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Pressure Effect of Spin Gap Substance $Cu_2(C_5H_{12}N_2)_2Cl_4$

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Spin gap substance $Cu_2(C_5H_{12}N_2)_2Cl_4$ single crystals were grown and the g principle axes were determined by X-band ESR measurement at room temperature for the first time. We found that the g principal axes are parallel to the $K_1K_2K_3$ orthogonal coordinate system, where the K_3 axis is the twofold screw axis (b-axis) of the system and the K_1 axis is an axis with an angle of 195.9° from the c-axis clockwise. High pressure magnetization measurements at low temperature were performed on several nonoriented single crystals. They show almost no change up to 0.42 GPa, and an intermediate state suddenly at 0.62 GPa which is reproduced by the Curie-Weiss law, followed by the stable state above 0.83 GPa. It turned out that the system above 0.83 GPa can be described well with a four spin model where two ferromagnetic dimers are connected antiferromagnetically.

KEYWORDS: spin gap, $Cu_2(C_5H_{12}N_2)_2Cl_4$, g principle axes, magnetization, high pressure

1. Introduction

The spin gap substances consisting of $S = 1/2$ antiferromagnetic dimers have attracted much attention both experimentally and theoretically for their various quantum critical phenomena which appear by applying the pressure [1–6]. The observation of novel excitation mode called amplitude mode in the pressure-induced ordered state of $TlCuCl_3$ is a good example [4, 7]. Title substance Cu_2(1,4-diazacycloheptane)$_2Cl_4$ [$Cu_2(C_5H_{12}N_2)_2Cl_4$] (abbreviated as CuHpCl) also shows typical magnetic behavior for the spin gap system. Reflecting the non-magnetic singlet ground state, the temperature dependence of magnetic susceptibility ($\chi - T$) shows a broad maximum at 8.8 K, and the magnetization curve ($M - H$) at low temperature does not show finite magnetization up to 7.5 T [8, 9]. This system also shows a remarkable pressure effect. Mito *et al*. observed the gradual increase of free spins with the application of pressure [10].

The system was regarded as a two-leg ladder model from its stacking manner of the Cu-Cu binuclear units along the [101] direction [Fig. 1(a)]. However, the magnetic network has been reviewed and it is now considered as three-dimensionally connected binuclear units [11, 12]. According to the latest model based on the density functional theory (DFT), the interaction between Cu ions in the binuclear unit is rather ferromagnetic (-6.6 K) than antiferromagnetic, and the weak (1.1 K) and strong (11.2 K) antiferromagnetic interactions are alternating along the [101] direction [12]. This strong antiferromagnetic interaction is the origin of the singlet state of this system.

In this study, we restudied the pressure effect of this system with newly prepared samples in order to investigate its origin in detail. As a result, we observed a pressure effect which is different from

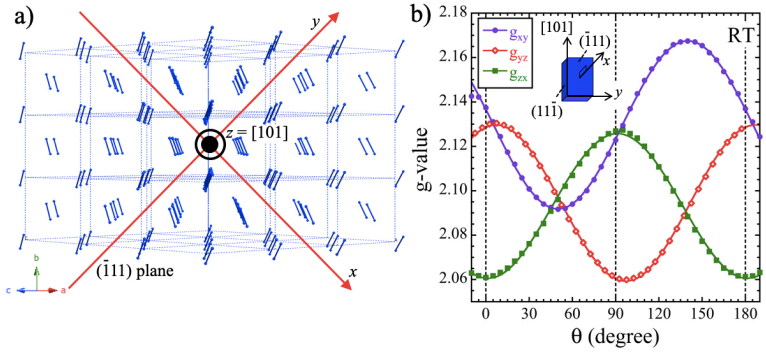

Fig. 1. (a)Stacking manner of Cu-Cu binuclear units seen from the z = [101] direction. (b) Magnetic field angle dependence of g-values in the experimentally defined xyz orthogonal coordinate system for a CuHpCl single crystal obtained at room temperature. x and z axes correspond to the direction normal to the $(\bar{1}11)$ plane and the [101] axis, respectively.

that obtained by Mito *et al*. We will discuss the result with taking the latest DFT calculation [12] into account, as well as the origin of the difference between these two results. Moreover, the fundamental characterization for the g anisotropy of this system which has not been investigated so far will be also provided for the first time.

