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Field-Induced Ferromagnetic Order and Colossal Magnetoresistance in $La_{1.2}Sr_{1.8}Mn_2O_7$: A ^{139}La NMR Study

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In order to gain insights into the origin of colossal magnetoresistance (CMR) in manganese oxides, we performed a ^{139}La NMR study in the double-layered compound $La_{1.2}Sr_{1.8}Mn_2O_7$. We find that above the Curie temperature $T_C = 126$ K, applying a magnetic field induces a *long-range* ferromagnetic order that persists up to $T = 330$ K. The critical field at which the induced magnetic moment is saturated coincides with the field at which the CMR effect reaches a maximum. Our results therefore indicate that the CMR observed above T_C in this compound is due to the field-induced ferromagnetism that produces a metallic state via the double exchange interaction.

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Since the discovery of giant magnetoresistance in magnetic superlattices, spin-dependent conductivity has become an important subfield of research in both condensed matter and applied physics. In recent years, the Ruddlesden-Popper series of manganese oxides, $(La, Sr)_{n+1}Mn_nO_{3n+1}$, has been found to show even larger magnetoresistance, the so-called colossal magnetoresistance (CMR) [1–4]. These compounds have perovskite crystal structure that also houses high temperature superconductivity. It has become clear that in these compounds, the degrees of spin, charge, electronic orbital, and lattice interact with each other and are responsible for the rich physical properties [5].

Among them, the $n = 2$ compounds, $La_{2-2x}Sr_{1+2x}Mn_2O_7$ have attracted a great deal of attention. The carrier content (hole content) can be systematically tuned by changing x. Correspondingly, the magnetic structure and the electrical conductivity change [2,3]. The c-axis length is about fivefold larger than the a axis; the ferromagnetic MnO_2 double layers and nonmagnetic, insulating $(La, Sr)_2O_2$ block are stacked along the c axis, forming a quasi-two-dimensional structure. This composes a natural ferromagnetic-nonmagnetic-ferromagnetic superlattice. The resistivity along the c axis, ρ_c, through a tunneling magnetoresistance process, is larger than the resistivity along the a axis, ρ_a, by a factor of $(10^3$–$10^4)$ [2]. The magnetic properties are complicated, depending on the coupling between adjacent MnO_2 double layers. For $x \leq 0.48$, the ground state is a ferromagnetically ordered state. For larger x, however, the low temperature state is an antiferromagnetically ordered state [6–8].

The most extensively investigated composition is the $x = 0.4$ compound, which orders ferromagnetically at $T_C = 126$ K and shows a negative magnetoresistance of $(2 \times 10^4)\%$ around T_C [2,3]. Intriguingly, this CMR effect persists in the paramagnetic state up to $T \sim 300$ K [2]. The most straightforward, existing interpretation for the CMR might be through the double exchange interaction theory [9]. Namely, applying a magnetic field aligns the Mn spins of the three electrons in the t_{2g} orbit, which in turn forces the spin in the e_g orbit to align in the same direction through Hund coupling so that the e_g electron can hop to the neighboring site with minimal energy cost. However, this mechanism cannot explain the CMR effect above T_C where a small field brings about a huge magnetoresistance effect [2]. Thus, the fundamental question of what is the origin of the CMR in this series of compounds remains unanswered. So far, several classes of theories have been proposed, which include the ''random resistor network'' theory [10] on the basis of phase separation suggested by neutron scattering [6], polaron effect [11], and the multicritical point scenario [12].

In this Letter, we report a ^{139}La NMR (nuclear magnetic resonance) study in $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.4$), focusing on the relationship between the magnetic properties and the occurrence of CMR. There are two crystallographically different sites of La; one lies in the middle of the MnO_2 bilayer (hereafter we call this site the in-bilayer site), and the other outside the MnO_2 bilayer (out-bilayer site). Therefore, La NMR is a powerful tool to probe the magnetic state of the MnO_2 bilayer. First, if Mn is in the ferromagnetic state, an NMR signal enhancement effect that is unique to such a state will be observed. Second, the in-bilayer La site will experience a larger internal field than the out-bilayer site. In contrast, if the MnO_2 bilayer is in an antiferromagnetic state, then the internal field at the in-bilayer La site will cancel.

We found, unprecedentedly, that applying a magnetic field induces ferromagnetism above T_C, which is primarily responsible for the CMR. The field induces a long-range ferromagnetic order, which drives the system metallic via the double exchange interaction.

