

## Spin state and orbital ordering in $\text{CuCr}_2\text{O}_4$ investigated by NMR

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(Received 20 June 2013; revised manuscript received 8 August 2013; published 12 September 2013)

$^{63,65}\text{Cu}$  and  $^{53}\text{Cr}$  nuclear magnetic resonance spectra for  $\text{CuCr}_2\text{O}_4$  were measured at various magnetic fields and temperatures. The microscopic evidence of orbital ordering in  $\text{CuCr}_2\text{O}_4$  was obtained from a dipolar hyperfine field, NQR, and magnetic anisotropy analysis of the linewidth broadening of the Cu and Cr NMR spectra measured in the external magnetic field. The energy gap in the dispersion relation of the spin wave excitation was measured from the temperature dependence of the resonance frequency of Cu and Cr ions in  $\text{CuCr}_2\text{O}_4$ . The energy gap of the Cu ions is about 10 K ( $\pm 5$  K), and that of the Cr ions is about 40 K ( $\pm 5$  K). These values imply that the spin-orbit coupling of Cr ions is stronger than that of Cu ions related to the orbital ordering in  $\text{CuCr}_2\text{O}_4$ . The magnetic field dependence of the Cr NMR frequency shows that the angle between the  $\text{Cr}^{3+}$  magnetic moment and the  $\text{Cu}^{2+}$  magnetic moment is about  $98^\circ$  ( $\pm 2^\circ$ ).

DOI: [10.1103/PhysRevB.88.094417](https://doi.org/10.1103/PhysRevB.88.094417)

PACS number(s): 76.60.-k, 75.25.-j, 75.25.Dk, 75.50.Gg

### I. INTRODUCTION

Coupling between the lattice, spin, and orbital in a spinel ( $\text{AB}_2\text{O}_4$ ) compound that has geometrical frustration has attracted interest. The frustration is induced by magnetic ions in  $B$  sites at the corners of the tetrahedron of the cubic spinel structure. The frustration is released as a result of the structural phase transition from cubic to lower structural symmetry. In the case of spinels that have magnetic ions in both  $A$  and  $B$  sites, the magnetic ground states are complex because of the  $A$ - $A$ ,  $A$ - $B$ , and  $B$ - $B$  exchange interactions. Magnetic phase transition can be induced by structural phase transition. Also, the orbital ordering related to the structural phase transition is affected by the magnetic ground state. For example,  $\text{MnV}_2\text{O}_4$  shows magnetostriction, orbital ordering, and complex magnetic ground states.<sup>1-3</sup>

$\text{ACr}_2\text{O}_4$  chromium spinels show complex noncollinear magnetic order with three magnetic sublattices. This noncollinear magnetic order was caused by sufficiently strong coupling between the spins of neighboring  $A^{2+}$  and  $\text{Cr}^{3+}$  ions.<sup>4</sup> The magnetic moment and the orbital degeneracy of the  $A$ -site ions can change the magnetic and structural properties. For example the magnetoelasticity, which is closely related to the magnetocapacitance and other magnetoelectric phenomena, was affected by the orbital degeneracy of the  $A$ -site ion in  $\text{ACr}_2\text{O}_4$ .<sup>5</sup>

The spinel  $\text{CuCr}_2\text{O}_4$  has two kinds of magnetic ions at the cation sites. The magnetic ions in the tetrahedral ( $A$ ) sites are related to orbital ordering (Fig. 1). The structural phase transition temperature is 850 K ( $=T_S$ ). Above  $T_S$ ,  $\text{CuCr}_2\text{O}_4$  has cubic symmetry; below  $T_S$ , it has compressed tetragonal symmetry. The lattice parameters of the tetragonal  $\text{CuCr}_2\text{O}_4$  are  $a = 8.5 \text{ \AA}$  and  $c = 7.8 \text{ \AA}$  at room temperature.<sup>6-9</sup> Recently, an additional phase transition from a tetragonal structure to an orthorhombic structure was observed at the magnetic phase transition temperature.<sup>10,11</sup>  $\text{Cu}^{2+}$  magnetic ions are in the  $A$  sites, surrounded by four oxygen neighbors, at the corners of a tetrahedron;  $\text{Cr}^{3+}$  magnetic ions are in the  $B$  sites, surrounded by six oxygen neighbors, at the corners of an octahedron. The  $\text{Cu}^{2+}$  ions have a  $3d^9$  spin configuration, while the  $\text{Cr}^{3+}$  ions have a  $3d^3$  spin configuration. The cooperative Jahn-Teller effect at the tetrahedral site induces

