Temperature Dependence of Magnetization at Zero Applied Magnetic Field in Nearly Two Dimensional Ferromagnets

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Abstract. NMR measurement have been made at low temperatures on the crystal structure of K$_2$CuF$_4$ and (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ at zero applied magnetic field. $^{63}$Cu, $^{65}$Cu and $^{35}$Cl NMR have been used to measure spontaneous magnetization at the temperature range 2 K down to 30 mK. We have made the NMR experiments using a $^3$He-$^4$He dilution refrigerator by conventional pulsed NMR method without external magnetic field. The magnetization at zero applied magnetic field in the nearly two-dimensional ferromagnet K$_2$CuF$_4$ of the experimental data is in a good agreement with Yamaji-Kondo theory and $\theta_c = 0.3$, which is applied the double-time Green’s function method incorporated with Tyablikov’s decoupling. For temperature 1.1 K down to 0.26 K, the spontaneous magnetization of (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ is support ($t \log t'$)-formalism from the spin wave theory.

1. Introduction

Ferro magnetism is one of research interest, however until now the theory cannot be regarded satisfactory [1][2]. The K$_2$MF$_4$ type crystal with (M = Mn, Fe, Co, Ni, or Cu) are known as the most typical two dimensional magnets. The crystal structure which are composed of magnetically nearly isolated layers of two dimensioanal Heisenberg ferromagnets of spin 1/2 are K$_2$CuF$_4$ [3] and (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ [4]. The crystal structure of K$_2$CuF$_4$ is of the K$_2$NiF$_4$ type with orbital order predicted by Khomskii and Kugel. The lattice constant are $a = 4.155$ Å and $c = 12.74$ Å at room temperature. This compounds consists of magnetic CuF$_2$ layers separated by nonmagnetic K and F atoms. All Cu$^{2+}$ ions are surrounded by six florin atoms with a distorted octahedral coordination. The crystal structure of (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ is ferromagnet with lattice constant $a = 7.65$ Å, $b = 24.66$ Å and $c = 7.33$ Å at room temperature. Magnetic properties of transition-metal layered materials have been studied extensively, because they are good examples of two-dimensional magnetic systems, while ideal two-dimensional Heisenberg spin systems are theoretically predicted not to show magnetic ordering at any finite temperature [6]. The phase transition in the isotropic two dimensional Heisenberg magnetic has been studied. It is stated [13] that the two-dimensional Heisenberg magnet could not exhibit spontaneous magnetization at any non zero temperature, if the interactions are limited within a finite range. A Small inter-layer exchange interaction and the Ising-like anisotropy can stabilize the long order at finite temperature whereas the XY-like anisotropy cannot produce a spontaneous magnetization at any non-zero temperatures [3]. The intraplane exchange coupling constant $J/k_B$ of K$_2$CuF$_4$ in
the c-plane is 11.2 K from the susceptibility measurement [7]. The interplane exchange coupling constant \( J' \) is estimated to be \( J'/J = 6.6 \times 10^{-4} \) from the neutron scattering experiment [8]. The anisotropy field in the c-plane is less than a few gauss from the susceptibility measurements.

The spontaneous magnetization of \( \text{K}_2\text{CuF}_4 \) depends on temperature such as \( T^{3/2} \) at low temperature above 1.6 K [3]. Below 1 K, the spontaneous magnetization has not \( T^{3/2} \)-dependence but \( T \log T' \) dependence, based on calculation with the renormalized spin wave theory [9]. In \((\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4\), the main perturbation to the isotropic intralayer exchange interaction leading to three-dimensional long-range order is here the anisotropy in the intraplanar interaction [10]. The dependence of the spontaneous magnetization on temperature can be measured using NMR measurement of the magnetic ions with zero external magnetic fields.

In order to study the temperature dependence of spontaneous magnetization due to various interaction, we measure the NMR frequencies of the \( ^{63}\text{Cu} \), \( ^{65}\text{Cu} \) and \( ^{35}\text{Cl} \) nuclei in samples.

2. Experimental Result and Discussion

The NMR study in zero applied field using NMR at low temperature with a \(^3\text{He}-^4\text{He} \) dilution refrigerator (as shown in Fig. 1) [11]. The NMR measurements have been made using a conventional pulsed method without external magnetic field. Temperature was controlled by Carbon resistance thermometers (by MATSUSHITA 0.25 watt), which are calibrated against the susceptibility of CMN. Measurements of spontaneous magnetization were taken at temperature range 2 K down to 30 mK. The NMR frequency of \( ^{63}\text{Cu} \) have been measured spontaneous magnetization in a single crystal of \( \text{K}_2\text{CuF}_4 \) with dimension (5x5x10) mm, whereas the NMR frequency of \( ^{65}\text{Cu} \) and \( ^{35}\text{Cl} \) have been measured spontaneous magnetization in a single crystal of \((\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4 \) with dimension (3x3x7) mm. In previous paper [12], the NMR frequency due to \( ^{63}\text{Cu} \) nuclei of \( \text{K}_2\text{CuF}_4 \) is observed to be 158 MHz at temperature of 470 mK.

