Giant magnetic anisotropy in Mn_3O_4 investigated by $^{55}Mn^{2+}$ and $^{55}Mn^{3+}$ NMR

Changsoo Kim, Euna Jo, Byeongki Kang, Sangil Kwon, and Soonchil Lee*
Department of Physics, KAIST, Daejeon 305-701, Korea

Jeong Hyun Shim
Fakultät Physik, Technische Universität Dortmund, Dortmund, Germany

Takehiko Suzuki and Takuro Katsufuji
Department of Physics, Waseda University, Tokyo 169-8555, Japan
(Received 14 August 2012; published 26 December 2012)

In Mn_3O_4, the magnetization along the c axis is different from that along the ab plane even in the strong field of 30 T. To investigate the origin of the huge magnetic anisotropy, Mn^{2+} and Mn^{3+} nuclear magnetic resonance spectra were measured in the 7-T magnetic field. The canting angle of the magnetic moments was estimated for various directions of field by rotating a single-crystalline Mn_3O_4 sample. One of the main results is that Mn^{3+} moments lie nearly in the ab plane in the external field perpendicular to the plane, meaning that the macroscopic magnetic anisotropy of Mn_3O_4 originates from the magnetic anisotropy of Mn^{3+} in the ab plane. The anisotropy field is estimated to be about 65 T. It is obvious that the Yafet-Kittel structure made of Mn^{2+} and Mn^{3+} spins lies in the ab plane due to this huge magnetic anisotropy, contrary to the previous reports. By the least-squares fit of the canting angle data for various field directions to a simple model, we obtained that $J_{BB} = 1.88J_{AB} - 0.09$ meV and $K_A = -14.7J_{AB} + 2.0$ meV, where J_{AB}, J_{BB}, and K_A are the exchange interaction constants between Mn^{2+} moments, Mn^{2+} and Mn^{3+} moments, and an anisotropy constant of Mn^{2+}, respectively.

DOI: 10.1103/PhysRevB.86.224420 PACS number(s): 75.30.Gw, 76.60.−k, 75.30.Et

I. INTRODUCTION

It is interesting that Mn_3O_4 has both orbital order and large magnetic anisotropy because magnetic anisotropy is due to spin-orbit coupling while observation of orbital order usually means well-quenched orbital angular momentum. This material has two different magnetic ions: Mn^{2+} ($3d^5$) at the center of oxygen tetrahedron called A sites and Mn^{3+} ($3d^4$) ions, octahedron called B sites in its spinel structure. Both the Mn^{2+} and Mn^{3+} ions are in the high-spin state. At 1440 K, Mn_3O_4 undergoes a structural phase transition from a cubic to a tetragonal structure with $c > a = b$ due to the Jahn-Teller effect. This distortion results in the orbital order of Mn^{3+} ions in which one electron in the e_g level occupies the z^2 orbital.[1]

This material undergoes several magnetic phase transitions with temperature. Below the Néel temperature (43 K), the Mn^{2+} moment aligns in the [110] direction and two Mn^{3+} moments are canted in the opposite direction, making the so-called Yafet-Kittel spin structure. When temperature decreases below 39 K, two different magnetic sublattices appear, one of which is incommensurate and another which is commensurate. Below 33 K, the spin structure changes back to the Yafet-Kittel structure but with two different magnetic unit cells. The magnetic unit cell of the sublattice that was commensurate above 33 K is the same with the chemical unit cell, while that of the incommensurate sublattice is twice as large as the chemical unit cell.[2–4] Various magnetic properties of Mn_3O_4 have attracted intense interest again recently and several new works have been reported. The most interesting new discovery would be the quantum phase transition by magnetic field.[5] The specific heat[6] and magnetoelectric coupling[7] were studied near magnetic phase transitions, and magnetic property of nanoparticle ensembles was also studied.[8]

The magnetization of Mn_3O_4 along the c axis is about half of that in the perpendicular direction in the 5-T magnetic field at liquid-helium temperature.[9] The two magnetizations are different even in 30 T.[10] Moreover, anisotropy in magnetic susceptibility is observed at up to 100 K, which is much higher than the Néel temperature. This magnetic anisotropy energy is comparable with that of recently studied materials with giant magnetocrystalline energy $Fe_{0.25}TaS_2$ and $LuFe_2O_4$.[11,12] Their magnetic anisotropy field along the easy axis is 60 ∼ 70 T and coercive field is large, 6 ∼ 11 T, at low temperature. Contrary to these, Mn_3O_4 has a relatively small coercive field, ∼1 T, and a magnetic easy plane rather than easy axis.

