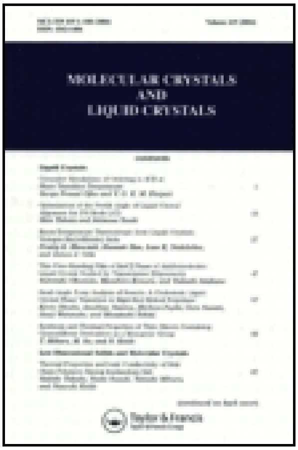

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High-Field Magnetization and High-Frequency ESR Study on the Tetranuclear Cluster Composed of π -Electrons (S =1/2) and d-Electrons (S =5/2)

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High-Field Magnetization and High-Frequency ESR Study on the Tetranuclear Cluster Composed of π -Electrons (*S* =1/2) and *d*-Electrons (*S* =5/2)

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Recently, Iwamura's group has succeeded in synthesizing the interesting new tetranuclear cluster composed of two paramagnetic Mn^{2+} ions (S=5/2 per ion) and two organic free radicals (S=1/2 per radical) as bridging ligand, $[\{Mn(hfac)_2\}_2(bnn)]$ (bnn=2,2'-bis[(1-oxyl-3-oxide-4,4,5,5-tetramethyl-imidazolinyl)]). The crystal structure is triclinic (space group *P1*) and each cluster is composed of two triangles which share their own base like a "butterfly". There are two kind of exchange pathways within the cluster and both of them are likely to be antiferromagnetic. Therefore, spin frustration may occur and we expect many possible ground states with different total spins (S_T=0 to S_T=6), depending on the relevant interactions and magnetic field.

We wish to discuss the important magnetic parameters such as exchange interactions and anisotropy which characterize this interesting system through measurements of high-field magnetization and high-frequency electron spin resonance.

Keywords: tetranuclear cluster; spin frustration; anisotropy

INTRODUCTION

There are much interesting subjects in the various magnetically interacting many body systems, however, it is not so easy task to identify their physical properties even in low dimensional magnet. With so much improvement on synthesizing technique in the field of organic chemistry, spin cluster systems have been studied actively in recent years. High spin molecules lie in a magnetic mesoscopic regime that bridges the atomic and macroscopic scales, and nowadays in principle we can obtain any desired systems of magnetically interacting cluster, so returning to the element of many body system, as a first step, studying with finite spin cluster, in which the system is described in terms of explicit form of spin Hamiltonian, is very useful in a sense that it contributes to understand the magnetic properties in more complicated compounds. Moreover, in the nanosized finite spin system, the energy levels are well separated each other, thus, masking of discreteness due to the thermal averaging is excluded at appropriate low temperatures, which makes us possible to observe the novel type of quantum phenomena such as quantum tunneling of magnetic moment (QTM) through the macroscopic measurements[1].

Recently, Iwamura's group has succeeded in synthesizing the tetranuclear cluster composed of two paramagnetic Mn^{2+} ions (S=5/2 per ion) and two organic free radicals (S=1/2 per radical) as bridging ligand, $[\{Mn(hfac)_2\}_2(bnn)]$ (bnn=2,2'-bis[(1-oxyl-3-oxide-4,4,5,5-tetramethyl-imidazolinyl)]) and examined its magnetic properties from the measurements of susceptibility and magnetization[2]. The crystal structure is triclinic (space group *P1*) and each cluster is composed of two triangles which share their own base like a "butterfly" as shown in Fig.1. There are possible two kind of exchange pathways within the cluster, namely J (between wing and body) and J_{13} (within body) (see Fig.1). Appropriate spin hamiltonian for this system and the eigenvalues are given as follows,

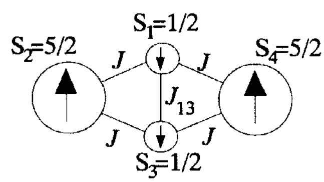

FIGURE 1 Schematic structure of $[\{Mn(hfac)_2\}_2(bnn)]$.

