NMR Studies of the Spinel-Type Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$

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Abstract. To investigate the magnetic properties of the Hf-rich side (0.5 \( \leq x \leq 1.0 \)) of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ from a microscopic point of view, $^{65}$Cu NMR has been performed at temperatures between 4.2 and 300 K. Temperature dependencies of the Knight shift and spin-lattice relaxation time ($T_1$) have been measured. As for $0.7 \leq x \leq 1.0$, the Knight shift gradually shifts to a negative side with decreasing temperature due to the core polarization of d conduction electrons. The temperature dependence of $1/T_1T$ in this range of $x$ indicates that the $T_1T$ is constant in all temperature region. On the other hand, in the range of $0.5 \leq x \leq 0.7$, the Knight shift rapidly shifts to negative side below about 130 K because of the core polarization of d conduction electrons. In this range of $x$, the values of $1/T_1T$ at high and low temperatures take constant values. The value at low temperatures is approximately twice compared with those at high temperatures. The density of state at the Fermi level in the low temperature region would be about 1.3 times larger than that in the high temperature region.

1. Introduction
Chalcogenide thiospinel CuX$_2$S$_4$ including transition metals has a large variety of physical properties because the ions at X site have a mixed valence X$^{3.5+}$ (i.e., combination of X$^{3+}$ and X$^{4+}$) [1, 2]. Cu is a monovalent cation. The cation sites, which are occupied by Cu and X ions, are located at the centers of tetrahedrons and octahedrons surrounded by S$^{2-}$ ions, respectively. The spinel-type structure has cubic symmetry. Much research on the metal-insulator transition in CuIr$_2$S$_4$ has been conducted in the last decade [1, 2, 3]. A few ferromagnetic spinel compounds exist, such as CuCr$_2$S$_4$ [4], CuCr$_2$Se$_4$ [4], and CuCr$_2$Te$_4$ [5].

The chalcogenide thiospinel CuCr$_2$S$_4$ with a mixed valence state of CuCr$^{3+}$Cr$^{4+}$S$_4$ [4] is a metallic ferromagnet with a Curie temperature $T_C = 380$ K; its net magnetic moment is close to $5.0$ \( \mu_B \), consisting of Cr$^{3+}$ ion with $3\mu_B$ ($S = 3/2$) and Cr$^{4+}$ ion with $2\mu_B$ ($S = 1$). Conversely, CuHf$_2$S$_4$ [6], which also has the spinel structure, shows metallic properties without any magnetic anomaly. Increasing values of $x$ in the mixed spinel Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ system [7] produce successive changes from a dominant ferromagnetic ($x \leq 0.5$) to a re-entrant spin-glass ($x \simeq 0.5$), then a spin-glass ($0.5 \leq x \leq 0.7$ ), and finally to a pure paramagnetic state ($0.8 \leq x \leq 1.0$). Hf substitutions cause the magnetic frustration, which originates from competition between ferromagnetic and antiferromagnetic interactions. A step-like anomaly in the magnetization in the range of $0.5 \leq x \leq 0.7$ of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ is also found around 160 K because of a spin crossover phenomenon.
To investigate the magnetic properties of the Hf rich side of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ from a microscopic point of view, $^{63}$Cu NMR has been performed at temperatures between 4.2 and 300 K. Temperature dependencies of the Knight shift and spin-lattice relaxation time ($T_1$) have been measured.

2. Experimental
The polycrystalline specimens were prepared by a solid state reaction method [7]. Mixtures of high-purity fine powders of Cu (purity 99.99%), Cr (99.99%), Hf (99.8%) and S (99.999%) with normal stoichiometry were calcined in sealed quartz tubes at 950 $^\circ$C for 5 days. Subsequently, the specimens were reground and pressed to form pellets, and then annealed at 400 $^\circ$C for 4 h. No secondary phase in the specimens was detected in the powder X-ray diffraction profiles. The powdered specimens were prepared for NMR measurements. A conventional pulse NMR spectrometer was used in $^{63}$Cu NMR measurements. A magnetic field of about 6.9 T (about 78 MHz) was applied by a superconducting magnet with magnetic field homogeneity of $10^{-5}$. Shifts in $^{63}$Cu-NMR were obtained at a gyro-magnetic ratio of 11.285 MHz/T. The NMR spectrum was derived from a summation of the FFT spectrum as a function of frequency. The resonance frequency was determined from a peak position of the spectrum. The spin-lattice relaxation time $T_1$ was measured by saturation recovery method.