The macroscopic magnetic anisotropy of Mn_3O_4 can be explained by either easy-axis anisotropy along the c axis or easy-plane anisotropy in the ab plane of either Mn^{3+} or Mn^{2+} ions. Therefore, there has been controversy about the microscopic origin of the macroscopic anisotropy and the plane direction of the Yafet-Kittel structure. Dwight measured low-field magnetization of a single crystal at 4 K and claimed that the magnetic moments forming the Yafet-Kittel structure lie in a plane perpendicular to ab plane due to the easy-axis anisotropy of Mn^{3+} that leads to the macroscopic anisotropy.[13] Nielsen pointed out that strong crystal-field effects in the A site could result in macroscopic anisotropy, but the easy-axis anisotropy of Mn^{3+} along the c axis is mostly responsible for macroscopic anisotropy. He also claimed that Mn^{3+} moments turn from the c axis to the ab plane as the field along the c axis increases.[10] There was a report, however, proposing that the spins of the Yafet-Kittel structure are in the ab plane even in the absence of external field.[14] Recent works assume again that Mn^{3+} moments are canted to the [001] and [00$\bar{1}$] directions.[9] These claims on the spin structure and origin of magnetic anisotropy have not been proved by microscopic observation.

In this work, we investigate the spin structure of the ground state and the origin of the magnetic anisotropy in Mn_3O_4 using nuclear magnetic resonance (NMR). The canting angle of a selected magnetic moment can be estimated by NMR and, therefore, it is a very useful tool to study complex magnets having more than one magnetic ion with canted spins such as Mn_3O_4. From the data of canting angles of Mn^{2+} and Mn^{3+} moments that vary with the direction of the magnetic field, we could quantitatively analyze the exchange interactions and anisotropy energies of Mn^{2+} and Mn^{3+}. The result clearly shows that the *ab* plane anisotropy of Mn^{3+} is the origin of the macroscopic anisotropy of Mn_3O_4.

II. EXPERIMENT

A high-quality single-crystalline Mn_3O_4 sample with the size of $5 \times 5 \times 1$ mm^3 was made by the floating zone method. The Hahn echo pulse sequence (90° pulse$-\tau-$180° pulse$-\tau-$signal) was used to obtain NMR spin echo signals. In 7 T, the NMR signal of Mn^{3+} was measured in the frequency range from 250 to 320 MHz and the NMR signal of Mn^{2+} was from 450 to 550 MHz. To change the direction of magnetic field at liquid-helium temperature, a homemade rotator with several worm gears was attached to our NMR probe.

III. RESULT AND DISCUSSION

In magnetic materials, ordered electron spins generate a hyperfine field at a nuclear spin. In an external magnetic field, the resonance frequency of NMR is proportional to the magnitude of the vector sum of the hyperfine field and external field as

$$f = \gamma_n |\vec{H}_{hf} + \vec{H}_{\text{ext}}|, \quad (1)$$

where $\vec{H}_{hf}$ and $\vec{H}_{\text{ext}}$ are the hyperfine and external magnetic fields, respectively, and the nuclear gyromagnetic ratio γ_n is 10.5 MHz/T for Mn nuclei. If we know the hyperfine and external fields, the angle between two fields can be calculated using this equation. In transition metals, the hyperfine field is usually antiparallel to the magnetic moment producing the hyperfine field.[15] Consequently, the angle between the magnetic moment and external field can be obtained by measuring the shift of the resonance frequency in the external magnetic field.