the structural phase transition, splitting the triply degenerated  $t_{2g}$  orbital into a nondegenerated  $xy$  orbital at higher energy and doubly degenerated  $yz$  and  $zx$  orbitals at lower energy [Fig. 1(b)]. An unpaired electron among the  $3d$  electrons of the  $\text{Cu}^{2+}$  ion occupies the  $xy$  orbital. Therefore, orbital ordering in the  $\text{CuCr}_2\text{O}_4$  spinel oxide is expected. However, most investigations regarding orbital ordering in  $\text{CuCr}_2\text{O}_4$  have focused on the structural phase transition and changes of the lattice parameter.

$\text{CuCr}_2\text{O}_4$  becomes a noncollinear ferrimagnet below 135 K ( $=T_c$ ), with three magnetic sublattices.<sup>9,12</sup> The triangular magnetic moment configuration of  $\text{CuCr}_2\text{O}_4$  [Fig. 1(c)], in which a  $\text{Cu}^{2+}$  magnetic moment is coupled antiferromagnetically to the net magnetization of two canted  $\text{Cr}^{3+}$  magnetic moments, was investigated using neutron diffraction experiments.<sup>6</sup> The magnetic moment of  $\text{CuCr}_2\text{O}_4$  is 0.5–0.7  $\mu_B$  per formula unit.<sup>6,9,11</sup> According to Prince's neutron diffraction experiment, the directions of the Cr magnetic moments in the same (001) planes are identical.

In the present work, we measured  $^{63,65}\text{Cu}$  and  $^{53}\text{Cr}$  nuclear magnetic resonance (NMR) spectra for  $\text{CuCr}_2\text{O}_4$  at various magnetic fields and temperatures. To investigate orbital ordering in  $\text{CuCr}_2\text{O}_4$ , the linewidths of the Cu and Cr NMR spectra measured in an external magnetic field of 2 T were compared. Also, to analyze the linewidths of the Cu and Cr NMR spectra, the resonance frequency shift caused by the dipole fields, the nuclear quadrupole effect, and the magnetic anisotropy were calculated. The energy gaps in the dispersion relation of the spin wave were obtained from the temperature dependence of the Cu and Cr NMR frequencies. The canting angle of the  $\text{Cr}^{3+}$  magnetic moment was estimated from the external magnetic field dependence of the Cr NMR frequency.

### II. EXPERIMENT

The sample was commercially available polycrystalline powder  $\text{CuCr}_2\text{O}_4$  of 99.9% purity (Kojundo). A continuous flow cryostat was placed within the bore of a superconducting magnet. Cu and Cr NMR spectra were obtained by recording spin-echo signal intensities at various frequencies. A conventional spin-echo pulse sequence ( $90^\circ$ - $\tau$ - $180^\circ$ ) was used. Because the Cu NMR frequency for  $\text{CuCr}_2\text{O}_4$  was not known,

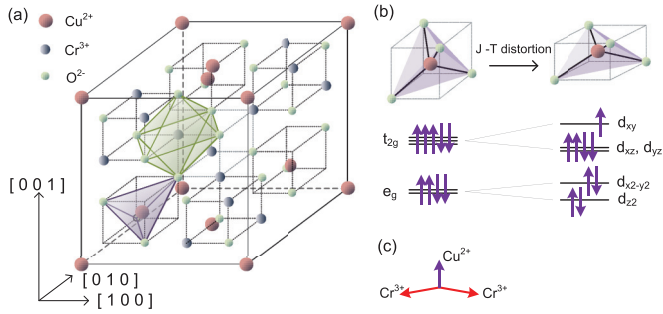


FIG. 1. (Color online) (a) Spinel oxide  $\text{CuCr}_2\text{O}_4$ . The largest brown circles are  $\text{Cu}^{2+}$  ions, the middle-sized blue circles are  $\text{Cr}^{3+}$  ions, and the smallest light green circles are  $\text{O}^{2-}$  ions. (b) Jahn-Teller distortion of the  $\text{CuO}_4$  tetrahedron. (c) The triangular magnetic moment configuration of  $\text{CuCr}_2\text{O}_4$ , in which a  $\text{Cu}^{2+}$  magnetic moment is coupled antiferromagnetically to the net of two canted  $\text{Cr}^{3+}$  magnetic moments.