3. Results and Discussion
The Knight shift in $^{63}$Cu NMR of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ for 0.5 $\leq x \leq$ 1.0 has been measured at temperatures between 4.2 and 300 K. The Knight shift vs. temperature of $^{63}$Cu NMR in Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ for 0.5 $\leq x \leq$ 1.0 are shown in Fig. 1. The behavior of the Knight shift in the vicinity of 300 K for 0.8 $\leq x \leq 1.0$ is different from that for 0.5 $\leq x \leq 0.7$. Especially the Knight
shift for $x = 0.9$ is largely deviated from others. Since the magnetization shows a diamagnetic state for $x = 1.0$ [2] and paramagnetic states for $x \leq 0.9$ [6], this difference of the magnetization may affect the large discrepancy of the Knight shift around 300 K. But the detailed reasons are not clear now.

To compare the temperature dependence of Knight shift for each concentration $x$, we examine the value gained by subtracting the Knight shift at 300 K from the Knight shift at each temperature. Figure 2 shows the temperature dependence of the deviation of the $^{63}$Cu Knight shift. Here, $K_{T=300}$ represents the value obtained by subtracting the Knight shift at 300 K from the Knight shift at each temperature. The Knight shift gradually shifts to a negative side with decreasing temperature for all samples because of the core polarization of $d$ conduction electrons at Cu site. For $x = 1.0$, 0.9, and 0.8, the negative shift becomes larger with decreasing $x$. The Knight shift for $x = 0.7$ rapidly shifts to negative side below 130 K and the deviation toward negative side represents a maximum. Therefore, the ratios of negative shift for $x = 0.6$ and 0.5 become smaller compared with that for $x = 0.7$.

In the range of $0.5 \leq x \leq 0.7$, the magnetization in the spin glass phase keeps an almost constant value in field cooling process due to the freezing of moments [7]. The Knight shift of $^{63}$Cu NMR would take the almost constant value if internal field at Cu site is mainly affected by the Cr static moment in the spin glass phase. However, as shown in Fig. 2, the Knight shift shifts to negative side below 10 K. In the range of $0.5 \leq x \leq 0.7$, a step-like anomaly is found in the magnetization measurements around 160 K [7]. However, no anomaly can be seen in theKnight shift measurements around this temperature.

The Spin-lattice relaxation time $T_1$ in $^{63}$Cu NMR of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ for $0.5 \leq x \leq 1.0$ has been measured at temperatures between 4.2 and 300 K. The nuclear longitudinal magnetization recovery $f(t) = 1 - (M(t)/M_0)$ cannot be expressed by a single exponential type. For $x = 1.0$, 0.9 and 0.8, the recovery $f(t)$ is explained well by $f(t) = a \exp(-t/T_{1S}) + (1-a)\exp(-t/T_{1L})$ consisting of two components: short recovery time $T_{1S}$ and long recovery time $T_{1L}$. Figure 3 shows the time dependence of the nuclear longitudinal magnetization recovery in $^{63}$Cu NMR for

**Figure 3.** Nuclear longitudinal magnetization recovery $f(t) = 1 - (M(t)/M_0)$ in $^{63}$Cu NMR of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ ($x = 1.0$).

**Figure 4.** Temperature dependence of $1/T_1T$ in $^{63}$Cu NMR of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ ($x = 1.0$, 0.9 and 0.8).
$x = 1.0$ at 250 K. The values of $a$ for $x = 1.0$, 0.9 and 0.8 are about 0.8 in all temperature region.

Since no secondary phase in cubic phase specimens of $x = 1.0$ was detected in the powder X-ray diffraction profile, it can be expected that the time dependence of the recovery for $x = 1.0$ should be expressed by a single exponential type. However, the experimental recovery curves represent two exponential types, indicating the distribution of $T_1$. The reason for the $T_1$ distribution in these materials is not clear. The same situation occurs in the $T_1$ measurements in $^{63}$Cu NMR of CuIr$_2$S$_4$ [3].

The temperature dependence of $1/T_1 T$ for $x = 1.0$, 0.9 and 0.8 at temperatures between 4.2 and 300 K is shown in Fig. 4. The $1/T_1 T$ for $x = 1.0$, 0.9 and 0.8 indicates that the $T_1 T$ is constant. According to the experimental results of the Knight shift of $^{63}$Cu NMR shown in Fig. 2, the Knight shift in the range of $0.8 \leq x \leq 1.0$ weakly shifts to the negative side due to the core polarization of $d$ electrons with decreasing temperatures. However, the $T_1 T$ is constant, which means that the contribution of $d$ electrons to the fluctuating local field at Cu site is small.