Figure 1(a) shows the Mn^{3+} NMR spectra of the single-crystalline Mn_3O_4 obtained in the 7-T magnetic field with various field angles from the *ab* plane at liquid-helium temperature. When the field direction is parallel with the *ab* plane, the center of the resonance signal is observed at 302 MHz. As the field rotates toward the *c*-axis direction, the resonance frequency decreases until it reaches the minimum in the *c*-axis direction and then the frequency increases symmetrically back to the initial value as the field rotates further back to the *ab* plane in the opposite direction. The macroscopic magnetization of Mn_3O_4 is parallel with the Mn^{2+} moment directed to [110] in the zero field. Since the magnetic anisotropy in the *ab* plane is much smaller than 7 T, the Mn^{2+} moment aligns along the field direction in the *ab* plane. Rotating the field within the *ab* plane made no change in the spectral position. It was reported that Mn^{3+}

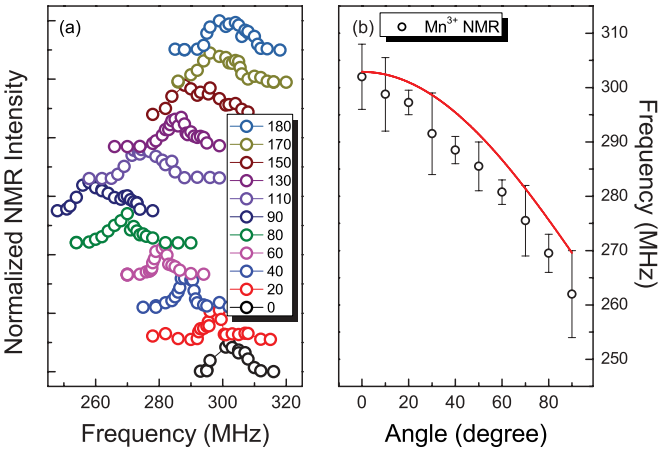

FIG. 1. (Color online) (a) Mn^{3+} NMR spectra measured while rotating the 7-T magnetic field from the *ab* plane to the *c* axis and then back to the *ab* plane in the opposite direction. The numbers in the inset represent the angle between the external field and the *ab* plane. (b) The resonance frequency versus the angle between the field and the *ab* plane. The red curve represents the resonance frequency predicted by Eq. (1) when Mn^{3+} moments are assumed to be fixed in the *ab* plane for any field angle.

NMR for Mn_3O_4 in the zero external field is observed at 258 ± 10 MHz.[16] Equation (1) and the difference between the resonance frequencies in the zero field and 7 T in the *ab* plane predict that the angle between the Mn^{3+} moment and the field or the Mn^{2+} moment is $120 \pm 5°$. This angle is similar to the value previously reported, $110 \sim 115°$.[2–4]

One of the controversies on the spin structure of Mn_3O_4 is about the direction of Mn^{3+} moments forming the Yafet-Kittel spin structure. It is accepted that Mn^{2+} moments lie in the *ab* plane, but it is under debate whether Mn^{3+} moments lie in the *ab* plane or its perpendicular plane. Many believe, without evidence, that one Mn^{3+} moment is tilted to the [001] direction and the other one is tilted to the [00$\bar{1}$] direction symmetrically due to the easy-axis anisotropy of Mn^{3+}.[13] In this case, the hyperfine field of one Mn^{3+} moment is parallel with the external field and the other is antiparallel. Then, it is expected that two peaks are observed in the Mn^{3+} spectrum, one above and the other below the resonance frequency in the zero field. In other words, one peak would split into two when the magnetic field is rotated from the *ab* plane to the *c* axis. The difference in resonance frequencies of the two peaks is estimated to be about 100 MHz when the field is in the *c*-axis direction. Contrary to this prediction, our experimental result shows only one peak shifted downward about 38 MHz. Observation of only one peak implies that two Mn^{3+} moments make the same angle with an external field.

When the magnetic field is parallel with the *c* axis, the spectrum is centered at 264 MHz, which is about 6 MHz different from the resonance frequency in the zero field. This indicates that Mn^{3+} moments are nearly perpendicular to the field. Equation (1) with 6 MHz of difference predicts the angle between the Mn^{3+} moment and the field is $87 \pm 5°$. The fact that the Mn^{3+} moments are nearly in the *ab* plane even in the 7-T perpendicular field means that Mn^{3+} ions have the strong easy *ab*-plane anisotropy rather than the easy *c*-axis

