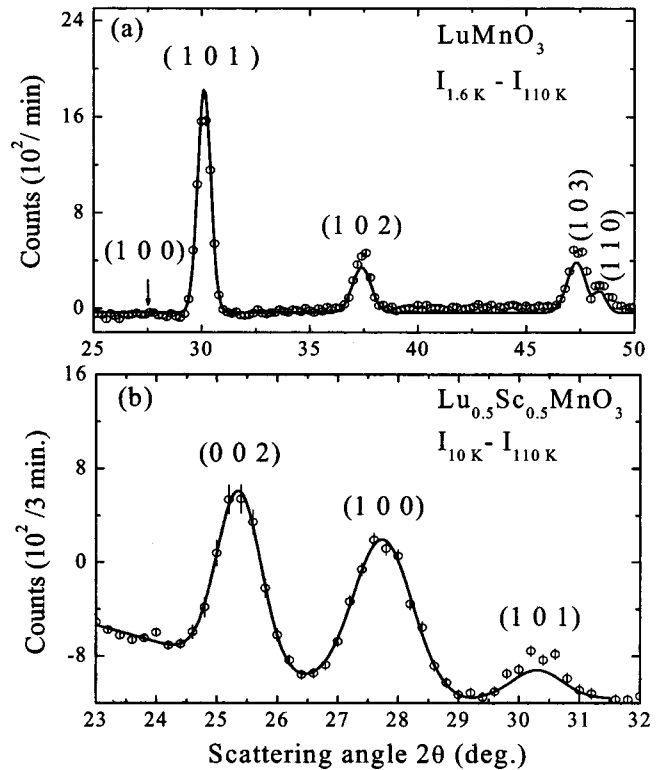
respectively, where the peak indices shown are based on the nuclear unit cell. These resolution-limited peaks developed at low temperatures are associated with the ordering of the Mn moments, and they appear at the positions as the nuclear ones. The relative magnetic intensities of the $x=0$ and of the $x=0.5$ compounds are significantly different, showing that the spin structure for the two compounds are quite different. A simple ferromagnetic arrangement for the Mn spins fits very poorly to the observed intensities and cannot be used to explain the observed $\chi'(T)$ discussed above, signaling the existence of antiferromagnetic components for the Mn moments in both compounds.

Displayed in Figs. 4(a) and 4(b) are the temperature dependencies of the peak intensities of the representative magnetic reflections, which are known as the order-parameter curves, for the $x=0$ and 0.5 compounds, respectively. The ordering temperatures of the Mn moments, determined from the inflection point of the order-parameter curves, are $T_N \approx 90$ and 95 K for the $x=0$ and 0.5 compounds, respectively. These ordering temperatures that we obtained agree well with a separate study.[8] On reducing temperature to below 67 K, the {100} intensity decreases which is accompanied by a further increase of the {101} intensity for the $x=0.5$ compound, as shown in Fig. 4(b). These behaviors are characteristics of spin reorientation, which was not observed in the $x=0$ compound. This reorientation of the Mn spins has also been observed in HoMnO$_3$ (Ref. 5) and ScMnO$_3$,[9] and is believed to be due to the thermal instability of the triangular antiferromagnetic coupling.

