

# Spin state of $\text{Mn}_3\text{O}_4$ investigated by $^{55}\text{Mn}$ nuclear magnetic resonance

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(Received 29 June 2011; published 18 November 2011)

The  $^{55}\text{Mn}$  nuclear magnetic resonance spectrum for the spinel oxide  $\text{Mn}_3\text{O}_4$  was measured at low temperature to investigate the spin structure in the ground state. The spectrum consists of three peaks in the frequency range of 250–265 MHz, which corresponds to the hyperfine field range of 24–25 T. The temperature dependence of the spectrum and the rf enhancement factor show that  $\text{Mn}^{3+}$  ions have two different magnetic moments, one of which is strongly related to the commensurate-incommensurate phase transition. This is consistent with the picture of two magnetic moments  $R$  and  $S$  claimed from the results of a neutron experiment. Comparison with a heat-treated sample suggests a relation between the two different magnetic moments and the occupation sites of manganese ions, the tetrahedral and octahedral sites. Theoretical estimations of the dipolar hyperfine field and the observed peak splitting predict that the magnetic moments of  $R$  and  $S$  differ by 5% at maximum. The spin-spin relaxation time has a frequency dependence that induces spectrum broadening and further splitting of the peak coming from  $S$ , indicating that the Suhl-Nakamura interaction is the major relaxation mechanism in  $\text{Mn}_3\text{O}_4$ .

DOI: [10.1103/PhysRevB.84.174423](https://doi.org/10.1103/PhysRevB.84.174423)

PACS number(s): 76.60.-k, 76.50.+g, 75.50.Gg, 75.25.-j

## I. INTRODUCTION

In ferromagnetic spinel oxides with transition metals, several different interactions between neighboring magnetic ions and the strong spin-orbit interaction generate a rich variety of interesting magnetic properties. Competition among the interactions with the nearest, next-nearest, and next-next-nearest magnetic ions induce various configurations of spin order. Strong spin-orbit coupling causes spin order interplay with charge and orbital orders and, therefore, macroscopically with structure. This results in many interesting and intriguing physical phenomena. The spinel oxide  $\text{Mn}_3\text{O}_4$  is a case where the competition among the interactions is high and the interplay of the spin order with the orbital order is strong.  $\text{Mn}_3\text{O}_4$  is known to have orbital order and geometrical frustration in the ground state and four different magnetic phases.<sup>1</sup> It exhibits two structural and three magnetic phase transitions, as well as a quantum phase transition.<sup>2</sup>

The manganese ions in  $\text{Mn}_3\text{O}_4$  exist in two different valence states,  $\text{Mn}^{2+}$  ( $3d^5$ ) in the tetrahedral site of the oxygen lattice and  $\text{Mn}^{3+}$  ( $3d^4$ ) in the octahedral site. The Jahn-Teller effect at the octahedral site induces a structural phase transition from the cubic to the tetragonal structure with the space group ( $I4_1/amd$ ) at 1443 K. The lattice parameters of the tetragonal  $\text{Mn}_3\text{O}_4$  are  $a = 5.76$  Å and  $c = 9.47$  Å.<sup>3,4</sup> Recently, a phase transition from the tetragonal to the monoclinic structure was also observed near 33 K.<sup>2</sup>

$\text{Mn}_3\text{O}_4$  undergoes a magnetic phase transition at  $T_N = 43$  K from a paramagnetic phase to the ferrimagnetic phase with a triangular spin arrangement (the Yafet-Kittel phase).<sup>5</sup> In this phase, the  $\text{Mn}^{2+}$  spins are aligned along the  $[110]$  direction, and the  $\text{Mn}^{3+}$  spins are aligned in the opposite direction but canted toward the  $[001]$  and  $[00\bar{1}]$  directions [Fig. 1(a)], resulting in a net magnetization in the  $[110]$  direction. Below 39 K,  $\text{Mn}^{2+}$  spins remain the same but  $\text{Mn}^{3+}$  spins have two different magnetic moment states, named  $R$  and  $S$ .<sup>6,7</sup> The magnetic moment  $S$  orders in a conical distribution along the  $[\bar{1}\bar{1}0]$  direction, which is incommensurate with the lattice,

while the  $R$  order is commensurate. Below 33 K, the spin structure becomes similar to that of the Yafet-Kittel phase between 39 and 43 K, but the magnetic unit cell of  $S$  is double the chemical one. In Fig. 1(b), illustrating the spin structure of the cell-doubled phase of  $\text{Mn}_3\text{O}_4$ , the spins of the  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions are represented by the purple long and red short arrows, respectively.