anisotropy. Because of this strong plane anisotropy, it is quite clear that Mn^{3+} moments lie in the ab plane in the zero field. Mn^{3+} moments tilt to the field direction by about 3° in the 7-T magnetic field applied along the c axis, while Mn^{2+} moments tilt by about 24° as discussed in the following. This means that the combined effect of the exchange interaction between the Mn^{3+} and Mn^{2+} moments and the Mn^{2+} anisotropy is an order of magnitude smaller than the Mn^{3+} anisotropy. Neglecting those two terms, the total energy of a Mn^{3+} magnetic moment in field along the c axis can be written as $E = K_B \cos^2(\frac{\pi}{2} - \Theta) - m_B H \cos\Theta$, where $\frac{\pi}{2} - \Theta$ is the tilting angle, K_B is the anisotropy constant at the site of Mn^{3+}, and m_B is the magnetic moment of Mn^{3+}. Differentiating the equation w.r.t. Θ gives the angle at equilibrium. Rough estimation of K_B obtained from the resulting equation with the experimentally measured angle 87° is 65 T (∼14 meV). The lower limit estimated in consideration of the experimental error is 25 T. The value is consistent with the temperature (100 K ∼ 8.6 meV) at which the anisotropy disappears in the magnetic susceptibility.

The large plane anisotropy of Mn^{3+} is also confirmed by the NMR spectra measured in magnetic fields with different directions. Figure 1(b) shows the resonance frequency of Mn^{3+} versus the angle between the ab plane and the field. The red curve represents the theoretical prediction of Eq. (1) for the case when two Mn^{3+} moments are fixed in the ab plane with 120° angle between them. The theory follows the experimental data qualitatively well but a bit larger, indicating that Mn^{3+} moments are slightly tilted to the magnetic field direction (Fig. 2).

We also measured the Mn^{2+} NMR spectrum for various magnetic field directions as in the Mn^{3+} NMR experiment at liquid-helium temperature [Fig. 3(a)]. As the field direction changes from the ab plane to the c axis and then back to the ab plane in the opposite direction, the resonance frequency shifts and gets back to the initial frequency symmetrically, such as Mn^{3+} NMR. The shift direction being opposite to Mn^{3+} reflects that the projection of Mn^{2+} moments on the

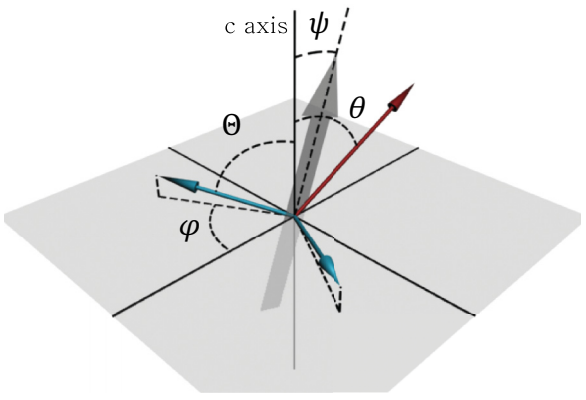

FIG. 2. (Color online) Magnetic moments of Mn_3O_4 in the external field. The red, blue, and gray arrows are the Mn^{2+} moment, Mn^{3+} moments, and magnetic field, respectively. ψ, θ, and Θ, are the angles of the magnetic field and Mn^{2+} and Mn^{3+} moments measured from the c axis. ϕ is the angle between the projection vector of Mn^{3+} moment on the ab plane and the plane including the magnetic field and Mn^{2+} moment and the c axis. Θ and θ are 90° and ϕ is 60° in the zero field.

