Magnetic properties of a Ni tetramer with a butterfly structure in high magnetic fields

M Hagiwara\textsuperscript{1,3}, Y Narumi\textsuperscript{2}, A Matsuo\textsuperscript{2}, H Yashiro\textsuperscript{1}, S Kimura\textsuperscript{1} and K Kindo\textsuperscript{2}

\textsuperscript{1} KYOKUGEN, Osaka University, 1-3 Machikaneyama, Toyonaka 560-8531, Japan
\textsuperscript{2} Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
E-mail: hagiwara@cqst.osaka-u.ac.jp

Abstract. We have performed magnetic susceptibility and low and high field magnetization measurements on single crystals of the Ni tetramer compound \([\text{Ni}_4(\mu\text{-CO}_3)_2(\text{aepy})_8](\text{ClO}_4)_4\) (aepy = 2-aminoethyl-pyridine) with a butterfly (diamond) structure. We observed a two-step-like magnetization curve and a further increase of magnetization around 63 T in magnetic fields up to 68 T perpendicular to the Ni tetramer plane (c-axis). From the magnetic fields at steep jumps of the magnetization, we determine broadly the short diagonal \((J_1)\) and the side \((J_2)\) antiferromagnetic exchange constants between the Ni ions \((J_1/k_B = 41.9 \text{ K} \text{ and } J_2/k_B = 9.2 \text{ K})\) in this compound. The long diagonal exchange interaction \((J_3)\) is ferromagnetic and the exchange constant is evaluated as \(J_3/k_B = −0.66 \pm 0.04 \text{ K}\) from the comparison between the magnetization measured in steady fields at 2 K and the calculated one. The origin of hysteresis of the magnetization in pulsed magnetic fields is discussed based on the calculated energy diagram.

\textsuperscript{3} Author to whom any correspondence should be addressed.
1. Introduction

Some current topics in magnetism are macroscopic emergence of quantum mechanical effects and novel phenomena caused by geometrical frustration. The observation of quantum tunnelling of magnetization in the molecular magnet Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$ [1]–[3], abbreviated as Mn$_{12}$-ac, has stimulated studies on nano-scale single molecular magnets which consist of a few or a few tens of metal ions. The Mn$_{12}$-ac is a small ferromagnet and the tunnelling occurs between two states separated by the axial anisotropy barrier with the help of thermal excitation. Later, a number of such kinds of molecular magnets were synthesized and investigated intensively in relation to mesoscopic quantum magnetism. Considerable attention has been paid not only to static but also dynamic properties of molecular magnets. Discrete level crossing or anticrossing in these systems sometimes causes interesting relaxation phenomena [2, 4]. In addition, potential applications in quantum computing and data storage have been considered for single molecular magnets [5].

Studies on magnetic systems with geometrical frustration have a long history and have renewed recently because of appearance of a number of novel physical phenomena, such as large residual entropy in the spin ice system Ho$_2$Ti$_2$O$_7$ [6], heavy fermion behaviour in LiV$_2$O$_4$ [7] and so on. The simplest cases of geometrically frustrated magnetic systems in two and three dimensions are an antiferromagnetically interacted spin system on an equilateral triangle and that on an equilateral tetrahedron, respectively. In short, the triangle shape formed by the nearest magnetic ions is a key framework of such kinds of frustrated magnets.

When these two interesting ingredients, namely quantum effects in nano-scale single molecular magnets and geometrical frustration, coexist in one system, we expect new curious physical phenomena in the system. In fact, geometrically frustrated molecular magnets have been synthesized recently and investigated by different experimental methods, and some interesting findings have been reported [8, 9].

In this paper, we report the results of magnetic susceptibility and magnetization measurements in magnetic fields up to about 70 T on the molecular magnet [Ni$_4$(μ – CO$_3$)$_2$(aetpy)$_8$] (ClO$_4$)$_4$ where the aetpy is (2-aminoethyl)-pyridine (C$_7$H$_{10}$N$_2$) abbreviated as NCAP [10].
The framework of this compound formed by Ni ions is a kind of diamond structures which is called a butterfly structure and is a two-dimensional version of a deformed tetrahedron. When the exchange interactions between Ni ions are antiferromagnetic, this is regarded as a geometrically frustrated nano-scale magnetic cluster.