Single crystal of $La_{1.2}Sr_{1.8}Mn_2O_7$ used in this study were grown by the traveling solvent floating zone method. X-ray diffraction indicates that the c-axis length is 20.20 Å. For NMR measurements, the single crystal was crushed

into a powder with particle size of ~20 μm to allow a maximal penetration of the oscillating (rf) magnetic field, H_1, since the NMR signal intensity is proportional to H_1^2. NMR experiments were performed using a homebuilt phase-coherent spectrometer. A standard $\pi/2$-τ-π-echo pulse sequence was used. The NMR spectra at zero magnetic field were taken by changing the rf frequency and recording the echo intensity step by step. The spectra at finite magnetic fields were taken by sweeping the field and recording the echo intensity with the aid of a boxcar integrator.

Figure 1 shows the NMR spectra at zero external magnetic field for various temperatures. Two peaks are observed. The signals were observed in a condition of strong H_1 enhancement. The pulse condition is $\pi/2$-τ-π = 1.0 μs–10 μs–2 μs with rf pulses of a power of 5 mW, which is a (10^3–10^4)-fold smaller power than requested for paramagnetic materials. This H_1 enhancement indicates that the signals come from the domain walls in a ferromagnetic state. In a domain wall of a ferromagnet, the rf field acting on the nucleus, which is perpendicular to the static magnetic field, is much larger than the applied H_1 because of the oscillating electron magnetic moment [13]. We have confirmed that the H_1 enhancement effect disappears and the signal to noise ratio decreases at high magnetic fields (above 0.4 T at T = 4.2 K) since there the magnetic domain walls are removed. Then, the peak seen at higher frequency is due to the La in-bilayer site.

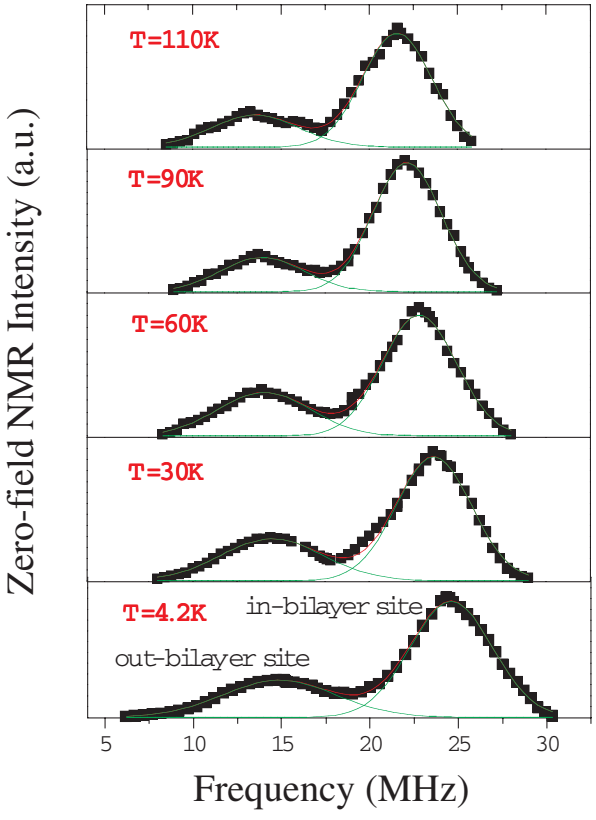

FIG. 1 (color online). The ^{139}La NMR line shape at zero magnetic field in $La_{1.2}Sr_{1.8}Mn_2O_7$. The red curve is the sum of two Gaussian functions (green) that best fit the data.

Figure 2 shows the temperature dependence of the internal field H_{in} extracted from the spectra, according to $\omega = \gamma H_{in}$, where ω is the Larmor (rf) frequency, and γ is the gyromagnetic ratio, which is 6.0146 MHz/T for ^{139}La. The large internal field is due mainly to the transferred hyperfine field from the ordered spins at Mn 3d orbitals. The signal has enough intensity at T = 120 K, but is lost above this temperature. This indicates that the Curie temperature T_C is around this temperature, in good agreement with the value T_C = 126 K reported from neutron scattering measurements [6–8]. Also, our result suggests that the ferromagnetic transition is of first order phase transition, although no appreciable hysteresis with respect to temperature was found around T_C. The first-order-like phase transition is similar to the cases of $La_{1-x}Ca_xMnO_3$ [14,15], and $La_{1-x}Na_xMnO_3$ [16].

