NMR study on the stability of the magnetic ground state in $MnCr_2O_4$

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The canting angles and fluctuation of the magnetic ion spins of spinel oxide $MnCr_2O_4$ were studied by nuclear magnetic resonance at low temperatures, which has a collinear ferrimagnetic order below T_C and a ferrimagnetic spiral order below $T_s < T_C$. Contrary to previous reports, only one spin canting angle of Cr ions was observed. The spin canting angles of Mn and Cr ions in the ferrimagnetic spiral obtained at a liquid-He temperature were 43° and 110°, respectively. The nuclear spin-spin relaxation was determined by the Suhl-Nakamura interaction at low temperatures but the relaxation rate T_2^{-1} increases rapidly as the temperature approaches T_s. This indicates that the fluctuation of the spiral component becomes faster as the temperature increases but not fast enough to leave an averaged hyperfine field to nuclei in the time scale of nuclear spin precession in the ferrimagnetic phase, which is on the order of 10^{-8} s. The spiral volume fraction measured for various temperatures reveals that the collinear and the spiral ferrimagnetic phases are mixed below the transition temperature of the spiral order. The temperature hysteresis in the volume fraction implies that this transition has first-order characteristics.

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I. INTRODUCTION

One of the reasons spinel oxides AB_2O_4 have been of interest is the various spin structures they show at low temperatures.[1–3] Cubic spinels MCr_2O_4 (M=Mn,Co) have drawn much attention recently in relation with multiferroics since it was found that their spin configuration leads ferroelectric.[4] The magnetic phase of MCr_2O_4 changes from paramagnetic to ferrimagnetic and from ferrimagnetic to spiral orders as the temperature decreases, even becoming glasslike at low temperatures. The complexity in the spin structure of cubic spinels results from geometrical frustration among the spins of B site ions, which form the lattice of corner-sharing tetrahedra. M (Cr) ions occupy the A (B) sites that locate at the center of a tetrahedron (octahedron) in the oxygen lattice. Both the M ions and Cr ions are magnetic, and their magnetization directions are opposed in the ordered states.

The antiferromagnetic exchange interaction J_{BB} among the spins of the B site ions does not induce ordered states due to the aforementioned frustration.[5] However, the addition of the exchange interaction J_{AB} between the A and B site ions can give rise to a magnetic order. The relative strength of J_{AB} to J_{BB} is the key factor determining the state of the magnetic order, including the spin canting angle. The Néel configuration, a collinear ferrimagnet, is expected to be the ground state when J_{BB} is much weaker than J_{AB}. As J_{BB} increases, both the M and Cr spins become canted and the magnetic structure becomes complex. A classical theory predicts that the ground state of a cubic spinel is determined by the parameter $u=4J_{BB}S_B/3J_{AB}S_A$, where S_A and S_B are the spin magnitudes at the A and B sites, respectively.[6] The Néel configuration is the ground state when $u<8/9$ and the ferrimagnetic spiral is locally stable when $8/9<u<1.3$. It becomes unstable when $u>1.3$.

An early neutron-diffraction experiment showed that the ferrimagnetic spiral is the ground spin state of the cubic spinel $MnCr_2O_4$.[7] Two different spin canting angle values were measured for the Cr ions while only one value was measured for the Mn ions. The cone angles of the Mn ions, Cr(I), and Cr(II) in the ferrimagnetic spiral were 24°, 104°, and 152°, respectively. The approximate u value estimated by these measurements is 1.6, which predicts that the ferrimagnetic spiral is unstable. In contrast, the cone angle of Mn ion spins measured by nuclear magnetic resonance (NMR) was 63° or 42° while those of Cr(I) and Cr(II) spins were 94° and 97°, respectively.[8–10] Theory poorly matches these numbers but it predicts a very unstable spiral state in general. The question as to whether the ferrimagnetic spiral is the stable ground state in the cubic spinels was raised again by a recent neutron-diffraction experiment involving $MnCr_2O_4$.[11] It was reported that the ferrimagnetic state is long-range ordered for all temperatures below $T_C \sim 50$ K and that the spiral component appears in the plane orthogonal to the direction of the ferrimagnetic order below $T_s \sim 20$ K. However, it is only short-range ordered.