we searched for the Cu NMR spectrum in a wide frequency range of 100–300 MHz, where the resonance signal of  $\text{Cu}^{2+}$  ions is usually found. The zero-field NMR frequency for  $\text{Cr}^{3+}$  ions in  $\text{CuCr}_2\text{O}_4$  was around 63 MHz, which is consistent with previous  $\text{Cr}^{3+}$  zero-field NMR experimental results.<sup>13</sup>

### III. RESULTS AND DISCUSSION

The nuclear magnetic resonance (NMR) frequency for the magnetic materials is given by

$$f = \frac{\gamma}{2\pi} |\mathbf{H}_{\text{ext}} + \mathbf{H}_{\text{hyp}}|, \quad (1)$$

where  $\gamma$  is the nuclei gyromagnetic ratio,  $\mathbf{H}_{\text{ext}}$  is the external magnetic field, and  $\mathbf{H}_{\text{hyp}}$  is the hyperfine field. In zero-field NMR, the resonance frequency is proportional to the hyperfine field, which is proportional to the magnetic moment. When the external magnetic field is applied, the resonance frequency is proportional to the vector sum of the hyperfine field and the external magnetic field.

Figure 2(a) shows the zero-field Cu NMR spectra measured in the temperature range of 7–45 K. Above 45 K, the spin-spin relaxation time was too short for the echo signal to be measured. The spectrum is positioned in the frequency range of 160–175 MHz at 7 K. The asymmetric and broad spectra, measured at various temperatures, were caused by unresolved  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  nuclear quadrupole resonance (NQR) lines. The Cu NMR frequency decreases with increasing temperature, while the spectrum shapes remained mostly unchanged. In the zero magnetic field, the NMR frequency is proportional to the magnetic moment. Therefore, when the temperature increased, the decrease of the resonance frequency indicates that the local magnetic moment is reduced by thermal fluctuation. Considering the energy gap ( $E_g$ ) in the dispersion relation of the spin waves, the temperature dependence of the sublattice magnetization ( $M$ ) at a sufficiently low temperature is given by<sup>14</sup>

$$M(0) - M(T) \propto T^{3/2} \exp(-E_g/kT). \quad (2)$$

Figure 2(b) shows the temperature dependence of the Cu NMR resonance frequencies at the maximal intensity of each

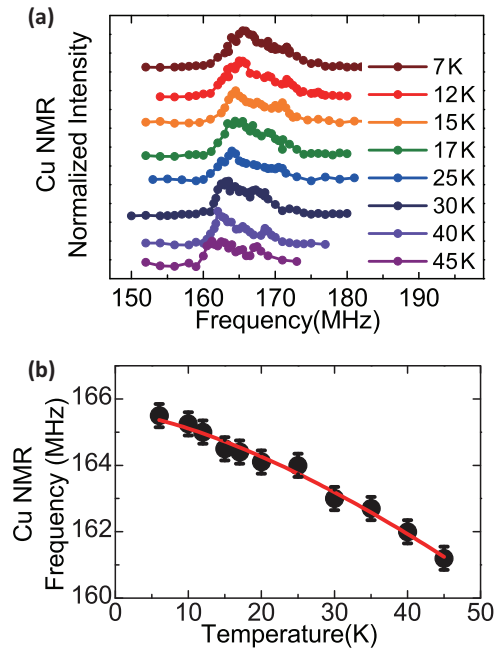


FIG. 2. (Color online) (a) Zero-field Cu NMR spectra measured in the temperature range of 7–45 K. (b) Temperature dependence of the Cu NMR frequency at 0 T. The solid red line is the fit to Eq. (2).

spectrum, measured at various temperatures. The temperature dependence of the resonance frequency in our data fits Eq. (2) well (solid red line). The energy gap of the Cu ions in  $\text{CuCr}_2\text{O}_4$ , obtained from the fitting, is about 10 K ( $\pm 5$  K).