![Figure 1. Schematic drawing of the apparatus for NMR: A: mixing chamber, B: supporting ring, C: sample cell, D: heat protector, E: receiver coil, F: tuned coil, G: transmitter coil, H: variable capacitor, I: connecting rod, J,K,L: thermometers, M: specimen](image)

In Yamaji-Kondo theory, the double-time Green’s function method incorporated with Tyablikov’s decoupling is applied to the nearly two-dimensional ferromagnets of layer-structure cooper compounds [5]. Spontaneous magnetization in the whole temperature region below \( T_c \) is:

\[
\frac{1}{2}\sigma(1 - \frac{\theta}{\theta_c}) = \frac{1}{\pi^2} \int_0^\infty du K\left(\sqrt{\frac{u}{2}}(1 - \frac{u}{8})\right) \times \left(\frac{1}{e^{u/\theta_c} - 1} - \frac{\theta}{\sigma_u} + \frac{1}{2}\right)
\]

where \( \theta_c \equiv k_BT_c/2J \) and \( K(x) \) is the complete elliptic integral.

This equation is independent of the kind of weak perturbation and equation for \( \sigma \) as a function...
of $\theta$ has only one parameter $\theta_c$. The magnetization at zero temperature $\sigma_0$ is 1/2 and otherwise magnetization is less than 1/2. For the system of the body-centered orthorhombic lattice, $K_2CuF_4$ with the calculated $\theta_c = 0.37$ and $J_x = J_y$ was found to agree with curve of $\sigma$ vs $\theta$ obtained from equation above. It is remarkable that $\sigma$ decreases proportionally to $\theta^{3/2}$ and it gives the same magnetization as Holstein-Primakoff’s spin wave theory does [5].

In this paper, we used the reduced temperature $(T/T_c)$ to change temperature, with $T_c = 6.25$ K for experimental data of $^{63}$Cu NMR of $K_2CuF_4$. Furthermore, we normalized frequency with $\nu(0)$, which is determined from extrapolation of experimental data, then we reduced frequency with $(\nu_{red} = (\nu(T)/\nu(0)) - 0.5)$. The magnetization $\sigma_0$ at zero temperature is set to 0.5 [5]. The experimental data compared with Yamaji-Kondo formalism, which is the magnetization curve $\sigma$ vs $(\theta/\theta_c)$ and $\sigma$ vs $(\theta/\theta_c)^{3/2}$ plotted in the graph of $(\nu_{red}$ vs $(T/T_c)$) and $(\nu_{red}$ vs $(T/T_c)^{3/2})$.

![Figure 2](image1.png)

**Figure 2.** $\nu_{red}$ vs $(T/T_c)$ curve for $^{63}$Cu NMR of experimental data of $K_2CuF_4$. For comparison, the full line has been calculated with the use $\theta_c=0.3$ from Yamaji-Kondo theory.

![Figure 3](image2.png)

**Figure 3.** The $\nu_{red}$ curve for $^{63}$Cu NMR of experimental data of $K_2CuF_4$ as plotted against $(T/T_c)^{3/2}$ scale. The full line shows calculation from Yamaji-Kondo theory with $\theta_c=0.3$.

![Figure 4](image3.png)

**Figure 4.** Temperature dependence of the $^{35}$Cl and $^{65}$Cu NMR frequency of $(C_3H_7NH_3)_2CuCl_4$. The solid line has been calculated with equation $\nu(T) = \nu(0) - C(t \log t')$. Formalism of $(t \log t')$ is obtained from a renormalized spin-wave theory of the nearly two dimensional ferromagnet [10].
The experimental results of $^{63}$Cu NMR in K$_2$CuF$_4$ is shown in Fig. 2 and Fig. 3 in which magnetization decreases proportionally to $(T/T_c)^{3/2}$. The results is in a good agreement with Yamaji-Kondo theory, with $\theta_c=0.3$.

The experimental data of $^{35}$Cl and $^{65}$Cu of (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ is plotted in the graph of (Freq vs $t \log t'$). The axis of $t \log t'$ calculated from a renormalized spin wave theory [10] is given by, $t = \frac{k_B T}{2\pi z_0 J S}$ and $t' = \frac{k_B T}{2\pi z'_0 J'S}$, with $z_0 = 4$, $z'_0 = 8$ and $\delta = 7.519 \times 10^{-3}$. The intraplane exchange coupling constant $J/k_B$ of (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ is 16 K.

The spontaneous magnetization of $^{35}$Cl and $^{65}$Cu of (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ decreases proportionally to $(t \log t')$ as is shown in Fig. 4. For temperature 260 mK to 1.1 K, the experimental results is in a good agreement with $(t \log t')$ formalism by Tsuru and Uryu [10] which is the spin-wave interactions have a significant effect on the temperature dependence of the magnetization for (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$, and in very low temperature (below 250 mK) spontaneous magnetization is divergen.

3. Conclusion

The magnetization at zero applied magnetic field in the nearly two-dimensional ferromagnet K$_2$CuF$_4$ of the experimental data is in a good agreement with Yamaji-Kondo theory and $\theta_c=0.3$, which is applied the double-time Green’s function method incorporated with Tyablikov’s decoupling. For temperature 1.1 K down to 0.26 K, the spontaneous magnetization of (C$_3$H$_7$NH$_3$)$_2$CuCl$_4$ is support $(t \log t')$ formalism from the spin wave theory.

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