Nuclear magnetic and quadrupole resonances of Cu in the low-dimensional magnets Cu$_2$M$_2$Ge$_4$O$_{13}$ (M = Fe, Sc)

J Kikuchi$^1$, S Nagura$^1$, H Nakanishi$^1$ and T Masuda$^2$

$^1$ Department of Physics, School of Science and Technology, Meiji University, Kawasaki, Kanagawa 214-8571, Japan
$^2$ International Graduate School of Arts and Sciences, Yokohama City University, Yokohama, Kanagawa 236-0027, Japan

E-mail: jkiku@isc.meiji.ac.jp

Abstract. We report on the results of nuclear magnetic and quadrupole resonances of Cu in Cu$_2$Fe$_2$Ge$_4$O$_{13}$ consisting of weakly coupled Cu dimers and Fe chains. In the antiferromagnetic state below 39 K, we observed nuclear resonance of Cu under the internal magnetic field at the Cu site. An analysis of the internal field based on the square-planar coordination of Cu$^{2+}$ suggests that the 3$d$ hole is mainly in the $d_{x^2-y^2}$ orbital. In Cu$_2$Sc$_2$Ge$_4$O$_{13}$ including only Cu dimers, we observed oscillation of Cu spin-echo intensity as a function of the separation time between $\pi/2$ and $\pi$ pulses. This is caused by indirect nuclear spin coupling mediated by strong intradimer exchange coupling of the electronic spins, indicating that the dimers are magnetically well isolated in these materials.

1. Introduction

Low-dimensional magnetic systems have received much interest because of their variety of exotic phenomena. Among a lot of fascinating model systems, Cu$_2$Fe$_2$Ge$_4$O$_{13}$ [1] seems to belong to a new category because it comprises of two distinct magnetic subsystems with contrasting nature: It includes both Cu$^{2+}$ ($S = 1/2$) dimers and Fe$^{3+}$ ($S = 5/2$) chains, each of which has gapped or gapless spin excitations if they were to exist independently. Cu$_2$Fe$_2$Ge$_4$O$_{13}$ orders antiferromagnetically below $T_N = 39$ K, and the ordered moments of Cu and Fe have been estimated as $m_{\text{Cu}} = 0.38 \mu_B$ and $m_{\text{Fe}} = 3.62 \mu_B$ at 0 K [1]. There are large and moderate reduction of the Cu and Fe ordered moments, indicating existence of quantum fluctuations. Besides, nonzero ordered moment of Cu suggests a crucial role of the Cu dimers in establishing long range magnetic order. In order to uncover the role of the Cu dimers for magnetic ordering and to clarify the electronic state of Cu$^{2+}$, we performed nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) experiments at $^{63}$Cu and $^{65}$Cu nuclei (both having nuclear spin $I = 3/2$) in Cu$_2$Fe$_2$Ge$_4$O$_{13}$. We also measured Cu NQR in Cu$_2$Sc$_2$Ge$_4$O$_{13}$ with Fe$^{3+}$ all replaced by nonmagnetic Sc$^{3+}$ [2] as an isostructural reference compound.

2. Experiments

Single crystals of Cu$_2$Sc$_2$Ge$_4$O$_{13}$ were grown by floating zone method [1]. Polycrystalline samples of Cu$_2$Sc$_2$Ge$_4$O$_{13}$ were prepared by solid reaction methods as described in [3]. NMR and NQR
experiments were performed with a standard phase-coherent pulsed spectrometer.

3. Results and Discussion

3.1. \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \)

\( \text{Cu}_2\text{M}_2\text{Ge}_4\text{O}_{13} \) (M = Sc, Fe) crystallizes in the monoclinic space group \( P2_1/m \) [3] in which Cu atoms occupy a unique site. A sharp \( ^{63}\text{Cu} \) NQR line was observed around 34.91 MHz at 50 K as shown in the inset of figure 1. Figure 1 shows temperature \( (T) \) dependence of the nuclear spin-lattice relaxation rate \( 1/T_{1,NQR} \) of \( ^{63}\text{Cu} \). \( 1/T_{1,NQR} \) exhibits thermally-activated behavior as expected for the spin-dimer system. By fitting the data to a formula \( 1/T_{1,NQR} = c \exp(-\Delta/T) \), we get \( c = (2.3 \pm 0.1) \times 10^5 \text{s}^{-1} \) and \( \Delta = 270 \pm 10 \text{ K} \). The value of a gap agrees well with those estimated from the susceptibility [2], \( ^{45}\text{Sc}-\text{NMR} \) [4] and neutron scattering experiments [2].

Figure 1. Temperature dependence of \( 1/T_{1,NQR} \) of \( ^{63}\text{Cu} \) in \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) (solid squares) and \( \text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13} \) (open circles). The dashed line indicates \( T_N \) of \( \text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13} \). Inset shows \( ^{63}\text{Cu} \) NQR spectra in \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) (solid line) and \( \text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13} \) (dashed line) at 50 K.