The present study investigates the characteristics of the ordered spin state of $MnCr_2O_4$ at a low temperature by NMR. First, the cone angles of Mn and Cr ion spins, to which the previous NMR and neutron-diffraction results gave different values, were measured. Information pertaining to accurate cone angles is important to understand not only the ground state of the spin order but also the electrical polarization.[12] We measured the nuclear spin-spin relaxation time T_2 as a function of the temperature to study the change in the spin fluctuation with temperature. The result indicates that the fluctuation of the spiral component increases rapidly as the temperature approaches the phase transition temperature of the spiral order T_s, above which the fluctuation is too fast for the spiral component to be measured by even local probes such as neutron diffraction or NMR. The temperature dependence of the NMR signal intensity reveals that the spi-

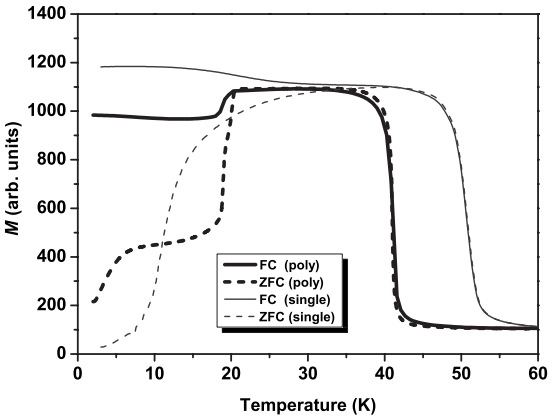

FIG. 1. Magnetization vs temperature curves obtained at 50 Oe: the thick solid and dashed lines represent the FC and ZFC $M(T)$ curves of the polycrystalline sample, respectively, and the thin lines represent those of the single crystal.

ral phase is mixed with the ferrimagnetic phase at temperatures below T_s.

II. EXPERIMENT

A polycrystalline $MnCr_2O_4$ sample was synthesized by a solid-state reaction from a molar ratio mixture of MnO and Cr_2O_3 powders. The mixture was sintered at 1100 °C for 12 h in an Ar environment, for 12 additional hours at 1200 °C, and finally for 24 h at 1300 °C. A single-crystalline sample was grown by the flux method using a mixture of $MnCO_3$, Cr_2O_3, PbF_2, and PbO (molar ratio=1:1:2:2). Saturation magnetization was measured in the temperature range of 4–20 K by a superconducting quantum interference device magnetometer. NMR signals were obtained by the conventional spin echo method using a custom-made spectrometer in the same temperature range. To estimate the spin canting angle, the resonance frequency was measured for various magnetic fields up to 4 T. The nuclear spin-spin relaxation time, T_2, was obtained by varying the time delay between the 90° and 180° pulses. The ^{53}Cr NMR spectrum was measured in the frequency range from 60 to 70 MHz, and the ^{55}Mn NMR spectrum was assessed from 530 to 560 MHz. As the spectral width was very broad, the signal intensity was measured as a function of the frequency after selective excitation.

III. RESULTS AND DISCUSSION

The magnetization versus the temperature curves show a discrepancy in the transition temperatures of the ferrimagnetic spiral and the collinear ferrimagnet of the polycrystalline and single-crystalline samples. In Fig. 1, the thick solid and dashed lines represent the field-cooling (FC) and zero-field-cooling (ZFC) $M(T)$ curves of the polycrystalline sample, respectively, and the thin solid and dotted lines represent those of the single crystal. T_C is relatively well defined by the abrupt increase in the magnetization in both samples of approximately 40 K for the polycrystalline sample and 50 K for the single-crystalline sample. T_s of the polycrystalline sample is more clearly defined by the abrupt decrease in the

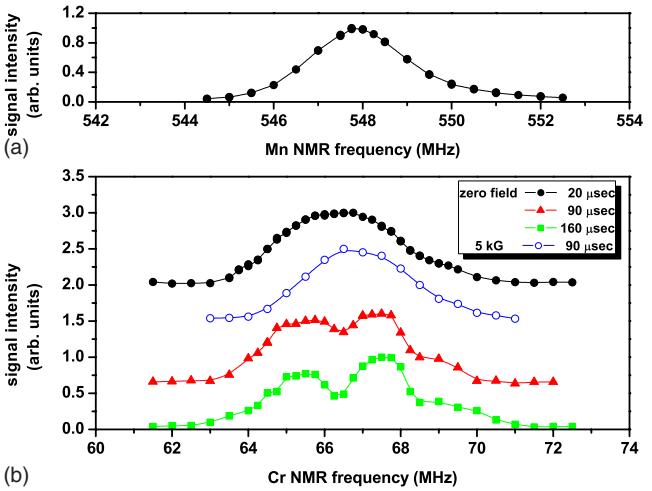

FIG. 2. (Color online) (a) The filled circles represent the zero-field Mn NMR spectrum obtained in a zero field at 6.5 K. (b) The filled circles represent the zero-field Cr NMR spectrum obtained at the echo time of 20, 90, and 160 μs, and the open circles represent the Cr NMR spectrum obtained in the external field of 5 kG and at the echo time of 90 μs.