Figure 3(a) shows the Cr NMR spectra measured in the external magnetic field range of 0–7 T at 5 K. The spectrum is positioned around 63 MHz in the zero-field. The Cr NMR frequency decreases with an increasing magnetic field because the hyperfine field direction is antiparallel with the external magnetic field. The resonance frequency is proportional to the vector sum of the external magnetic field and the hyperfine field, which is parallel or antiparallel to the magnetic moment. Therefore, the angle between the external magnetic field and the magnetic moment can be obtained from the magnetic field dependence of the resonance frequency. Figure 3(b) shows the magnetic field dependence of the Cr NMR frequencies, obtained from the Gaussian fitting of each spectrum. Since the hyperfine field of the Cr ions is one order of magnitude larger than the external magnetic field, the first-order approximation of the total field [Eq. (1)] can be taken. Then,  $f = \frac{\gamma}{2\pi} (\cos \theta H_{\text{ext}} + H_{\text{hyp}})$ , where  $\theta$  is a canting angle. The linear fitting result is represented by a solid red line in Fig. 3(b). The estimated canting angle between the Cr magnetic moment and the Cu magnetic moment is about  $98^\circ$  ( $\pm 2^\circ$ ). The magnetic moment of Cu is  $1 \mu_B$  when the orbital angular momentum is neglected. If the magnetic moment of  $\text{CuCr}_2\text{O}_4$  is  $0.5 \mu_B$ ,<sup>6</sup> the net magnetic moment of the two Cr magnetic moments should be either  $1.5 \mu_B$  or  $0.5 \mu_B$ . Then, the canting angles between the  $\text{Cr}^{3+}$  magnetic moments and the  $\text{Cu}^{2+}$  magnetic moments are estimated to be  $105^\circ$  and  $95^\circ$  for  $1.5 \mu_B$  and  $0.5 \mu_B$  of net magnetic moment of Cr ions, respectively, taking  $3 \mu_B$  as the Cr magnetic moment. The canting angle obtained from the Cr NMR experiments is

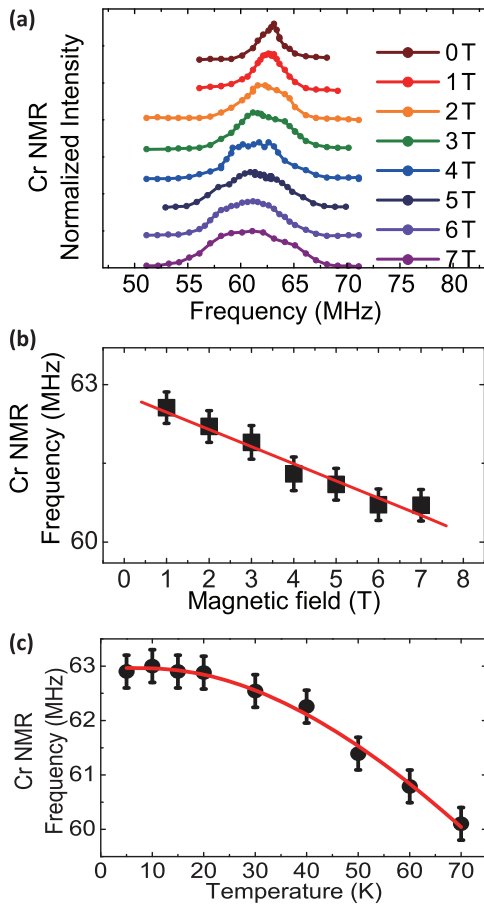


FIG. 3. (Color online) (a) Cr NMR spectra measured in the external magnetic field range of 0–7 T. The resonance frequency decreases as the magnetic field increases. (b) The magnetic field dependence of the Cr NMR frequency. The solid red line is a linear fit to the data. (c) Temperature dependence of the Cr NMR frequency at 0 T. The solid red line is the fit to Eq. (2).

close to  $95^\circ$ . That is, the Cr magnetic moments are almost antiparallel in the triangular spin configuration of  $\text{CuCr}_2\text{O}_4$ .