An interesting observation of \( \text{Cu} \) NQR in \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) is remarkable oscillation of the spin-echo intensity as a function of the separation time \( \tau \) between \( \pi/2 \) and \( \pi \) rf pulses as illustrated in figure 2. A ratio of the oscillation frequencies between the two isotopes \( ^{63}\text{Cu} \) and \( ^{65}\text{Cu} \) agrees with the square of the isotopic ratio of the gyromagnetic ratio \( (^{63}\gamma/^{65}\gamma)^2 \) within experimental accuracies. This type of oscillation results when the RKKY type indirect nuclear-spin coupling acts strongly in pairs [5]. It is likely that in spin dimer systems, strong intradimer exchange interaction between electronic spins enhances indirect coupling between the nuclear spins on that dimer. The observed spin-echo oscillation therefore suggests that the Cu dimers in \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \) are magnetically well isolated.

The spin-echo oscillation is damped strongly with increasing temperature. We found that the \( T \) dependence of the damping constant of the echo oscillation scales with that of \( 1/T_{1,NQR} \).

3.2. \( \text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13} \)

In the paramagnetic state at 50 K a sharp NQR line was observed around 34.90 MHz for \( ^{63}\text{Cu} \) (see inset of figure 1). The \( T \) dependence of \( 1/T_{1,NQR} \) of \( ^{63}\text{Cu} \) in \( \text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13} \) is shown in figure 1 in comparison with that in \( \text{Cu}_2\text{Sc}_2\text{Ge}_4\text{O}_{13} \). \( 1/T_{1,NQR} \) in \( \text{Cu}_2\text{Fe}_2\text{Ge}_4\text{O}_{13} \) increases
discovery indicates that the internal field at the Cu site due to ordering of Cu$^{2+}$ ions coordinating the Z principal axis by an angle $\theta_s$ of about 60° [1]. Thus, $\mathbf{B}_{\text{int}}$ and $\mathbf{m}_{\text{Cu}}$ are neither parallel nor antiparallel to each other. Such a large difference between $\theta$ and $\theta_s$ is ascribed to anisotropic hyperfine interaction characteristic of a Cu$^{2+}$ ion. Usually, $\mathbf{B}_{\text{int}}$ and $\mathbf{m}_{\text{Cu}}$ are related via the hyperfine tensor $\mathbf{A}$ as $\mathbf{B}_{\text{int}} = \mathbf{A} \cdot \mathbf{m}_{\text{Cu}}$. 

\section*{Figure 2.} Spin-echo intensity of $^{63}$Cu in Cu$_2$Sc$_2$Ge$_4$O$_{13}$ plotted against 2$\tau$ where $\tau$ is the separation time between $\pi/2$ and $\pi$ pulses. Solid lines are fits to an exponentially-decaying part plus a sinusoidally oscillating part with damping.

divergently on approaching $T_N = 39$ K from above, signaling critical slowing down of electronic-spin fluctuations. On the other hand, 1/$T_{\text{NQR}}$ well above $T_N$ increases gradually with increasing temperature. 1/$T_{\text{NQR}}$ above 60 K follows roughly a relation $1/T_{\text{NQR}} = c \exp(-\Delta/T) + d$ with $c = 4.8 \times 10^4$ s$^{-1}$, $d = 2.7 \times 10^3$ s$^{-1}$ and $\Delta = 270$ K. The value of $c$ is about one fifth of the corresponding value for Cu$_2$Sc$_2$Ge$_4$O$_{13}$, which might be due to difference of the hyperfine coupling constants between the two compounds.

We observed zero-field resonance of Cu in the antiferromagnetic (AF) state, indicating that there appears internal magnetic field at the Cu site due to ordering of Cu$^{2+}$ and Fe$^{3+}$ magnetic moments. Figure 3 shows the Cu NMR spectrum at 5 K. The $^{63}$Cu and $^{65}$Cu NMR frequencies in the AF state are determined by the Hamiltonian consisting of both the Zeeman and quadrupolar interaction terms:

$$\mathcal{H} = -\gamma h B_{\text{int}} \left[ \frac{1}{2} \sin \theta \left( I_x e^{-i\phi} + I_y e^{i\phi} \right) + I_z \cos \theta \right] + \frac{h \nu_Q}{6} \left[ 3I_z^2 - \mathbf{I}^2 + \frac{\eta}{2} (I_+^2 + I_-^2) \right].$$

Here $B_{\text{int}}$ is a magnitude of the internal field, $\nu_Q$ is the quadrupolar frequency, $\eta$ is the asymmetry parameter of the electric field gradient (EFG), $\theta$ and $\phi$ are polar and azimuth angles of the internal field with respect to the principal frame of the EFG tensor. We tried to reproduce the observed resonance frequencies by diagonalizing the Hamiltonian (1) and tuning $B_{\text{int}}$, $\theta$, $\phi$, $\nu_Q$ and $\eta$. The best fit was obtained with $B_{\text{int}} = 3.40$ T, $\theta = 4^\circ$, $\phi = 0^\circ$, $^{63}\nu_Q = 34.54$ MHz and $\eta = 0.25$. The line positions calculated from the above parameters are indicated by the arrows in figure 3. Although we have to check the existence of an unobserved line around 5 MHz, agreement seems fairly good.