The magnitude of the internal field is also confirmed by the NMR measurements under finite external fields. Figure 3 shows the NMR spectra at Larmor frequency of 91.2 MHz. By utilizing the strong magnetization (M) anisotropy that M_{ab} is larger by 1 order of magnitude than M_c [2], mechanical shocks were provided when the sample is in the magnetic field of 12–16 T so that the ab plane of the small grains align preferably to the direction of the external field. Therefore the spectra can be regarded as being under the condition of the $H \parallel ab$ plane. The broken line in Fig. 3 indicates the resonance field in the absence of an internal field. The distance between the actually observed peak and the broken line is therefore the internal field. As can been seen in Fig. 2, such an extracted internal field below T_C agrees excellently well with that obtained from zero-field NMR measurements. Note that, at low temperatures, there is no appreciable signal peak at the

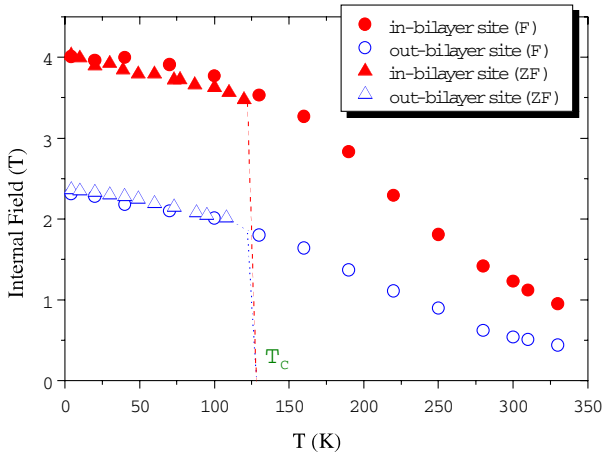

FIG. 2 (color online). Temperature dependence of the internal magnetic field at the La sites in $La_{1.2}Sr_{1.8}Mn_2O_7$. The triangles are the data obtained by zero-field (ZF) NMR. The circles are the data obtained by applying a finite magnetic field (F) of about 10 T (see text). The ZF Curie temperature is T_C = 126 K.

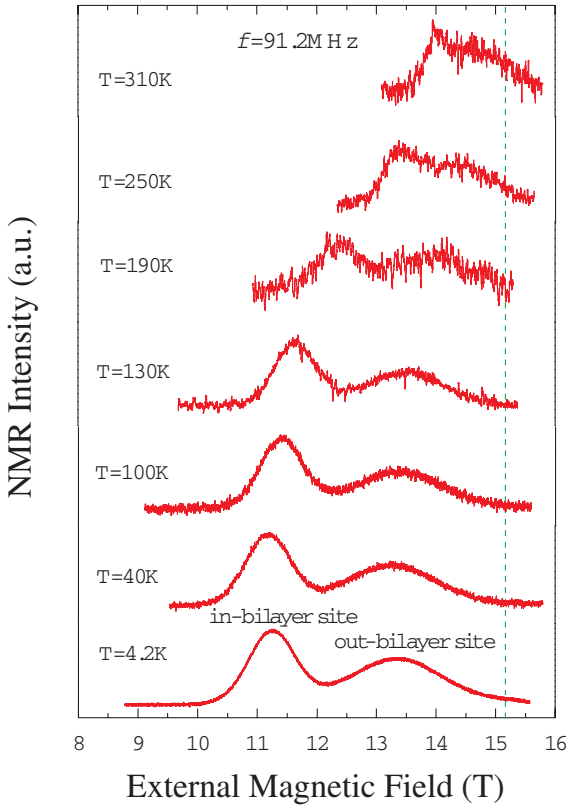

FIG. 3 (color online). Typical examples of the magnetic field swept ^{139}La NMR line shape at the Larmor frequency of $\omega_L = 91.2$ MHz at various temperatures. The vertical broken line is the resonance field position ω_L/γ, in the absence of internal field.

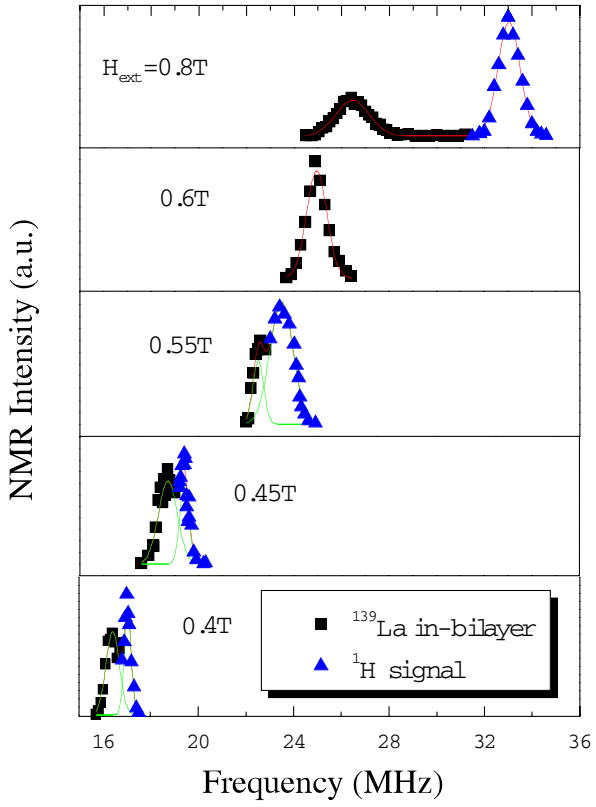

FIG. 4 (color online). Examples of ^{139}La NMR spectra for the in-bilayer La site at $T = 130$ K, in the presence of external magnetic fields, H_{ext}. The triangles indicate proton (^{1}H) spectrum, which, at $H_{ext} = 0.6$ T, coincides with ^{139}La spectrum. The red curve is the sum of two Gaussian functions (green) that best fit the data.