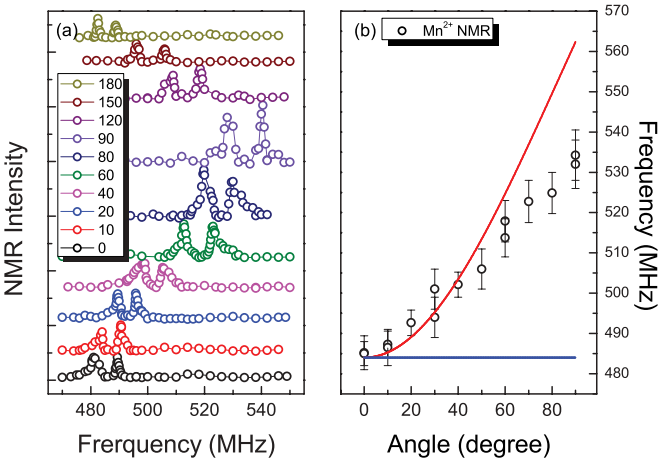

FIG. 3. (Color online) (a) Mn^{2+} NMR spectra measured while rotating the 7-T magnetic field from the ab plane to the c axis and then back to the ab plane in the opposite direction. The numbers in the inset represent the angle between the external field and the ab plane. (b) The resonance frequency versus the angle between the field and the ab plane. Solid curves: resonance frequency predicted by Eq. (1) when Mn^{2+} moments are fixed in the ab plane during the rotation of the field (red) and when the Mn^{2+} moment is always parallel with the field (blue).

field direction is antiparallel to that of Mn^{3+} moments. In all spectra, two peaks are observed. This is the splitting of one peak due to the Suhl-Nakamura interaction, which is the indirect interaction between nuclear spins by energy exchange with virtual spin waves which induces the fluctuation of nuclear spins.[17] The Mn^{3+} NMR spectrum suffers from the Suhl-Nakamura interaction, but its effect almost vanished in the strong magnetic field of 7 T. This is because the spin-spin relaxation time T_2 of Mn^{2+} is one order of magnitude shorter than that of Mn^{3+},[16,18] making the Mn^{2+} spectrum more vulnerable to the Suhl-Nakamura interaction.

In the zero field, the Mn^{2+} NMR signal is observed in the region of 552–562 MHz and centered at 558 MHz.[18] When the 7-T magnetic field is applied along the ab plane, the center of the peak is 485 MHz, which is the same as the frequency expected when the Mn^{2+} moment is parallel with the applied field within experimental error. As the field rotates from the ab plane to the c axis, the resonance frequency increases. Figure 3(b) shows the resonance frequencies of Mn^{2+} NMR predicted by Eq. (1) when the Mn^{2+} moment stays in the ab plane (red curve) and perfectly follows the direction of the magnetic field (blue curve) during rotation. Experimental data follow the red curve relatively well initially, but start to deviate from it as the angle increases. This deviation indicates that the Mn^{2+} moment points to the direction somewhere between the magnetic field and the ab plane. The maximum angle between the field and Mn^{2+} moment is $66 \pm 5°$ when the field is along the c axis.

Contrary to Mn^{3+} moments having overwhelming anisotropy, the direction of the Mn^{2+} moment is determined by the equilibrium condition among the torques due to the anisotropy energy, exchange interactions, and external field. When the magnetic field, Mn^{2+} moment, and the sum vector of Mn^{3+} moments lie in the same plane and two Mn^{3+} moments

are symmetrically placed with respect to the plane as in Fig. 2, the total energy of a unit Yafet-Kittel structure is expressed as

$$\begin{aligned} E = \; & K_A \cos^2\theta + 2K_B \cos^2\Theta \\ & - m_A H \cos(\theta - \psi) \\ & - 2m_B H(-\cos\phi \sin\Theta \sin\psi + \cos\Theta\cos\psi) \\ & + 12 \times 5J_{AB}(-\sin\theta\cos\phi\sin\Theta + \cos\theta\cos\Theta) \\ & + 4 \times 4J_{BB}(\sin^2\Theta\cos 2\phi + \cos^2\Theta), \end{aligned} \tag{2}$$

where K_A and K_B are the anisotropy constants at the sites of Mn^{2+} and Mn^{3+}, respectively, H is the external magnetic field, and J_{AB} and J_{BB} are the exchange constants between Mn^{2+}-Mn^{3+} and Mn^{3+}-Mn^{3+}, respectively. ψ, θ, and Θ are the angles of the magnetic field, Mn^{2+} and Mn^{3+} moments measured from the c axis. ϕ is the angle between the projection vector of the Mn^{3+} moment on the ab plane and the plane including the magnetic field, Mn^{2+} moment, and the c axis. The exchange interaction term between Mn^{2+} moments adds only a constant to the total energy because they are always parallel with each other. A Mn^{3+} ion has six nearest-neighbor Mn^{3+} ions. The Jahn-teller distortion makes the sign and amplitude of the interaction with two intrachain neighbors different from that with four interchain neighbors.[19,20] Among the four interchain pairs, two pairs always have the spins in the same direction and contribute a constant to the total energy. This interaction term was also excluded in the above expression. The exchange constant J_{BB} in the above equation represents the average value of the intrachain and interchain interactions.