It is quite interesting that the same magnetic ions in a magnetic material have two different magnetic moment states resulting in two independent sublattices with different spin orders. All the experimental evidence for the existence of two different magnetic moments of  $\text{Mn}^{3+}$  ions was provided by neutron scattering experiments. A neutron scattering study reported that the magnetic moments  $R$  and  $S$  have the same magnitude but different canting angles.<sup>8</sup> However, other works reported the same angles but different magnitudes.<sup>6,7</sup> The average magnetic moment of  $R$  and  $S$  is about  $3.4\mu_B$  and the magnetic moment of  $S$  is about 10% smaller than that of  $R$  when a difference is claimed. The main purpose of this study is to investigate the existence of two different magnetic moments of  $\text{Mn}^{3+}$  ions by experiments other than neutron scattering and to measure the magnitudes of the moments.

In this work, we report the observation of the zero-field  $^{55}\text{Mn}$  nuclear magnetic resonance (NMR) spectrum for  $\text{Mn}^{3+}$  ions in the spinel oxide  $\text{Mn}_3\text{O}_4$  at the temperature of liquid helium. NMR is a useful local probe to examine the microscopic spin structure of magnetic materials. The NMR spectrum in the ground spin state shows several peaks. To investigate the several peak features, we obtained an NMR spectrum for a heat-treated sample and compared it with that of an untreated one. The spectra obtained at several different temperatures show that the temperature dependence of each peak is different. The rf enhancement factor of each peak was also measured and compared. The dipolar hyperfine field was calculated based on the cell-doubled phase. The frequency dependence of the spin-spin relaxation time was measured to study the influence of the Suhl-Nakamura interaction on

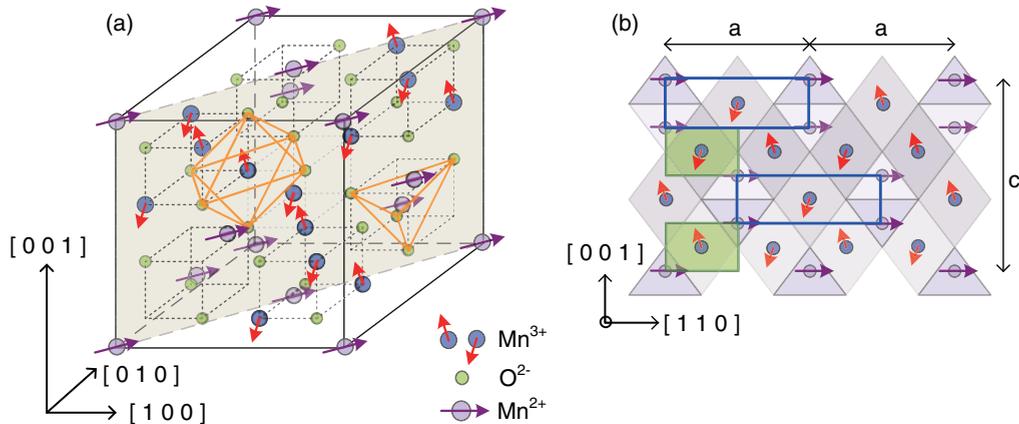


FIG. 1. (Color online) (a) Spin structure of spinel oxide  $\text{Mn}_3\text{O}_4$ . The purple long and red short arrows represent the spins of the  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions, respectively. (b) Cell doubled phase viewed along the  $[1\bar{1}0]$  direction. A  $\text{Mn}^{3+}$  ion having  $S$  spin is surrounded by a tetragonal lattice of  $\text{Mn}^{2+}$  ions whose axis is along the  $[110]$  direction (blue open rectangle), and that of  $R$  spin is surrounded by a tetragonal lattice along the  $[1\bar{1}0]$  direction (green closed rectangle).

the spectrum. The results provide additional evidence for the model of two different magnetic moments of  $\text{Mn}^{3+}$  ions.