position of the broken line in Fig. 3. This is in contrast to the case observed in the $x = 0.5$ compound [17], where there appears a peak around this position, due to the in-bilayer La site that is in the antiferromagnetically ordered state.

The most important finding of this work is that even above T_C, the internal field persists when an external field is present, as can be seen in Fig. 3. This means that ferromagnetism is induced by the applied field, which persists up to 330 K. This is the key to understanding the CMR effect above T_C in this compound.

The saturated magnetic moment at the critical external field, H_{cr}, at which the moment is fully polarized depends on temperature. Figure 4 shows an example of the spectra at $T = 130$ K at various external fields. Below $H_{cr} = 0.58$ T, the peak frequency ω_p increases with increasing field H_{ext} with $\partial\omega_p/\partial H_{ext} > \gamma$, indicating a significant contribution of the polarized Mn moment. Above H_{cr}, however, $\omega_p = \omega_0 + \gamma H_{ext}$, where ω_0 is a constant. This indicates that above H_{cr}, the induced moment reaches a fully polarized value. Figure 5 shows the field-induced moment as a function of the external magnetic field at different temperatures. Here, we have assumed that at $T = 4.2$ K, the saturated moment is $3.6\mu_B$ [2]. At $T = 4.2$ K, we have confirmed that the external field has no effect on the ordered moment because the moment is already fully polarized in the Curie state. Note that H_{cr} at 130 and 150 K is 0.58 and 2.93 T, respectively. These values agree excellently well with the H_{cr}^{ρ} at which the magnetoresistance effect reaches 90% of the maximal value [2]. At still higher

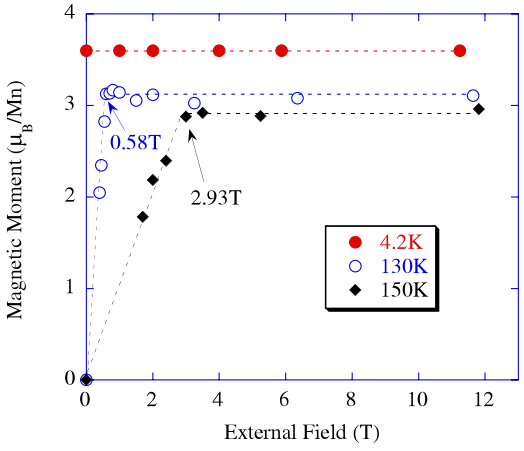

FIG. 5 (color online). Magnetic moment of Mn estimated from the NMR frequency (see text) as a function of field at different temperatures. The broken lines are guides to the eyes. The arrow indicates H_{cr} at $T = 130$ and 150 K, respectively.

temperatures, H_{cr} increases further, roughly tracking H_{cr}^{ρ} [18]. Therefore, our results indicate that the CMR in this compound is due to the field-induced magnetism that makes the compound metallic via the double exchange interaction.

Finally, it is an interesting future work to clarify the origin of the field-induced magnetism above T_C. A possible candidate might be that the susceptibility is highly enhanced due to competing interactions (double exchange interactions that favor ferromagnetic state and superexchange state that favors an antiferromagnetic order), or due to a proximity to a critical point in the phase diagram of T vs x [12]. The tendency of short-range order above T_C in the absence of external field suggested previously [19,20] is probably consistent with the former case. For the later case, Murakami and Nagaosa have recently shown that the fluctuations are largely enhanced around a multiple critical point [12], which gives an account for the first order ferromagnetic phase transition and the CMR effect in $R_{1-x}Sr_xMnO_3$ (R = La, Pr, Nd). We hope that our work will stimulate more theoretical studies in this regard.

In conclusion, we found that an external magnetic field induces a long-range ferromagnetic order above zero-field Curie temperature $T_C = 126$ K. The critical field at which the induced magnetic moment is saturated agrees excellently well with the field at which the CMR effect reaches a maximum. Our results indicate that the CMR observed above T_C in this compound is due to the field-induced ferromagnetism that produces a metallic state via double exchange interaction.

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