2. Experimental

CuHpCl sample was prepared by following the procedure described in Ref. [8]. It belongs to the monoclinic crystal system and the space group is $P2_1/c$ [8]. Plate-like single crystal samples were obtained. The typical size is about 1mm × 0.5mm × 0.3mm. From the X-ray structure analysis, the largest and the next largest planes were found to be the $(\bar{1}11)$ plane and the $(11\bar{1})$ plane, respectively, and the edge of these two planes was the [101] axis. With the X-band ESR magnetic field angle dependence measurements were performed at room temperature on a single crystal sample.

Magnetization measurements under pressure were performed on several nonoriented single crystal samples. A pressure cell made of CuBe with an inner diameter of 2.7 mm, a sample space height of about 10 mm, an outer diameter of 8.7 mm, and a cylinder length of 74 mm was used. Temperature dependence measurements were performed from 2 K to 100 K at 1 T. The change in pressure in this temperature region is considered to be small [13]. Magnetic field dependence measurements were performed up to 5 T at 1.8 K. The pressure was calibrated by the superconducting transition temperature of tin. Daphne 7373 was used as the pressure medium.

3. Results and Discussions

3.1 g Principle axes

As shown in Fig. 1 (a) and the inset of (b), the [101] axis is defined as the z axis, and the x axis is defined as normal direction to the $(\bar{1}11)$ plane. The y axis is perpendicular to these two axes. The z axis, or the [101] axis, is orthogonal to the b axis and the angle between the b axis and the x axis is 134.4°. Fig. 1 (b) shows the angle dependence of the g values in the xyz coordinate system. $g_{\alpha\beta}$ indicates the g value obtained by changing the angle from the α axis (0°) to the β axis (90°). From these results, the g principal axes and their values for this system were determined by the standard procedure [14]. The principal g values were determined to be g_1 = 2.092, g_2 = 2.059, and g_3 = 2.166. We found that the g_3 axis almost coincides with the b axis and the g_1 and g_2 axes are in the ac plane. The angle between the b axis and the g_3 axis is 4.4°. This is consistent with the result

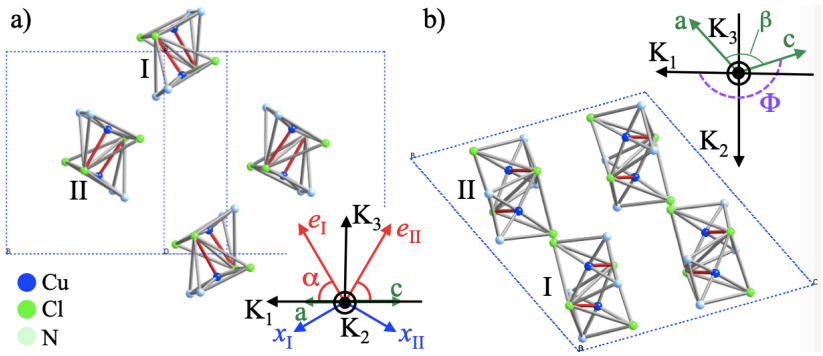

Fig. 2. Crystal structure of CuHpCl seen from the K_2 axis (a) and the K_3 axis (b). The red Cu-Cl bond indicates apical bond of square pyramid.

that the maximum value of g_{xy} was 2.167 at 140° [Fig. 1 (b)].

In the following, the $K_1K_2K_3$ orthogonal coordinate system, which is common to monoclinic crystal system with the twofold screw axis symmetry [15], is defined for this substance, and the g principle axes are compared with this coordinate system. CuHpCl consists of Cu-Cu binuclear units. Each Cu ion is in a distorted square-pyramidal geometry with two chlorine and two nitrogen atoms in the basal plane and and a chlorine atom at its apex (Fig. 2). The two pyramids in this unit are almost centrosymetric. If the two pyramids are completely centrosymetric, they have an identical g tensor. For simplicity, if we assume that this unit is described by one g tensor, the g tensor sites of the system are reduced to two (site I and II). In general, the g tensors are averaged by the exchange interactions. In this system, as the g tensors of site I and II as well as those in the Cu-Cu binuclear unit are averaged, the b axis is expected to be one of the g principle axes because it is the twofold screw axis of the system. This is consistent with the experimental result, considering that the accuracy of sample alignment is about ±5°. Here we define the b axis as the K_3 axis.