The zero-field Cr NMR spectra were measured in the temperature range of 5–70 K. The temperature dependence of the resonance frequencies at the maximum intensity in each spectrum is shown in Fig. 3(c). Equation (2) fits the data well [the solid red line in Fig. 3(c)], as it does in the case of Cu ions. The initial energy gap, obtained by fitting, is about 40 K ( $\pm 5$  K). The shift of the Cr NMR resonance frequency with increasing temperature is smaller than that of the Cu NMR resonance frequency, which might be caused by the larger energy gap for Cr ion than for Cu ion because the resonance frequency is proportional to the magnetic moment. Although we could not find a theory to explain the spin wave dispersion for ferrimagnets with the three magnetic sublattices, two spin waves with energy gaps are possible.<sup>15,16</sup> However, a more elaborate theory is necessary. The energy gap in the antiferromagnet is introduced by the interplay of anisotropy and exchange energy; it is given by  $E_g = (2E_A E_E)^{1/2}$ , where  $E_A$  and  $E_E$  are the anisotropy and the exchange energies, respectively. In the case of the ferromagnet,  $E_g = E_A$ . In both cases, the magnitude of the energy gap is increased as the anisotropy energy is increased. Therefore, it can be concluded

that a larger energy gap means a higher anisotropy energy in the ferrimagnet. If the spin-orbit coupling is strong, then the anisotropy energy is large. Therefore, it is expected that the spin-orbit coupling in Cr ions is stronger than that in Cu ions. This is consistent with the theory that predicts the orbital order of Cu ions in  $\text{CuCr}_2\text{O}_4$ .

The hyperfine field in Eq. (1) can be divided into two parts, the contact hyperfine field and the dipolar hyperfine field. The dipolar hyperfine field is generated either by the electron spins within the ion to which the referring nucleus belongs or by those in the neighboring magnetic ions. The former case will be referred to as a dipolar hyperfine field; the latter will henceforth be referred to simply as a dipole field. The dipole field affects the linewidth of the NMR spectra. In a simple ferromagnet or antiferromagnet, all of the nuclei of the magnetic ions are in equivalent positions; therefore, they experience the same dipole field. Thus, the dipole field induces the resonance frequency shift. However, in complex magnetic materials that have several magnetic sub unit cells, the dipole field at each magnetic ion site is different. That is, the nuclei in the various magnetic ion sites experience different total magnetic fields. Therefore, NMR spectrum broadening or peak splitting can be induced in complex magnetic materials.<sup>17,18</sup> We calculated the dipole fields at each magnetic ion site in  $\text{CuCr}_2\text{O}_4$ . In the calculation, the lattice parameter of the tetragonal structure was used;  $3 \mu_B$  and  $1 \mu_B$  were used as the magnetic moment of  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  ions, respectively. The dipole fields were summed from the nearest neighboring magnetic ions to the seventeenth nearest neighboring magnetic ions. The distance between the central ion and the seventeenth nearest neighboring ions is smaller than the general magnetic domain size. There are four Cr ion sites, in which the dipole fields are different. The linewidth broadening expected from the dispersion of the dipole field was about 0.3 MHz when the easy axis was along the [001] direction and the triangular configuration of the magnetic moments was in the (100) plane. The easy axis of  $\text{CuCr}_2\text{O}_4$  was not known; however, many spinel chromites have an easy axis in the [001] or [111] direction.<sup>9</sup> If the direction of the net magnetization was along the [111] direction, and the triangular configuration of the magnetic moments was in the (110) plane, the broadening expected from the dispersion of the dipole field was about 1.8 MHz. Therefore, in the zero-field NMR spectra for Cr ions, the linewidth caused by the dipole fields depends on the direction of the net magnetization; the linewidth magnitude is from 0.3 MHz to 1.8 MHz. When we applied the external magnetic field, because of the strong magnetic interactions between Cr and Cr, and between Cr and Cu, the relative angles between the two Cr moments and between the Cr and Cu moments do not change in whichever direction of magnetic field is applied. If the total magnetic moment, which should be parallel to the Cu magnetic moment in the triangular configuration, follows the magnetic field direction, the Cr spins will always be almost perpendicular ( $98^\circ$ ) to the magnetic field direction. Then, in the powder sample, the direction of the net magnetization varied in relation to the  $c$  axis of the unit cell. The dipole fields were calculated with rotating the direction of the net magnetic moments in relation to all axes. The linewidth broadening expected from the dispersion of the dipole field was about 2.8 MHz in the NMR spectrum in the external magnetic field.