There are six formula units per crystalline unit cell in the hexagonal RMnO$_3$, where three of the six Mn ions are lo-
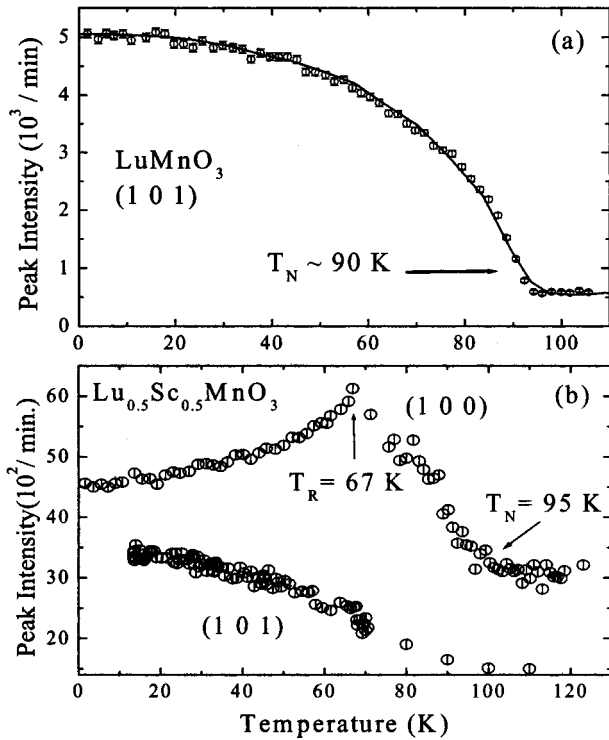
FIG. 4. Temperature dependencies of the representative magnetic reflections for the (a) $x=0$ and (b) $x=0.5$ compounds, showing ordering temperatures for the Mn moments of $T_N \approx 90$ and 95 K for the $x=0$ and 0.5 compounds, respectively. A spin reorientation occurs below 67 K for the $x=0.5$ compound is also evident.

cated in the $z=0$ layer while the other three in the $z=1/2$ layer. The Mn ions in each layer form a triangular lattice with the lattice orientations in the $z=0$ and in the $z=1/2$ layers are 60° apart. The possible magnetic structures for this type of lattice have been considered thoroughly by Muňoz *et al.*[9] We went through all the possible models and found that the observed magnetic intensities are consistent with the magnetic structure, where the Mn moments lie in the basal MnO_2 planes, with the nearest Mn moments in each layer are 120° apart, and the couplings between the adjacent MnO_2 planes are ferromagnetic for the $x=0$ compound and antiferromagnetic for the $x=0.5$ compound, as shown in Figs. 5(a) and 5(b), respectively. Unfortunately, the specific moment direction in the a-b plane cannot be determined from our powder data due to the similarity between the a and b axes. The low-temperature saturated moment is $\langle \mu_z \rangle = 3.22(3)\mu_B$
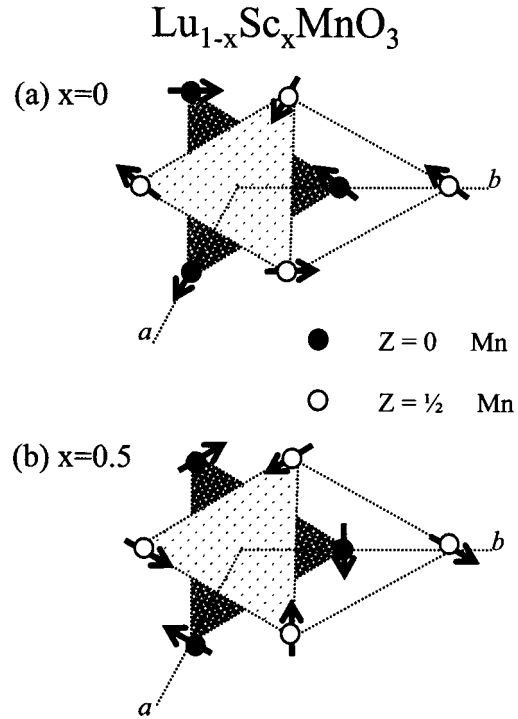

FIG. 5. The proposed magnetic structures of the Mn spin in (a) $LuMnO_3$ and (b) $Lu_{0.5}Sc_{0.5}MnO_3$.

and $3.15(3)\mu_B$ for the $x=0$ and 0.5 compounds, respectively. This saturated moment obtained for the Mn ions in $LuMnO_3$ is about 10% smaller than those found in the isostructural $ScMnO_3$.[9]

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