We also define the average direction of the Cu-Cl apical bonds of square pyramids in the unit as z_ν, (ν =I, II) [Fig. 2 (a)]. It is relevant to consider that the Cu-Cl apical bond direction z_ν is one of the principle axes of the local g tensor site because it is the longest among Cu-Cl and Cu-N distances in the square pyramid. Consequently, the symmetrical axes of the system can be further defined. One of two bisectors of z_I and z_II is the K_3 axis, the other is defined as the K_1 axis, and the axis which is perpendicular to both the K_3 and K_1 axes is defined as the K_2 axis. We found that the angle between the g_1 axis and the K_1 axis was 5.3° and the angle between the g_2 axis and the K_2 axis was 6.5°. Thus, within the accuracy it can be said that the g principle axes coincide with the $K_1K_2K_3$ coordinate system. The characteristic angles α and Φ [15], which connect this coordinate system to the crystal structure, were determined; the angle between the K_1 axis and the z_I or z_II direction in the K_3K_1 plane is α = 58.4° [Fig. 2 (a)], and the angle from the K_1 axis to the c axis is Φ = 195.9° counterclockwise [Fig. 2 (b)].

For the other local g principal axes at site I (II), it is obvious that they are parallel to the $\boldsymbol{x}_\mathrm{I}$ ($\boldsymbol{x}_\mathrm{II}$) and $\boldsymbol{K}_2$ ($-\boldsymbol{K}_2$) directions, where $\boldsymbol{x}_\nu$ is perpendicular to both z_ν and $\boldsymbol{K}_2$ [Fig. 2 (a)], from the twofold rotational symmetry around the b axis. This suggests that the hole orbital of Cu^{2+} ions in the basal plane of the square pyramid does not consist of the $d_{x^2-y^2}$ orbital alone, which should extend toward the negative ions [Fig. 2 (b)]. The d_{xy} orbital also likely mixes to the $d_{x^2-y^2}$ orbital and both contributions results in the direction of $\boldsymbol{x}_\nu$ and K_2 as the local g principal axes within the basal plane.

3.2 Pressure effect on magnetic behavior

Figure 3 shows the $\chi - T$ (a) and the $M - H$ (b) with nonoriented single crystal samples obtained at several pressures. At ambient pressure, both the $\chi - T$ and $M - H$ showed the typical behavior of the

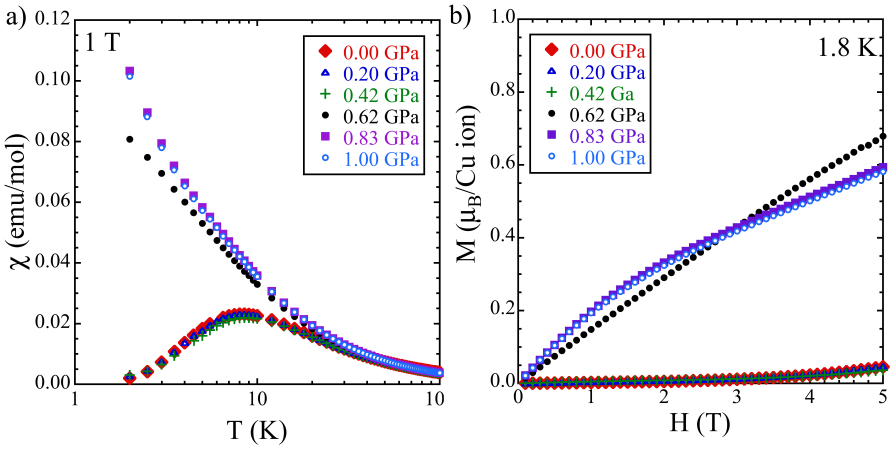

Fig. 3. $\chi - T$ at 1 T (a) and $M - H$ at 1.8 K (b) of CuHpCl nonoriented single crystals obtained at several pressures.

spin gap system, which was consistent with the previous results [8, 10]. The $\chi - T$ and $M - H$ showed almost no change from that at 0 GPa up to 0.42 GPa. However, at 0.62 GPa, they suddenly changed. Moreover, above 0.83 GPa, they became insensitive to the pressure again. We also confirmed that these pressure changes were completely reversible. Similar results were obtained in the 2nd run for the same sample from 0 GPa to 1.15 GPa.

On the other hand, Mito *et al*. observed free spin-like behavior which gradually increases by applying pressure in the $\chi - T$ measurement of powder sample up to 0.8 GPa. They proposed a model described as $\chi(P) = \alpha\chi(P = 0\,\mathrm{GPa}) + (1 - \alpha)C/T$, where C is the Curie constant and α indicates the ratio to the total number of spins [10]. They observed a monotonous decrease in α as the pressure is increased. However, the result obtained in this study cannot be fully explained by this model. We believe that the result obtained in this study is more intrinsic and the difference in these results is caused by the difference in the quality of samples. This will be mentioned later.