## II. EXPERIMENTAL DETAILS

The samples were commercially available polycrystalline powder  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  of 99.9% purity (Kojundo, Republic of Korea). The heat-treated  $\text{Mn}_3\text{O}_4$  sample was made by heating the untreated  $\text{Mn}_3\text{O}_4$  sample at 1000 °C for 15 h in vacuum and then cooled in air at room temperature. It was confirmed by using x rays that the heat-treated sample has the same chemical formula as the untreated one within the experimental error. A closed-cycle cryogenic system was used to reach liquid-helium temperature. The  $^{55}\text{Mn}$  NMR spectrum was obtained using a custom-built spectrometer. A conventional spin-echo pulse sequence ( $90^\circ\text{-}\tau\text{-}180^\circ$ ) was used, where the  $90^\circ$  pulse width was 4  $\mu\text{s}$ . For an accurate measurement, the probe coil was tuned and matched carefully at each frequency. We searched for the spectrum in the wide frequency range of 200 to 320 MHz, where the resonance signal of  $\text{Mn}^{3+}$  ions is usually found.

## III. RESULTS AND DISCUSSION

The resonance frequency of the zero-field NMR spectrum for nuclei of magnetic ions in magnetic materials is proportional to the hyperfine field at the nuclei. Figure 2(a) shows the zero-field  $^{55}\text{Mn}$  NMR spectrum for the spinel oxide  $\text{Mn}_3\text{O}_4$  measured in the temperature range of 6–30 K. It is quite evident that the spectrum has three peaks. The intensity of the peak around 264 MHz (peak 1) is larger than those of the peaks around 258 MHz (peak 2) and 249 MHz (peak 3). The intensities of the spectra were normalized in such a way that the intensities of peak 1 are the same at all temperatures. The frequency range of 250–265 MHz corresponds to the hyperfine field range of 24–25 T. The peak positions shift to the lower-frequency side as the magnetization decreases with increasing temperature.

The NMR frequency for the magnetic materials is proportional to the magnetic moment. Therefore, the first reason

for the several peaks in the spectrum could be the existence of several different magnetic moments, which are mainly determined by the valence state of the magnetic ion. The Mn ions in  $\text{Mn}_3\text{O}_4$  have two different valence states,  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ . Since it is already known that the NMR spectrum for  $\text{Mn}^{2+}$  ion in the tetrahedral site of  $\text{Mn}_3\text{O}_4$  is observed in the frequency range of 550–560 MHz,<sup>9,10</sup> none of the peaks in the spectrum of Fig. 2 are due to  $\text{Mn}^{2+}$  ions. It is also possible that some of the peaks come from other manganite phases included as impurities. We searched for the NMR spectrum for  $\text{MnO}_2$  in which manganese ions are in the  $\text{Mn}^{4+}$  state only to find that no signal is observed in the frequency range of the experiment.  $\alpha\text{-Mn}_2\text{O}_3$  also has  $\text{Mn}^{3+}$  ions but its Mn NMR spectrum is observed at around 315 MHz.<sup>11</sup> Since only three