Applying the equilibrium condition of torques to the derivative of the total energy with respect to the angle ϕ gives

$$m_B H \sin\psi - 30J_{AB}\sin\theta + 32J_{BB}\sin\Theta\cos\phi = 0, \tag{3}$$

and the derivative with respect to the angle θ in combination with Eq. (3) gives

$$\begin{aligned} & K_A \sin 2\theta - m_A H \sin(\theta - \psi) + 60J_{AB}\Bigg(\sin\theta\cos\Theta \\ & + \frac{-m_B H \sin\psi + 30J_{AB}\sin\theta}{32J_{BB}}\cos\theta\Bigg) = 0. \end{aligned} \tag{4}$$

To estimate K_A, J_{AB}, and J_{BB} qualitatively, the Mn^{2+} angle data were used in the least-squares fit of Eq. (4). Since Mn^{3+} moments lie nearly in the ab plane even when the magnetic field is in the perpendicular direction, we approximated $\Theta = \frac{\pi}{2}$. When the 7-T magnetic field is along the ab plane, the angle between the Mn^{3+} moment and the field is $120 \pm 5^\circ$ as mentioned above. From this angle and Eq. (3), we get the relation between J_{AB} and J_{BB}:

$$J_{BB} = 1.88J_{AB}(\pm 0.38) - 0.09(\pm 0.01) \tag{5}$$

in meV units. J_{AB} and J_{BB} have the linear relation for the same angle ϕ because J_{AB} tends to decrease the angle between Mn^{2+} moments and J_{BB} increases. Using the relation between J_{AB} and J_{BB}, the relation between K_A and J_{AB} we get from the least-squares fit is

$$K_A = -14.7J_{AB} + 2.0 < 0 \tag{6}$$

in meV units. The uniaxial anisotropy of Mn^{2+} and external magnetic field along the c axis tend to align the Mn^{2+} moment to the c-axis direction while the exchange interaction J_{AB} tends to align the Mn^{2+} moment in the opposite direction to the Mn^{3+} moment, which is in the ab plane. The angle of the Mn^{2+} moment in the external field is determined in order to make the torque due to the magnetic field equal to the sum of those due to the anisotropy field and exchange interaction, resulting in the linear relation between K_A and J_{AB}, as in Eq. (6). The sign of K_A is negative, that is, the anisotropy of the Mn^{2+} magnetic moment is not the plane but axial type along the c axis. The value of J_{AB} reported in previous works ranges from 0.27 to 0.59.[19–21] For this range of J_{AB}, Eqs. (5) and (6) predict $0.42 < J_{BB} < 1.02$ and $-6.7 < K_A < -2.0$, respectively. The strong antiferromagnetic exchange coupling holds the Mn^{2+} moment in the ab plane in the absence of field, overcoming the Mn^{2+} axial anisotropy. The range of K_A value presented here is quite larger than the typical values. One of the reasons might be the very low magnetic moment of Mn^{2+}. Neutron diffraction experiments[2–4] yielded about 4.5 μ_B as the magnetic moment of Mn^{2+} ions in Mn_3O_4. This suggests strong crystal-field effects on the A site, which may give rise to a strong magnetic anisotropy.[10] The simple mean-field approach might also be the reason for the unusually large K_A.