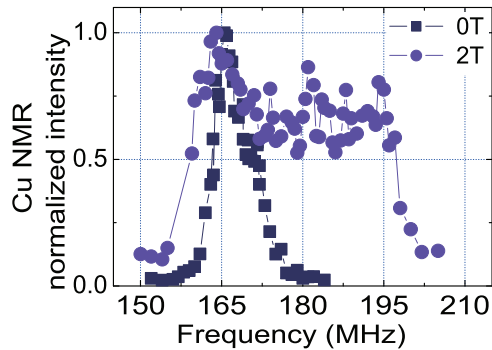


FIG. 4. (Color online) Cu NMR spectra measured at zero-field (squares) and at 2 T (circles).

The strong magnetic anisotropy could have caused the spectrum broadening in the powder NMR spectra measured in the external magnetic field. If the magnetic moments do not follow the external magnetic field and the magnetic moment is therefore along the magnetic easy axis of the structure even in the external magnetic field, then the angle between the magnetic moment and the magnetic field will be random in the powder sample. In the case of  $\text{CuCr}_2\text{O}_4$ , the directions of the two Cr magnetic moments are almost antiparallel; therefore, if there is a Cr magnetic moment parallel to the external magnetic field direction, there is also one antiparallel to the external magnetic field. Then, the NMR resonance frequencies of the two Cr magnetic moments, which are almost antiparallel, shift from the center frequency of the zero-field NMR spectrum to the opposite directions. The shift expected under an external magnetic field of 7 T is about 15 MHz; the expected linewidth of the Cr spectrum is about 30 MHz. However, in the Cr NMR spectrum measured in the magnetic field of 7 T [Fig. 3(a)], the linewidth is much smaller than 30 MHz. This means that the directions of the Cr magnetic moments are not random but retain mostly the same angle to the external magnetic field direction. The linewidth of the Cr NMR spectra measured in the external magnetic field was explained by the dipole field that originated from the magnetic moments of the neighboring magnetic ions, which follow the external magnetic field well.

Figure 4 shows the Cu NMR spectra measured at an external magnetic field of 2 T. Note that the linewidth in the external magnetic field strikingly increases compared to that of the Cr spectrum. The linewidth of the spectrum in the zero field is about 10 MHz. However, the linewidth of the spectrum measured in the external magnetic field of 2 T is more than three times larger than that in the zero field, while the linewidth of the Cr NMR spectrum is less than twice that in the zero field in Fig. 3(a).

To investigate the linewidth broadening of the Cu NMR spectra, the dipole fields Cu nuclear experiences were also calculated while the direction of the magnetic moments was rotated. The dipole field was the same at all the Cu ion sites. Therefore, in the zero field, the dipole field does not affect the linewidth of the Cu NMR spectrum. However, the magnitude of the dipole field depends on the direction of the net magnetic moment. In an external magnetic field, the magnetic moment direction varies for the powder sample. The expected linewidth broadening of the powder NMR spectra, caused by the various angle dependencies of the dipole field,

was about 4 MHz. The linewidth of the Cu NMR spectra measured in the external magnetic field of 2 T cannot be explained by the dipole field only.

The nuclear quadrupole effect in the NMR spectrum was also considered because the angle between the magnetic field and the  $c$  axis varies in the powder sample. The typical nuclear quadrupole coupling constant  $\frac{e^2qQ}{h}$  for Cu ions is 60 MHz. Then, the quadrupole frequency  $\nu_Q (= \frac{3e^2qQ}{2I(2I-1)\hbar})$  is calculated and found to be 30 MHz because the nuclear spin  $I$  is  $3/2$ . If the linewidth broadening was caused by the first-order quadrupole effect, then the linewidth should broaden from 160 MHz to 230 MHz because, in a magnetic field of 2 T, the central resonance frequency is in the range of 190–200 MHz. The linewidth, caused by the angle dependence in the presence of second-order quadrupole effects, is about 3 MHz. The dipolar and NQR broadening expected in the powder spectrum of  $\text{CuCr}_2\text{O}_4$  is 7 MHz at most, while the observed linewidth is about 40 MHz. Therefore, the main cause of the spectrum broadening of Cu NMR in the external magnetic field is not the dipole field originating from the neighboring magnetic ions and the NQR.