One feature of the $M - H$ obtained at 0.62 GPa is that no α can reproduce it with the above model [Fig. 4 (a), (b)]. Both the $\chi - T$ and $M - H$ at this pressure were explained well by the Curie-Weiss law defined as $\chi = C/(T + \Theta)$ with the averaged g value $g = 2.106$ and $\Theta = 3.1$ K.

Interestingly, however, the result at 0.8 GPa by Mito *et al*. and that at 0.83 GPa in this study are in good agreement quantitatively irrespective of their intermediate states and both can be explained by the model with $\alpha = 0.5$ [10] [Fig. 4 (c), (d)]. The value of $\alpha = 0.5$ means that half of the total number of spins form the singlet ground state and it reminds that the $M - H$ shows a plateau at half of the saturation magnetization. It should be noted that there is no parameter to satisfy both the $\chi - T$ and $M - H$ simultaneously with the Curie-Weiss law [Fig. 4 (c), (d)]. The facts that the $\chi - T$ and $M - H$ are insensitive to pressure with $\alpha = 0.5$ above 0.83 GPa suggests that the magnetic network of this system changes into that with a fourfold periodicity and it is stable above 0.83 GPa. We use following minimal model to analyze the result,

$$\mathcal{H} = J_{\mathrm{F}}(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_4) + J_{\mathrm{AF}}\mathbf{S}_2 \cdot \mathbf{S}_3 \tag{1}$$

where, J_{F} and J_{AF} represent ferromagnetic and antiferrometric interactions, respectively. Obtaining the eigenvalues of this Hamiltonian, the magnetization $M(T, H)$ at arbitrary temperature T and magnetic field H was calculated from its partition function. Figures 4 (c) and (d) show the best fits to the experimental results and the interactions are obtained as $J_{\mathrm{F}} = -4.4$ K and $J_{\mathrm{AF}} = 11.9$ K. Compared to the calculation results of $\alpha = 0.5$, the four spin model more appropriately reproduced both the $\chi - T$