IV. CONCLUSION

Mn_3O_4 has two different magnetic ions: Mn^{2+} and Mn^{3+}. Two Mn^{3+} moments and one Mn^{2+} moment form the Yafet-Kittel structure where the Mn^{2+} moment lies in the ab plane and the Mn^{3+} moments are aligned along the canted direction opposite to the Mn^{2+} moment. The NMR experiment in the external field along the ab plane shows that the angle between Mn^{2+} and Mn^{3+} moments is 120°. When the field direction rotates from the ab plane to the c axis, the Mn^{2+} moment is tilted to the field direction, while the Mn^{3+} moments nearly stay in the ab plane. In the 7-T magnetic field along the c axis, Mn^{3+} moments are tilted to the c-axis direction by only about 3°. This indicates that the Mn^{3+} moment has the easy-plane anisotropy and the anisotropy field of Mn^{3+} is estimated to be 65 T. Therefore, it is clear that the Yafet-Kittel structure consisting of one Mn^{2+} moment and two Mn^{3+} moments lies in the ab plane in zero field, contrary to previous reports. In the 7-T field along the c axis, Mn^{2+} moments are tilted from the ab plane by about 25°. The direction of a moment in the external field is determined by anisotropy constants K_A and K_B and exchange constants J_{AB} and J_{BB}. From the least-squares fit of the angle data for various directions of magnetic field, we obtained $J_{BB} = 1.88J_{AB} - 0.09$ and $K_A = -14.7J_{AB} + 2.0$ in meV units.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation under Grants No. NRF-2009-0078342 and No. 2012R1A2A2A01003598.

*soonchillee@kaist.ac.kr

[1]T. Suzuki, K. Adachi, and T. Katsufuji, J. Magn. Magn. Mater. **310**, 780 (2007).
[2]B. Boucher, R. Buhl, and M. Perin, J. Appl. Phys. **42**, 1615 (1971).
[3]G. B. Jensen and O. V. Nielsen, J. Phys. C: Solid State Phys. **7**, 409 (1974).
[4]B. Chardon and F. Vigneron, J. Magn. Magn. Mater. **58**, 128 (1986).
[5]M. Kim, X. M. Chen, Y. I. Joe, E. Fradkin, P. Abbamonte, and S. L. Cooper, Phys. Rev. Lett. **104**, 136402 (2010).
[6]F. Guillou, S. Thota, W. Prellier, J. Kumar, and V. Hardy, Phys. Rev. B **83**, 094423 (2011).
[7]R. Tackett, G. Lawes, B. C. Melot, M. Grossman, E. S. Toberer, and R. Seshadri, Phys. Rev. B **76**, 024409 (2007).
[8]R. J. Tackett, J. G. Parsons, B. I. Machado, S. M. Gaytan, L. E. Murr, and C. E. Botez, Nanotechnology **21**, 365703 (2010).
[9]T. Suzuki and T. Katsufuji, Phys. Rev. B **77**, 220402 (2008).
[10]O. V. Nielsen and L. W. Roeland, J. Phys. C: Solid State Phys. **9**, 1307 (1976).
[11]K.-T. Ko, K. Kim, S. B. Kim, H.-D. Kim, J.-Y. Kim, B. I. Min, J.-H. Park, F.-H. Chang, H.-J. Lin, A. Tanaka, and S-W. Cheong, Phys. Rev. Lett. **107**, 247201 (2011).
[12]K.-T. Ko, H.-J. Noh, J.-Y. Kim, B.-G. Park, J.-H. Park, A. Tanaka, S. B. Kim, C. L. Zhang, and S-W. Cheong, Phys. Rev. Lett. **103**, 207202 (2009).
[13]K. Dwight and N. Menyuk, Phys. Rev. **119**, 1470 (1960).
[14]O. V. Nielsen, J. Phys. (Paris) Colloq. **32**, Suppl. C1-51 (1971).
[15]E. A. Turov and M. P. Petrov, *Nuclear Magnetic Resonance in Ferro- and Antiferromagnets* (Wiley, New York, 1972).
[16]E. Jo, K. An, J. H. Shim, C. Kim, and S. Lee, Phys. Rev. B **84**, 174423 (2011).
[17]D. Y. Yoon, S. Lee, Y. S. Oh, and K. H. Kim, Phys. Rev. B **82**, 094448 (2010).
[18]H. Yasuoka and T. Kubo, J. Phys. Soc. Jpn. **29**, 1102 (1970).
[19]A. Chartier, P. D'Arco, R. Dovesi, and V. R. Saunders, Phys. Rev. B **60**, 14042 (1999).
[20]J.-H. Chung, J.-H. Kim, S.-H. Lee, T. J. Sato, T. Suzuki, M. Katsumura, and T. Katsufuji, Phys. Rev. B **77**, 054412 (2008).
[21]G. Srinivasan and M. S. Seehra, Phys. Rev. B **28**, 1 (1983).