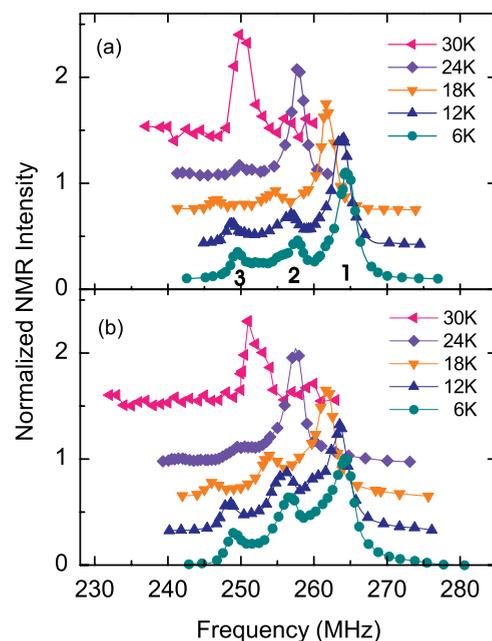


FIG. 2. (Color online)  $^{55}\text{Mn}$  NMR spectrum for (a) the untreated  $\text{Mn}_3\text{O}_4$  sample and (b) the heat-treated sample.

peaks are observed, the possibility of splitting due to a nuclear quadrupole coupling is also excluded.

The magnetic moment of a magnetic ion in spinel oxides varies depending on whether it is in the tetrahedral or octahedral site because of the different chemical environments, even though its valence state remains the same. In a normal spinel, 2+ and 3+ ions occupy the tetrahedral and octahedral sites, respectively, and in an inverse spinel, the occupation sites are exchanged. The normal spinel  $\text{Mn}_3\text{O}_4$  is known to become partly inverted near the structural phase transition temperature,<sup>12</sup> where both the  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  ions occupy not only the octahedral site but also the tetrahedral site. To check whether some of the peaks come from the inverted  $\text{Mn}^{3+}$  ions, we measured the NMR spectrum for the heat-treated  $\text{Mn}_3\text{O}_4$  [Fig. 2(b)] and compared it with that for the untreated one [Fig. 2(a)]. In the NMR spectrum for the heat-treated  $\text{Mn}_3\text{O}_4$ , the intensity of peaks 2 and 3 relative to peak 1 seems to increase a little. The NMR signal intensity depends on the number of nuclei and the nuclear relaxation times. The spin-spin relaxation times ( $T_2$ ) of the treated and untreated samples were similar. Therefore, the relative intensity change implies the possibility that peaks 2 and 3 come from the  $\text{Mn}^{3+}$  ions in the tetrahedral sites. The temperature dependences of the NMR spectra are also similar, as shown in the figure.

Figure 2(a) shows that the normalized intensities of peaks 2 and 3 decrease faster than that of peak 1 with increasing temperature. In the spectrum measured at 30 K, peaks 2 and 3 are barely observable, while peak 1 is still clearly observed. This indicates that the  $\text{Mn}^{3+}$  ions in  $\text{Mn}_3\text{O}_4$  have two different magnetic moments with different temperature dependences. Peak 1 comes from the manganese ions with the magnetic moment with higher transition temperature, and peaks 2 and 3 come from those with the lower one. This observation is consistent with the previous picture of two different magnetic moments  $R$  and  $S$  for  $\text{Mn}^{3+}$  ions. It was reported that only the  $S$  spins are involved in the commensurate-incommensurate phase transition at 33 K.<sup>6</sup> Therefore, it is plausible to assign peaks 2 and 3 to the  $S$  spin and peak 1 to the  $R$  spin, which is irrelevant to the transition at 33 K.

The rf enhancement factor observed at each peak position also indicates that the peaks can be divided into two groups as above. In the NMR experiment on the ferromagnetic materials, rf power is enhanced by the accompanying electron spin oscillation. Therefore, the maximal signal intensity is obtained with less external power if the rf power is enhanced. Figure 3 shows the normalized NMR signal intensity versus rf power observed at three peak positions. In the graph, the normalized echo intensities of peaks 2 and 3 reach a maximum together around 20 mV, while that of peak 1 continues to increase. Therefore, the enhancement factors for the peaks 2 and 3 are the same and larger than that for peak 1. Since the enhancement factor depends on the anisotropy field, the result implies that the magnetic moment related to peak 1 is in a magnetic environment different from that of peaks 2 and 3. This is also consistent with the  $R$  and  $S$  picture, where the different magnetic environments of  $R$  and  $S$  generate the different spin orders.