magnetization at 20 K compared to that of the single-crystalline sample, whose magnetization decreases smoothly at approximately 12 K only in the ZFC case. The $M(T)$ curves of our polycrystalline and single-crystalline samples are in good agreement with those in previous reports.[11,13] One of the reasons for the difference in the characteristics of the two samples is the site disorder in the single-crystalline sample. X-ray absorption spectroscopy showed that the Mn ions occupy only the A sites and the Cr ions occupy the B sites in our polycrystalline sample whereas both ions are found in both sites in the single-crystalline sample.[14] All of the experimental data described below were obtained from the polycrystalline sample.

Figure 2(a) shows the ^{55}Mn NMR spectrum obtained in a zero field at 6.5 K. The spectrum shows a well-defined single Gaussian peak centered around 548 MHz. The nuclear spin-spin relaxation time T_2 at the central part of the spectrum is on the order of microseconds. The linewidth is about 8 MHz that is much greater than $1/T_2$, implying that it is the inhomogeneous broadening. Figure 2(b) shows the ^{53}Cr NMR spectrum obtained in a zero field at 6.5 K for several different echo times. The spectrum obtained at the echo time of 20 μs shows a very well-defined single peak whose width is about 5 MHz. The single peak centered around 67 MHz at a short echo time of 20 μs appears to split into a double peak as the echo time supasses 90 μs. This is not a splitting but a suppression of the spectral intensity around the center due to the frequency-dependent nuclear spin-spin relaxation rate. In an ordered magnetic insulator containing a high concentration of identical magnetic nuclear spins, the Suhl-Nakmura (SN) interaction, in which nuclear spins are indirectly coupled by virtual magnons, is expected to play a major role in the NMR relaxation at low temperatures. It is known that the SN interaction generates a field- and frequency-dependent T_2 with a minimum occurring in the center of the spectrum, as the majority of nuclear spins precess at this

frequency.[15–17] Therefore, the central part of the spectrum decays faster than the rest as the echo time increases, making a dip in the spectrum at a long-enough echo time. The double peak feature of the spectrum obtained at 90 μs disappears in the spectrum obtained at the same echo time, however, in a magnetic field, as denoted by the open circles in the figure. This is consistent with the fact that the spin-spin relaxation rate due to the SN interaction decreases as the field increases. The dependence of T_2 on the frequency and field confirms that the SN interaction is the main source of Cr nuclear interaction in $MnCr_2O_4$. This most likely explains why a double peak was observed in the previous NMR work, rather than the difference in the sample quality.[10] The difference of only 3% in the canting angles of the two Cr spins associated with the two peaks in the previous NMR report supports this claim because the experimental error of the canting angle as estimated by NMR is larger than this in general.

The spin canting angles of the Mn^{2+} and Cr^{3+} ions relative to the magnetization direction are determined by the shift of the spectrum with an external field. The NMR resonance frequency f is proportional to the magnitude of the total field, which is the vector sum of the hyperfine field H_{hf} and external field H_{ext}. This is expressed as follows:

$$f = \gamma/2\pi|\vec{H}_{ext} + \vec{H}_{hf}| \simeq \gamma/2\pi(H_{hf} - H_{ext}\cos\theta),$$

where γ is the gyromagnetic ratio, and θ is the angle between H_{hf} and H_{ext}. The direction of the hyperfine field is antiparallel to the local magnetization in most magnetic materials, providing the minus sign in the equation. As the hyperfine fields of the Mn^{2+} and Cr^{3+} ions in $MnCr_2O_4$ are more than one order of magnitude larger than the external magnetic field used in the experiment, the first-order approximation of the total field can be taken. The slope of the frequency shift with external field is then determined as $\gamma/2\pi\cos\theta$.