The linewidths of the NMR spectra of Cu and Cr ions are very different from each other in the external magnetic field since the orbital of Cu ions is ordered, while that of Cr is not. In special magnetic insulators that have orbital ordering, the magnitude of the dipolar hyperfine field originating from the electrons within the ion is large enough that a resonance frequency shift in the NMR spectra can be obtained.<sup>19,20</sup> The dipolar hyperfine field is a function of the angle and the distance between the nucleus and the magnetic moment of the nucleus's own electrons. If the magnetic moment direction is changed by rotation of the external magnetic field direction, the resonance frequency is changed. The resonance frequency shift type and the number of peaks in the NMR spectrum show the orbital state because the orbital is the electron's spatial distribution. In the case of the  $\text{Cu}^{2+}$  ions in  $\text{CuCr}_2\text{O}_4$ , there is an unpaired electron in the  $xy$  orbital. The NMR frequency shift due to the dipolar hyperfine field can be obtained from the expectation value of the dipole field operator. For the  $xy$  state, this NMR frequency shift is given by  $f_0(3(\hat{n} \cdot \hat{z})^2 - 1)$ , in which the vector  $\hat{n}$  represents the spin direction and  $f_0$  is a constant. In the powder NMR experiments, the effect of the orbital ordering due to rotation of the magnetic moment, which is parallel to the external magnetic field, appears as NMR spectrum broadening because the angles between the  $z$  axis and the magnetic moments are random. In previous research, V NMR spectra were measured in external magnetic field using powder  $\text{MnV}_2\text{O}_4$  samples.<sup>21</sup> Large linewidth broadening was also seen in the data. The V ion in  $\text{MnV}_2\text{O}_4$  is related to the orbital ordering. These facts indicate that orbital ordering induced the large linewidth broadening. However, the linewidth broadening in this case is not as large as Cu NMR because of magnetostriction. The magnetostriction causes angles between the  $z$  axis and the magnetic moments to be not completely random because the  $c$  axis is aligned along the external magnetic field direction.

The resonance frequency shift caused by the angle dependence of the dipolar hyperfine field is larger than that of the



dipole field and the NQR in  $\text{CuCr}_2\text{O}_4$ , in which orbital ordering in  $\text{Cu}^{2+}$  ions is expected. Therefore, if we had rotated the single crystal sample, then the rotation angle dependence of the resonance frequency would have been  $f_0(3(\hat{n} \cdot \hat{z})^2 - 1)$ . In the powder NMR spectrum, the large broadening of the spectrum, as seen in our data, occurred because the angles between the  $c$  axis and the magnetic moments are random; therefore, the resonance frequency shift was seen simultaneously. The  $f_0$  is proportional to  $\langle r^{-3} \rangle$ , where  $r$  is the distance between the nucleus and the electrons. Usually the value  $\langle r^{-3} \rangle$  for ions in a crystal is smaller than that of the corresponding value calculated for free ions. In our data,  $f_0$  was about 10 MHz. The linewidth broadening of 33 MHz, in which the effects of the NQR and dipole field were excluded, was caused by the dipolar hyperfine field. Therefore, the main cause of the Cu NMR spectrum broadening is the orbital ordering of Cu ions in  $\text{CuCr}_2\text{O}_4$ .

#### IV. CONCLUSION

We investigated the spin state and orbital ordering of  $\text{CuCr}_2\text{O}_4$ . The temperature dependence of the Cu and Cr

NMR resonance frequencies shows that there is an initial energy gap in the dispersion relation of the spin wave. The energy gap for Cr ions is larger than that for Cu ions, which indicates that the spin-orbit coupling of Cr ions is stronger than that of Cu ions. This is consistent with the orbital ordering of Cu ions in  $\text{CuCr}_2\text{O}_4$ . In order to investigate the orbital ordering in  $\text{CuCr}_2\text{O}_4$ , the linewidths of the Cu and Cr NMR spectra, measured with an external magnetic field of 2 T, were compared. According to the calculations of the resonance frequency shifts caused by the magnetic anisotropy, the dipolar hyperfine field, and the nuclear quadrupole effect, the main cause of the linewidth broadening of the Cu NMR spectra is the orbital ordering in Cu ions. The external magnetic field dependence of the Cr NMR frequency shows that the canting angle between the Cr magnetic moment and the Cu magnetic moment is about  $98^\circ (\pm 2^\circ)$ .

#### ACKNOWLEDGMENTS

This work was supported by Korea Research Foundation Grant No. 2012R1A2A2A01003598.

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