The resonance frequency of the zero-field NMR for a magnetic ion is determined by the total hyperfine field, which is the vector sum of the contact and dipolar hyperfine fields.

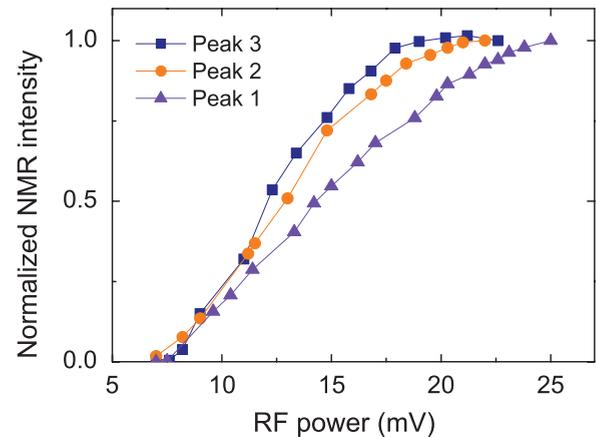


FIG. 3. (Color online) NMR signal intensity vs rf power.

The former is given by  $A\mu$ , where  $A$  is the hyperfine coupling constant and  $\mu$  is the magnetic moment. The difference in the magnetic moments of  $R$  and  $S$  can generate a difference in their resonance frequencies. In  $\text{Mn}_3\text{O}_4$ ,  $R$  and  $S$  experience different dipole fields due to their different magnetic environments. Therefore, different resonance frequencies are expected even if the magnetic moments of  $R$  and  $S$  are the same. To estimate the amount of peak splitting in the NMR spectrum of  $\text{Mn}_3\text{O}_4$ , we calculated the dipolar hyperfine field based on the magnetic cell-doubled structure. Although  $\text{Mn}_3\text{O}_4$  has a monoclinic structure below 33 K, we approximated it as a tetragonal structure because the tilting is so small that the angle between the  $a$  and  $b$  axes is almost  $90^\circ$ . The dipolar hyperfine field is generated by the magnetic moments of all the neighboring manganese ions. In the calculation,  $4.34\mu_B$  was used as the magnetic moment of a  $\text{Mn}^{2+}$  ion and  $3.64\mu_B$  and  $3.25\mu_B$  were used for the  $R$  and  $S$  spins of the  $\text{Mn}^{3+}$  ions, respectively.<sup>6</sup> For each  $\text{Mn}^{3+}$  ion at an octahedral site, the dipolar fields were summed from the nearest-neighbor to the seventh-neighbor ions. The distance between the central ion and the seventh-neighbor ions is smaller than the general domain size. The result showed that the expected difference in the resonance frequencies of  $R$  and  $S$  is about 5 MHz.

The exact magnitude of the magnetic moments of  $R$  and  $S$ , which is controversial, matters little in the dipole field calculation because the dipole field at a  $\text{Mn}^{3+}$  position is mostly determined by the magnetic moment of the neighboring  $\text{Mn}^{2+}$  ions. A  $\text{Mn}^{3+}$  ion having  $S$  spin is surrounded by a tetragonal lattice of  $\text{Mn}^{2+}$  ions whose axis is along the  $[110]$  direction [blue open rectangle in Fig. 1(b)], and one having  $R$  spin is surrounded by a tetragonal lattice along the  $[\bar{1}\bar{1}0]$  direction [green closed rectangle in Fig. 1(b)]. In both cases  $\text{Mn}^{2+}$  spins align along the  $[110]$  direction. If we simply assume that the magnetic moments of the  $R$  and the  $S$  spins are the same,  $4\mu_B$ , and that of  $\text{Mn}^{2+}$  is  $5\mu_B$ , for example, the expected peak splitting is about 6 MHz.