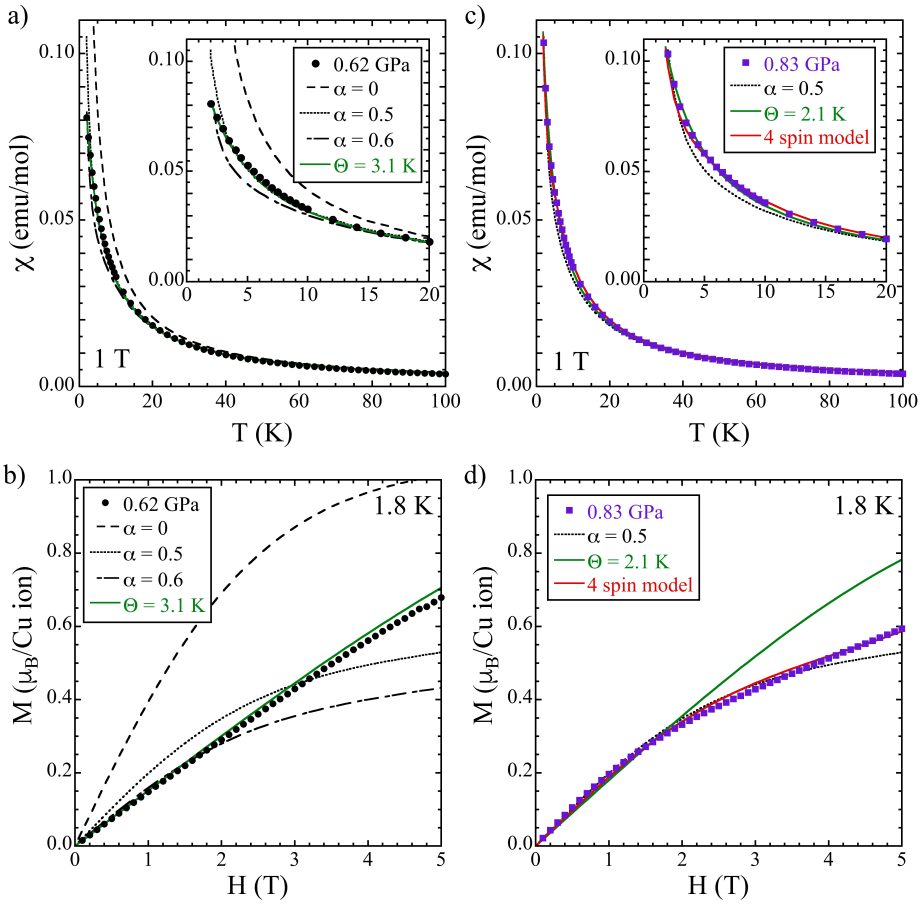

Fig. 4. Comparison of the $\chi - T$ (a) and the $M - H$ (b) at 0.62 GPa, and those at 0.83 GPa [(c), (d)] with the calculation results. For the comparison in (d), an example that the $M - H$ can not be reproduced by $\Theta = 2.1$ K obtained by the fitting to the $\chi - T$ (c) is shown.

and $M - H$ behaviors in whole regions.

The linkage within the Cu-Cu binuclear unit is expected to be rigid compared to the packing of units. Therefore, it is natural assumption that the ferromagnetic interaction comes from that in the binuclear unit. On the other hand, it seems that the inter-binuclear unit interaction can be easily changed through the shrink of the lattice parameters by applying pressure. A slight difference in the Cu-Cu distances along the [101] direction of 0.006 Å , for example, yields the tenfold different antiferromagnetic interactions [12]. Thus, there is a possibility that the magnetic network with fourfold periodicity like two ferromagnetic dimers connected antiferromagnetically is realized above 0.83 GPa through an intermediate state at 0.62 GPa.

If the four spin model with $J_F = -4.4$ K and $J_{AF} = 11.9$ K is appropriate, the ground state of the system is still gapped though the gap energy is very small (~ 0.5 K). Moreover, a 1/2 plateau will become clear as the temperature is lowered. Further investigation is required to clarify magnetic networks realized under pressures, including the intermediate state at 0.62 GPa, in addition to the magnetization measurement under pressure at a lower temperature. ESR measurements under pressure [16] is helpful to investigate the deformation of the square pyramid via changes in the g principal axes and their values. They will give information about the change of the ferromagnetic interaction of the binuclear unit.

Finally, we mention the reason of the difference between the result obtained in this study and that by Mito *et al*. in the intermediate pressure region. We also measured the magnetization of CuHpCl powder sample under pressure, and obtained the same results with the single crystal samples. Therefore, it does not depend on the sample morphology. We also measured a bromine substituted substance CuHpBr. As a result, it showed sample dependence. We found that most of the samples in CuHpBr are twin from the X-ray structure analysis and we observed splitting of ESR signal in the X-band ESR measurement. It was also found that the lattice constants a and c are close each other (a = 13.416Å, c = 13.930Å in space group $P2_1/c$), and this may be a reason that twins are likely to be produced. Similarly, for CuHpCl, although no splitting of ESR signal was observed in our sample, the lattice constants are relatively close (a = 13.354Å, c = 12.724Å [8]) and twin might be yielded depending on the preparation conditions. If the sample has domain structures such as twin, pressure is concentrated at the boundary. In general, when stress concentrates on the boundaries of the domains, it is expected that the sample does not deform uniformly and deforms mainly at the domain boundaries. In other words, the magnetic structure represented by the 4-spin model can be formed at the domain boundaries even below 0.42 GPa, and the change in magnetization resulting from this boundaries may appear. This affects the pressure change of magnetic behavior for CuHpCl.

In summary, the detailed X-band ESR measurements at room temperature and the magnetization measurements under pressure were performed on CuHpCl. It was found that the g principal values are g_1 = 2.092, g_2 = 2.059, and g_3 = 2.166. The g principle axes almost correspond to the $K_1K_2K_3$ orthogonal coordinate system which consists of the twofold screw axis (the b axis) as the K_3 axis, and the K_1 axis with an angle $\Phi = 195.9^\circ$ to the c axis counterclockwise. Magnetization measurements under pressure suggested that the $M - H$ curve showed a 1/2 plateau when the pressure is applied above 0.83 GPa. We constructed the minimal model that the ferromagnetic dimers are connected by antiferromagnetic interaction and both the $\chi - T$ and $M - H$ were explained well with $J_F = -4.4$ K and $J_{AF} = 11.9$ K. The experimental results suggest that this phase is stable to the pressure above 0.83 GPa, which follows an intermediate phase found at 0.62 GPa.

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