2. Experimental

2.1. Sample preparation and crystal structure

Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution. Single crystal samples of NCAP were prepared with a slow evaporation method from an aqueous solution of stoichiometric amounts of nickel perchlorate hexahydrate and aetpy after vigorously stirring the solution for 24 h according to the method described in [9]. Blue single crystals of NCAP with about $3 \times 3 \times 2$ mm$^3$ in size were obtained from this method. The crystallographic axes were determined with an x-ray diffractometer. This compound crystallizes in a tetragonal system (space group $P4(2)(1)2$). The lattice constants at room temperature are $a = 14.523(4)$ Å and $c = 16.566(5)$ Å. The Ni tetramer unit structure is depicted in the upper part of figure 1 for two crystal orientations. The Ni tetramer units are well separated from each other by aetpy ligands in the $c$ plane and perchlorate anions along the $c$ direction. Each nickel atom is surrounded octahedrally by two nitrogen atoms from (ethylamino)pyridine and two oxygen atoms from the carbonate bridges and forms a deformed octahedron with them. Two kinds of Ni sites exist in this unit from the local symmetry of the Ni site. The local environment around the upper Ni ions, namely bond lengths and bond angles, is equivalent to that around the lower Ni ones in figure 1 and the same situation is realized for the left and right Ni ions. None of the bond directions from the Ni ions, however, coincide with the $c$-axis. Therefore, strictly speaking, the $c$-axis is not the quantized $z$-axis for each Ni ion, but we assume that the $c$-axis is the $z$-axis for each Ni ion.
for simplicity in the succeeding analysis and discussion. The framework of the Ni tetramer is also drawn in the lower part of the same figure. From the framework, there are three exchange pathways which are denoted by $J_1$ for the short diagonal path, $J_2$ for the side path, and $J_3$ for the long diagonal path. The crystal packing viewed from the [0 0 1] direction is shown in figure 2. The planes formed by Ni tetramers are stacked along the $c$-axis and the Ni tetramers point to the same direction in each plane and alter the direction plane by plane by 90°.

2.2. Magnetic susceptibility

We measured magnetic susceptibility of this compound with a super conducting quantum interference device (SQUID) magnetometer (MPMS-XL7). The magnetic susceptibility along the $c$-axis increases monotonically with decreasing temperature as shown in figure 3. Therefore, we plot the magnetic susceptibility ($\chi$) times temperature ($T$) as a function of temperature in the same plane. The $\chi T$ decreases with decreasing temperature down to 10 K and slightly increases below this temperature. This indicates the dominant exchange interaction in this compound is antiferromagnetic. For the magnetic susceptibility along the $a$-axis, similar behaviour to that along the $c$-axis has been obtained.

2.3. Apparatus

We have performed high field magnetization utilizing pulsed magnets developed at KYOKUGEN, Osaka University [11]. The pulsed magnet is made by winding with a Cu–Ag wire and reinforced by a maraging steel cylinder. The magnet can generate magnetic fields up to 80 T a few times without destruction, but it usually generates the field up to about 70 T for conventional use. We measured the magnetization at the temperature down to about 100 mK in magnetic fields up to about 60 T utilizing a dilution refrigerator and down to 1.3 K up to about 70 T using a $^3$He pumping system.
Figure 3. Temperature \((T)\) dependence of magnetic susceptibility \((\chi = M/H)\) along the \(c\)-axis in the magnetic field of 1000 Oe (solid circles). The \(\chi T\) values as a function of \(T\) are plotted with solid squares. The solid line is calculated \(\chi T\).

Figure 4. High field magnetization curves at 1.3 K along (a) the \(c\) direction and (b) the \(a\) direction. The broken line above 68 T in figure 4(a) is an expected magnetization curve up to the saturation magnetization. Arrows indicate the direction of the field sweep.

2.4. High field magnetization

Figures 4(a) and (b) show the results of high field magnetization measurements for the magnetic field along the \(c\)- and \(a\)-axes, respectively. The magnetization curves along the \(c\)- and \(a\)-axes were measured at 1.3 K up to about 68 and 56 T, respectively. A two-step-like magnetization curve was obtained for the \(c\)-axis and a further increase was observed around 63 T. Since the \(g\) value of this compound is about 2.2 which is obtained from ESR measurements and the saturation magnetization is expected to be about 2.2 \(\mu_B/\text{Ni}\), the magnitudes at the plateaux are almost a half and three quarters of the saturation magnetization. In figures 4(a), expected magnetization curve up to the saturation magnetization (2.2 \(\mu_B\)) is drawn with a broken line by smoothly extrapolating
Figure 5. Schematic magnetization curve calculated at \( T = 0 \) K. The magnitudes of the magnetization plateaux from low fields correspond to 1/2, 3/4 and 1 of the saturation magnetization. Above the magnetization curve, a valence bond picture [12, 13] corresponding to each plateau state is depicted. The large open circles and the small solid ones indicate the Ni\(^{2+}\) ions \((S = 1)\) at the shortest diagonal sites and the spin 1/2 degrees of freedom, respectively. The thin lines between the solid circles represent the singlet bonds. The thin and thick arrows correspond to the magnetic moments of spin 1/2 and 1, respectively. In the middle, the energy scheme near the lowest energy branch in magnetic fields is depicted and the rightmost energy represents expanded energy branches of the lowest level in the middle figure.