In Fig. 3, the center frequencies of the Cr and Mn NMR spectra obtained at 4.2 K are plotted as a function of the external field. Both of the frequencies change linearly in the experimental field range, as expected. The resonance frequency of the Mn spectrum decreases as the field increases whereas that of the Cr spectrum increases. This visually shows that the spin directions of the Mn and Cr ions are opposite to each other because the signs of the hyperfine fields of the ions are identical. From the slope of the linear fit to the data, the spin canting angles of the Mn and Cr ions were determined to be $43\pm5°$ and $110\pm5°$, respectively. This is contrary to the previous neutron-diffraction or NMR experiments that reported two different values of spin canting angles for Cr ions. The canting angle of the Mn spin is identical to that in one of the previous NMR reports[9] but twice as large as the value of the neutron result.[7] The canting angle of the Cr spin is consistent with the previous NMR measurement[10] and one of the values given by the neutron diffraction.[7] Considering that no single value of u can result in these cone angles, the classical theory fails to explain the result. However, both of the values corresponding to the Mn and Cr spin canting angles indicate that the ferrimagnetic spiral configuration is unstable in $MnCr_2O_4$. This reminds us of the fact that a long-range order of the ferrimagnetic component accompanies a short-range order of the spiral component below T_s in $MnCr_2O_4$.[11]

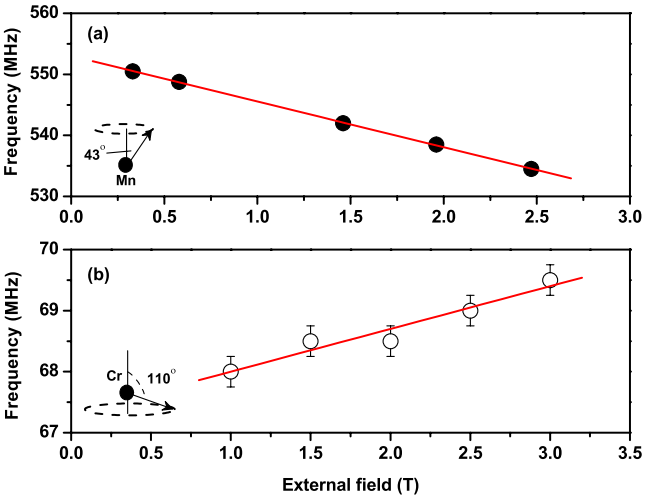

FIG. 3. (Color online) (a) The filled circles represent the central frequency of the Mn NMR spectrum obtained in the external field at 4.2 K. (b) The open circles represent the central frequency of the Cr NMR spectrum obtained in the external field at 4.2 K. The red lines denote the linear fit, of which the slope is $\gamma/2\pi\cos\theta$.

Figure 4 shows the nuclear spin-spin relaxation rate T_2^{-1} of Cr ions at temperatures ranging from 6.5 to 14.5 K. The relaxation rate increases relatively slowly with the temperature below 11 K, above which the slope becomes steep. The main interaction a Cr ion nucleus experiences is the interaction with the electron spins of magnetic ions and the prominent relaxation source is SN interaction that is mediated by spin wave as mentioned above. The relaxation due to SN interaction is normally temperature independent. Therefore, the weakly temperature-dependent relaxation with the rate of 2×10^4 s^{-1} near 7 K should be mainly due to SN interaction. The additional relaxation increasing fast with temperature indicates that the spin fluctuation becomes too large to be described in the framework of SN interaction, which is formulated for the case the spin fluctuation is small enough to

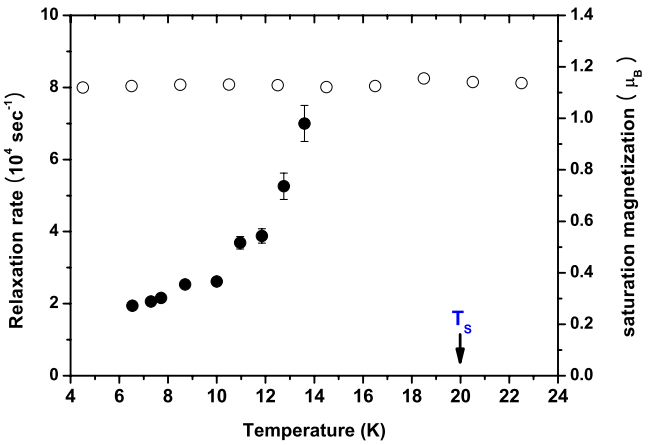

FIG. 4. (Color online) The filled circles show the relaxation rate T_2^{-1} at the central frequency of the Cr NMR spectrum with the temperature. The open circles denote the saturation magnetization.