The difference between the resonance frequency of peak 1 and the average resonance frequency of peaks 2 and 3 estimated in Fig. 2 is about 10 MHz. The sum of this value and the theoretical estimation of the dipolar hyperfine field, which is about 15 MHz, is attributable to the difference in the contact hyperfine fields of  $R$  and  $S$ . If the hyperfine coupling constant

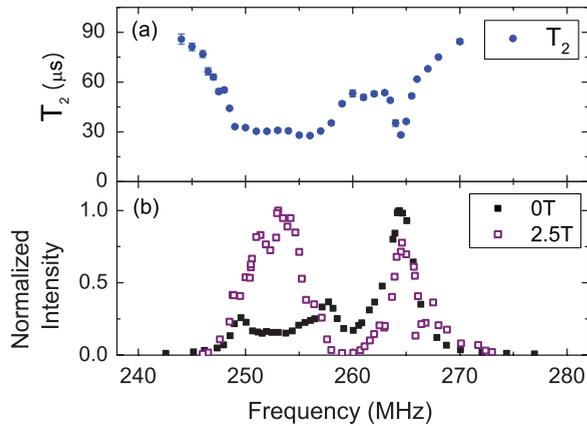


FIG. 4. (Color online) (a) The spin-spin relaxation time and (b) the spectra obtained at zero-field (closed squares) and at 2.5 T (open squares).

is the same, this difference predicts a difference of less than 5% in the magnitudes of the magnetic moments of  $R$  and  $S$ .

One of the reasons for the further splitting of peaks 2 and 3 is the distribution of the spin-spin relaxation time. In Fig. 4(a), the spin-spin relaxation time obtained at 6 K is depicted for various frequencies. The figure shows that the spin-spin relaxation time changes greatly with frequency. The signal intensity is relatively suppressed in the region between peaks 2 and 3 by the spin-spin relaxation, which is faster there than at the peak positions. In an ordered magnetic insulator, the Suhl-Nakamura interaction, in which the nuclear spins are indirectly coupled by virtual magnons, plays a major role in NMR relaxation at low temperature. The interaction induces a frequency- and field-dependent spin-spin relaxation time.<sup>13</sup> The spin-spin relaxation due to the Suhl-Nakamura interaction gets slower with increasing external field. In Fig. 4(b), the spectrum obtained in a magnetic field of 2.5 T is depicted together with that obtained at zero field for comparison. The

central parts of peaks 2 and 3 are fully recovered in a magnetic field, as theory predicts. The Suhl-Nakamura interaction plays a role in suppressing the central parts of the peaks related to  $S$  and splitting them into peaks 2 and 3.

#### IV. CONCLUSIONS

The zero-field  $^{55}\text{Mn}$  NMR spectrum for  $\text{Mn}^{3+}$  ions in the spinel oxide  $\text{Mn}_3\text{O}_4$  consists of three peaks. The results of measurements of the enhancement factor and the temperature dependence of the spectra show that the peaks are divided into two groups coming from two different magnetic moments in different magnetic environments. Peaks 2 and 3 come from a magnetic moment that is related to the commensurate-incommensurate magnetic phase transition, while peak 1 is irrelevant to that transition. This provides evidence for the picture that  $\text{Mn}^{3+}$  ions have two different magnetic moments  $R$  and  $S$ . The relative intensities of peaks 2 and 3 increases a little when the sample is heat treated. If the heat treatment induces inversion, the result means that  $R$  and  $S$  are somehow related to the occupation sites, the tetrahedral and octahedral sites. The observed difference in the resonance frequencies of  $R$  and  $S$  is due to the difference in their magnetic moments and the dipolar hyperfine fields, and/or the difference in hyperfine coupling constants of the tetrahedral and octahedral sites. A comparison of theory with experiment indicates that the difference in the magnitudes of the magnetic moments  $R$  and  $S$  is 5% at maximum. One of the main reasons for the splitting of peaks 2 and 3 for the same magnetic moment  $S$  is the frequency-dependent spin-spin relaxation due to the Suhl-Nakamura interaction.

#### ACKNOWLEDGMENTS

This work was supported by the Korea Research Foundation Grant No. KRF-2008-313-c00290 and the Korea Science and Engineering Foundation Grant No. 2009-0078342.

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