On the other hand, for $x = 0.7$, 0.6 and 0.5, nuclear longitudinal magnetization recovery can be analyzed as a stretched exponential relaxation (SER) type as follows [8, 9]:

$$f(t) = y_0 \exp \left\{ - \left( \frac{t}{T_1} \right)^p \right\}. \quad (1)$$

Figure 5 shows the time dependence of the nuclear longitudinal magnetization recovery $f(t) = 1 - (M(t)/M_0)$ in $^{63}$Cu NMR for $x = 0.7$ at 140 K. According to the magnetization measurements [7], the magnetization in the region of $0.5 \leq x \leq 0.7$ is much larger than that in the region of $0.8 \leq x \leq 1.0$. Since the local field caused by magnetic Cr atoms in the region of $0.5 \leq x \leq 0.7$ is very large compared with that in the region of $0.8 \leq x \leq 1.0$, the $T_1$ in the region of $0.5 \leq x \leq 0.7$ would be distributed widely. Because of this reason, the recovery would be analyzed as the SER type.

The plot of $1/T_1 T$ vs. temperature for $x = 0.7$, 0.6 and 0.5 measured at temperatures between 4.2 and 260 K is shown in Fig. 6. The temperature dependence of $1/T_1 T$ for $x = 0.7$ above 140 K shows a constant value. However, the value of $1/T_1 T$ for $x = 0.7$ abruptly changes about 140
K and the $1/T_1T$ below about 90 K indicates a constant value which is about two times larger than that above 140 K. For $x = 0.6$ and 0.5, the values of $1/T_1T$ remain constant above about 60 K, increase below about 60 K and below about 20 K take constant values which are about twice compared with those above 60 K. From these results, for $x = 0.7, 0.6$ and 0.5, the density of state at the Fermi level in the low temperature region would be about 1.3 times larger than that in the high temperature region.

In summary, to investigate the magnetic properties of the Hf-rich side ($0.5 \leq x \leq 1.0$) of Cu(Cr$_{1-x}$Hf$_x$)$_2$S$_4$ from a microscopic point of view, $^{63}$Cu NMR has been performed at temperatures between 4.2 and 300 K. Temperature dependencies of the Knight shift and spin-lattice relaxation time ($T_1$) have been measured. The Knight shift for $0.7 \leq x \leq 1.0$ gradually shifts to a negative side with decreasing temperature due to the core polarization of $d$ conduction electrons. The temperature dependence of $1/T_1T$ in this range of $x$ indicates that the $T_1T$ is constant in all temperature region. On the other hand, in the range of $0.5 \leq x \leq 0.7$, the Knight shift rapidly shifts to negative side below about 130 K because of the core polarization of $d$ conduction electrons. In this range of $x$, the values of $1/T_1T$ at high and low temperatures take constant values. The value at low temperatures is approximately twice compared with those at high temperatures. The density of state at the Fermi level in the low temperature region would be about 1.3 times larger than that in the high temperature region.

References
[1] Nagata S 2005 Chin. J. Phys. 43 722.
[2] Kawashima K, Horibe N, Awaka J, Yamamoto H, Ebisu S and Nagata S 2007 Physica B 387 208.
[3] Niki H, Okuda H, Okada Y, Higa K, Oshiro M, Fukuyoshi N, Mahoe R, Yogi M, Nakama T, Yagasaki K, Ebisu S and Nagata S 2011 J. Phys.: Conf. Ser. 273 012139.
[4] Wohlfarth E P (Ed.) 1982 Ferro-Magnetic Materials in A Handbook on the Properties of Magnetically Ordered Substances, vol. 3 (Amsterdam: North-Holland) p 603.
[5] Suzuyama T, Awaka J, Yamamoto H, Ebisu S, Ito M, Suzuki T, Nakama T, Yagasaki K and Nagata S 2006 J. Solid State Chem. 179 140.
[6] DiSalvo F J and Waszczak J V 1982 Phys. Rev. B 26 2501.
[7] Kariya F, Ebina K, Hasegawa H, Koshimizu K, Wuritunasitu B, Hondou K, Ebisu S and Nagata S, 2009 J. Solid State Chem. 182 2018.
[8] Sobol W T, Cameron I G, Pintar M M and Blinc R 1987 Phys. Rev. B 35 7299.
[9] Palmer R G, Stein D L, Abrahams E and Anderson P W 1984 Phys. Rev. Lett. 53 958.