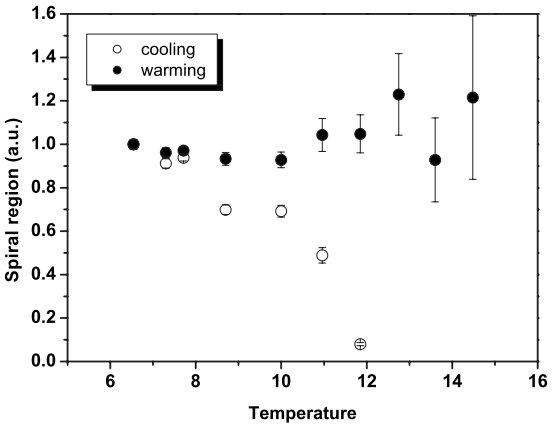

FIG. 5. The volume fraction of the ferrimagnetic spiral phase vs the temperature. The open circles represent the volume fraction of the ferrimagnetic spiral obtained while cooling and the filled circles represent that obtained while warming.

be described by spin waves, as the temperature approaches T_s. The previous observation that the spiral component of the spin order is unstable and short ordered implies that it is the spiral component of the Cr ion spins that fluctuates. This interpretation is also consistent with the saturation magnetization plotted together with the nuclear relaxation rate in Fig. 4. The value of the saturation magnetization stays at $1.1\mu_B$ independent of temperature even when the temperature crosses T_s, where the spiral component is generated or vanishes. This means that the component along the easy axis remains the same while the spiral component perpendicular to it is averaged out by fluctuation crossing T_s, leaving only the ferrimagnetic order.

The NMR signal intensity is in general a function of the temperature, T_2, and the number of nuclei. The data points in Fig. 5, where the Cr NMR signal intensity vs the temperature is plotted, were obtained from the raw experimental data after temperature and T_2 correction. Thus, they represent the number of the nuclei producing the signal. The signal intensity obtained while warming the sample stays constant while that obtained while cooling it changes. It is worthwhile to note that the NMR signal is observed not in the ferrimagnetic phase but only in the spiral phase of $MnCr_2O_4$. Therefore, the corrected signal intensity in the figure is proportional to the volume of the ferrimagnetic spiral phase. Upon warming, the entire volume of the $MnCr_2O_4$ sample maintains its ferrimagnetic spiral phase until the change to the ferrimagnetic phase at T_s. Upon cooling, however, $MnCr_2O_4$ remains in the ferrimagnetic phase well below T_s. In the temperature region where the signal intensity changes, the two phases coexist. Depending on the temperature change history, the ferrimagnetic spiral phase is embedded in the matrix of the collinear ferrimagnet phase. The mixed phase may cause some error in the data analysis of the experiments assuming a single phase below T_s such as the spin canting angle measurement in neutron diffraction, we think. The temperature hysteresis in the volume of the ferrimagnetic spiral phase can be ascribed to a first-order transition at T_s. An electron spin resonance work on the similar cubic spinel $CoCr_2O_4$ showed an abrupt shift of the frequency at T_s, also indicating a first-order transition.[18] The experimental evidence is in conflict to the second-order transition on which the classical theory is based. The Mn NMR signal intensity also showed a similar temperature hysteresis.

IV. CONCLUSION

Neutron-diffraction experiments investigated the magnetic property of $MnCr_2O_4$ in detail. The works showed that the spiral component is short-range ordered through the observation of the diffusive satellite peaks and measurement of the canting angle, and claimed that the spin glasslike behavior is caused by the fluctuation of the spiral component. In this work, we measured again the canting angles to which neutron-diffraction and NMR experiments gave quite different results, and showed that the fluctuation of the spiral component is the key factor explaining the magnetic behavior of $MnCr_2O_4$. The spin fluctuation makes the spiral component short range ordered and causes a transition to the ferrimagnetic phase, as well as the glasslike behavior. Only one canting angle of Cr spins was observed in our NMR study, contrary to that observed in previous neutron and NMR experiments. The measured canting angles predict an unstable ferrimagnetic spiral state at a low temperature. This instability is consistent with the measurement of the spin-spin relaxation rate. The relaxation rate increases more rapidly as the temperature increases until it appears to diverge at T_s. The rapid increase in the relaxation rate near T_s can be explained by the fluctuation of the spiral component. The NMR signal is not observed due to this strong relaxation near T_s. The NMR signal is unobservable above T_s as well, where the magnetic phase is collinear ferrimagnetic. The magnetization remains the same, crossing T_s, indicating that the canted spins in the ferrimagnetic spiral phase do not line up along one direction, entering the ferrimagnetic phase; instead, the fluctuation of the spiral component averages out to leave only the magnetic component along the easy axis. The fluctuation accelerates as the temperature approaches T_s, and past T_s, it becomes fast enough to make the spiral component unobservable in neutron diffraction experiments but not fast enough to leave an averaged hyperfine field to nuclei in the time scale of nuclear spin precession, which is on the order of 10^{-8} s. The temperature hysteresis of the spiral volume fraction indicates that the spiral and collinear ferrimagnetic phases are generally mixed below T_s.

ACKNOWLEDGMENTS

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