The magnetization curve for the \( a \)-axis is similar to that for the \( c \)-axis and the magnetic fields at the steep magnetization jumps are very close to each other. Both magnetization curves have large hystereses near the fields at a steep increase of magnetization which will be discussed later.

3. Analyses and discussion

3.1. Magnetization analyses

The magnetization curves are analysed by the following spin Hamiltonian describing the exchange interactions of the Ni tetramer.

\[
\mathcal{H} = J_1 S_1 \cdot S_2 + J_2 (S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4) + J_3 S_3 \cdot S_4 - g_1 \mu_B (S_1^z + S_2^z) H - g_2 \mu_B (S_3^z + S_4^z) H, \tag{1}
\]

where \( J_1, J_2 \) and \( J_3 \) are the exchange constants between Ni ions which are already defined in the previous section, \( S_1, S_2, S_3, \) and \( S_4 \) the Ni spins as denoted in figure 1, \( g_1 \) and \( g_2 \) the \( g \) values along the \( z \)-axis for \( S_1, S_2 \) and \( S_3, S_4 \), respectively, \( \mu_B \) the Bohr magneton, \( H \) the external magnetic field along the \( z \)-axis. When assuming that the exchange constants \( J_1 \) and \( J_2 \) are \( J_1 > J_2 > 0 \), namely antiferromagnetic and the absolute value of \( J_3 \) is smaller than \( J_2 \), \( g_1 = g_2 = g \) and no single ion anisotropy for simplicity, we get the magnetization curve analytically at \( T = 0 \) K as depicted in figure 5, which reproduces the overall experimental magnetization curve at 1.3 K including the expected part around the saturation magnetization.

We notice in the analyses that the small exchange constant \( J_3 \) does not affect the transition fields. The transition fields \( H_1 \) and \( H_2 \) are given by \((J_1 + 2J_2)/g\mu_B\) and \((2J_1 + 2J_2)/g\mu_B\), respectively.
Figure 6. Magnetization curves at 2 and 4.2 K measured with a SQUID magnetometer up to 7 T. The solid line is the magnetization calculated by assuming that the spins are populated in energy branches of the lowest level separated by the ferromagnetic exchange interaction $J_3$ as shown in the rightmost picture of figure 5.

respectively. From the comparison with the experimental values $H_1 = 40.7$ T and $H_2 = 69$ T which are determined as the maximum of field derivative of magnetization for field descending process and the field at the middle point (1.93 $\mu_B$) of the expected magnetization, respectively, we get $J_1/k_B = 41.9$ K (29.1 cm$^{-1}$) and $J_2/k_B = 9.2$ K (6.4 cm$^{-1}$). These values are close to those reported in [9] ($J_1 = 28.6$ cm$^{-1}$ and $J_2 = 7.9$ cm$^{-1}$) determined from the susceptibility fit.

When $J_3 \sim 0$, a quintet, a triplet and a singlet are nearly degenerate so as to form the ground state and the first excited state (triplet) is located at $J_1 - 3J_2$ ($\sim$14 K) as shown in the middle picture of figure 7. The low field magnetization at low temperature, especially the start of the magnetization from zero field, must be affected by the small exchange constant $J_3$. Therefore, we measured the magnetization up to 7 T at 2 and 4.2 K with the SQUID magnetometer. Figure 6 shows the magnetization curves for these two temperatures. Accordingly, we know that the energy splitting of the ground states (singlet, triplet and quintet) due to a finite $J_3$ is required for the calculation of the magnetization at sufficiently low temperature (2 K). The solid line in figure 6 is the calculated magnetization by using $J_3/k_B = -0.66 \pm 0.04$ K and $g = 2.191 \pm 0.004$. The agreement between the experiment and the calculation is excellent. From the fit of the low field magnetization, we know the exchange interaction $J_3$ is weakly ferromagnetic. The solid line in figure 3 is a fit of the susceptibility to that calculated for the spin Hamiltonian under the same conditions $g_1 = g_2 = g$, and the following parameters $J_1/k_B = 49.7 \pm 0.5$ K, $J_2/k_B = 9.3 \pm 0.2$ K, $J_3/k_B = -0.63 \pm 0.02$ K and $g = 2.229 \pm 0.002$ are determined from the fit. We get a very close value of $J_3$ to that determined from the low field magnetization.
3.2. Origin of hysteresis