We now discuss briefly the electronic state of a Cu$^{2+}$ ion in Cu$_2$Fe$_2$Ge$_4$O$_{13}$. We assume here that the Z principal axis of the EFG tensor at the Cu site, along which the EFG takes a maximum value, is perpendicular to the plane formed by four O$^{2-}$ ions coordinating the Cu$^{2+}$ ion. The above analysis then indicates that the internal field $B_{\text{int}}$ at the Cu site makes a relatively small angle ($\theta = 4^\circ$) with the Z principal axis. On the other hand, the ordered moment $\mathbf{m}_{\text{Cu}}$ of the Cu$^{2+}$ ion is tilted away from the Z principal axis by an angle $\theta_s$ of about 60° [1]. Thus, $B_{\text{int}}$ and $\mathbf{m}_{\text{Cu}}$ are neither parallel nor antiparallel to each other. Such a large difference between $\theta$ and $\theta_s$ is ascribed to anisotropic hyperfine interaction characteristic of a Cu$^{2+}$ ion. Usually, $B_{\text{int}}$ and $\mathbf{m}_{\text{Cu}}$ are related via the hyperfine tensor $\mathbf{A}$ as $B_{\text{int}} = \mathbf{A} \cdot \mathbf{m}_{\text{Cu}}$. 

\section*{Figure 3.} Spin-echo intensity of $^{63}$Cu in Cu$_2$Sc$_2$Ge$_4$O$_{13}$ plotted against 2$\tau$ where $\tau$ is the separation time between $\pi/2$ and $\pi$ pulses. Solid lines are fits to an exponentially-decaying part plus a sinusoidally oscillating part with damping.
Although the principal values of $A$ for Cu$_2$Fe$_2$Ge$_4$O$_{13}$ are unknown at present, the dependence of $\theta$ on $\theta_s$ may be calculated for the two limiting cases of a Cu$^{2+}$ ion being in either $d_{x^2-y^2}$ or $d_{3z^2-r^2}$ orbital state, using the known principal values of $A$ for the two orbitals [6]. We found that when $\theta_s = 60^\circ$, the angle $\theta$ is 10$^\circ$ and 60$^\circ$ for the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states, respectively. Concerning the magnitude of $B_{\text{int}}$, both orbitals yield $B_{\text{int}} \approx 4.5$ T for $m_{\text{Cu}} = 0.38 \mu_B$ [1] which is not very different from the estimated value of 3.40 T. Though qualitative, it is clear that the $d_{x^2-y^2}$ orbital gives better agreement with the experiment because $\theta$ remains small for large $\theta_s$. This implies a dominant $d_{x^2-y^2}$ character of the Cu$^{2+}$ ion in Cu$_2$Fe$_2$Ge$_4$O$_{13}$.

![Cu NMR spectrum](image)

**Figure 3.** Cu NMR spectrum in the antiferromagnetic state of Cu$_2$Fe$_2$Ge$_4$O$_{13}$ at 5 K. Arrows indicate line positions for the two isotopes ($^{63}$Cu: solid, $^{65}$Cu: dashed) calculated using parameters given in the text.

### 4. Summary

We presented the results of Cu NQR and NMR experiments in Cu$_2$M$_2$Ge$_4$O$_{13}$ (M = Sc, Fe). In Cu$_2$Sc$_2$Ge$_4$O$_{13}$, thermally-activated behavior of $1/T_1$NQR of $^{63}$Cu was observed. Remarkable oscillation of the Cu NQR spin-echo intensity is attributed to nuclear spin coupling within the dimer via the strong intradimer exchange interaction between the Cu$^{2+}$ electronic spins. In Cu$_2$Fe$_2$Ge$_4$O$_{13}$, we determined parameters characterizing the internal magnetic field and the electric field gradient at the Cu site in the AF state. The direction of the internal field is very different from the direction of Cu$^{2+}$ ordered moment, which is accounted for qualitatively by large anisotropy of hyperfine interaction of a Cu$^{2+}$ ion in the $d_{x^2-y^2}$ orbital state.

### References

[1] Masuda T, Zheludev A, Grenier B, Imai S, Uchinokura K, Ressouche E and Park S 2004 *Phys. Rev. Lett.* **93** 077202

[2] Masuda T and Redhammer G J 2006 *Phys. Rev. B* **74** 054418

[3] Redhammer G J and Roth G 2004 *J. Solid State Chem.* **177** 2714

[4] Lue C S, Kuo C N, Su T H and Redhammer G J 2007 *Phys. Rev. B* **75** 014426

[5] Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Oxford University Press)

[6] Abragam A and Bleaney B 1980 *Electron Paramagnetic Resonance of Transition Ions* (New York: Oxford University Press)