Finally, we discuss the origin of hystereses in the magnetization curve. Figure 7 displays the energy diagram of the low energy levels of this compound calculated by using the parameters obtained from the magnetization measurements. The transition field $H_1$ corresponds to the field at the intersection between the lowest branch of the quintet and that of the septet and the $H_2$ corresponds to that between the lowest branch of the septet and that of the nonatet. Magnetization curve for the field ascending process shows a gradual increase compared to that for the field descending one. The magnetization curve for the field ascending process intersects that for the field descending one twice around 20 and 40 T in figure 4(a). This is probably explained by the calculated energy diagram. Since the energy branches are well separated at high fields except at the transition fields as shown in figure 7, it is expected during the field descending process from the field maximum that most of the spins stay in the lowest branch of the energy levels. That is to say, most spins move from the lowest branch of the septet to that of the quintet for the $c$ direction.

On the other hand, the field ascending process is largely different. At zero field and low temperature, most spins are populated in the lowest quintet state as shown in figure 7. On applying magnetic fields, level splitting of the quintet state occurs due to the Zeeman effect. We used pulsed magnetic fields with the duration of about 7 ms and a nearly symmetric waveform, resulting in the nearly same sweep time during the field ascending and descending processes. This field sweep rate must be comparable to or slightly faster than the thermal relaxation time in magnetic systems. A field sweep in pulsed magnetic fields faster than thermal relaxation time
causes non-equilibrium of the spin population. This makes the magnetization near the zero field in the field ascending process smaller than that in the field descending one, because some spins remain in the second lowest or higher quintet branch.

In the energy diagram, the second lowest branch of the quintet state intersects the lowest branch of the septet one around 20 T ($H_0$). If these two states are mixed by an antisymmetric interaction term such as Dzyaloshinsky–Moriya interaction and the avoided level crossing takes place, the spins on the second lowest branch of the quintet state move into the lowest branch of the septet one and the magnetization becomes larger than that for the field descending process. At the transition field $H_1$ of about 40 T, the lowest state changes from the lowest branch of the quintet state to that of the septet one. In this case, the magnetization must be lower than that in the field descending process for the same reason as occurred around 20 T. This scenario has been confirmed by high field magnetization measurements at low temperatures between 90 mK and 1.3 K as shown in figure 8. Magnetization curves in the field descending process at 90 mK, 300 mK, 600 mK, 900 mK and 1.3 K are almost superposed over the whole field range, while those in the field ascending process are different and the magnetization becomes close to that in the field descending one with decreasing temperature. This is because the number of thermally excited spins are very small at sufficiently low temperatures.

4. Conclusions

We have performed magnetic susceptibility, and high and low field magnetization measurements on single crystals of the Ni tetramer compound NCAP with a butterfly structure. A magnetization curve with two steps and a further increase of magnetization around 63 T was observed in magnetic fields up to about 70 T and the main two exchange constants are determined roughly from the transition fields. We understand each plateau state in the following way in terms of the valence bond picture [12, 13] as depicted in figure 5. In this picture, the large open circles and the small solid ones indicate the Ni$^{2+}$ ions ($S = 1$) at the shortest diagonal sites and the spin 1/2 degrees of freedom inside the Ni$^{2+}$ ion, respectively. The spin 1 in the large circle is obtained by symmetrization of two $S = 1/2$ variables, thus obeying the Hund’s rule in each Ni site. The thin
lines between the solid circles represent the singlet bonds. The thin and thick arrows correspond to the magnetic moments of spin 1/2 and 1. At the one half plateau, the singlet state is formed by the Ni spins ($S = 1$) at the shortest diagonal sites and the other Ni spins behave almost freely or are weakly coupled by the ferromagnetic $J_3$ interaction. One of the singlet bonds within the Ni dimer is broken at the second plateau corresponding to the three quarters of the saturation magnetization, and the singlet bonds are fully broken at the saturation field to direct all the moments to the field. This valence bond picture corresponds to the spin state $S = 0, 1$ and 2 formed by the coupling of two $S = 1$ spins.

From the magnetization measured in steady fields and its analysis, we determine the exchange constant $J_3$. As for magnetic susceptibility, we also analyse the experimental data using the same Hamiltonian and evaluate the parameters. The evaluated exchange constants $J_1$, $J_2$ and $J_3$ are close to those determined from magnetization measurements, but slightly different from them. Fine tuning of the parameters including single ion anisotropy terms must be required to get much better agreement between magnetization and susceptibility experiments. Hystereses of the magnetization curve in pulsed magnetic fields is discussed based on the energy diagram calculated by using the above parameters. This work provides us with one of the advantages of high field measurements when determining magnetic parameters of nano-scale single molecular magnets. The number of magnetic ions in the Ni tetramer unit is only four, but we hope that this compound can be one of the key materials to study much more complicated frustrated nano-scale single molecular magnets.

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