$$H = -2J(\vec{S}_1\cdot\vec{S}_2 + \vec{S}_2\cdot\vec{S}_3 + \vec{S}_3\cdot\vec{S}_4 + \vec{S}_4\cdot\vec{S}_1) - 2J_{13}\vec{S}_1\cdot\vec{S}_3 \qquad (1)$$

$$E = -2J\left[S_T(S_T+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)\right] - J_{13}\left[S_{13}(S_{13}+1)\right] \qquad (2)$$

where

$$\vec{S}_T = \vec{S}_{13} + \vec{S}_{24},\ \vec{S}_{13} = \vec{S}_1 + \vec{S}_3 \text{ and } \vec{S}_{24} = \vec{S}_2 + \vec{S}_4.$$

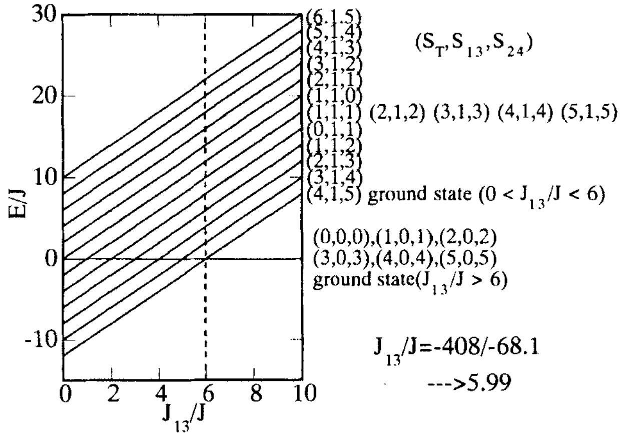

FIGURE 2 Energy level scheme based on eq. (2) (see text).

Then, the energy diagram is calculated straightforwardly as shown in Fig.2. From fitting the theoretical curve to the temperature dependence of susceptibility measurement from 300 to 2K at 500 G, both exchange interactions are likely to be antiferromagnetic (J=-68.1±4.6K, J_{13}=-408±28K). Therefore, spin frustration may occur and we expect many possible ground states with different total spins (S_T=0 to S_T=6), depending on the relevant interactions and magnetic field Magnetization measurement up to 4 T at 2 K revealed the ground state is S=4. This fact implies that two S=1/2 spins align in parallel configuration as shown in Fig.1, in spite of the fact that the antiferromagnetic interaction within body J_{13} is relatively large compare to wing-body interaction J.

In this report, we wish to discuss the ground state and energy levels in this interesting system from the evaluation of important magnetic parameters such as exchange interactions and anisotropy. The anisotropy is expected to be very small because of isotropic nature of manganese(II) and organic free radical.

RESULTS AND ANALYSIS

Using pulsed high magnetic field up to 40 T, the magnetization process were measured by induction method at the temperature 1.8 K at ISSP. Submillimeter wave ESR measurements have been performed up to about 1 THz and in pulsed magnetic fields up to about 30T at the temperature down to 1.6 K at IMR. A far-infrared laser, Gunn oscillators and InSb have been employed as the radiation source and detector, respectively.

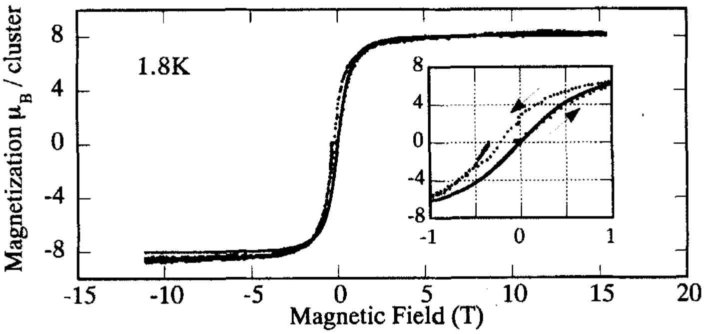

FIGURE 3 Magnetization process at 1.8K. Solid line shows the theoretical Brilouin curve for S=4. Low field region is also shown in the inset.

AC susceptibility measurements were performed down to 100 mK in a helium dilution refrigerator at Faculty of Engineering, Kyushu University. The sample [{Mn(hfac)2}2(bnn)] was provided from Iwamura's group. Detailed prescription for sample preparation is available in Ref. [2]. All of the measurements were performed on less than ca. 30 mg of powder sample.

According to the published results, the ratio J_{13}/J of this system is almost equal to 6, but still under critical as is seen in the energy scheme. Therefore, if it is the case, it may be possible to induce an excited state with higher spin value by applying high magnetic field. So we performed high field magnetization measurements up to 40 T at 1.8 K. Fig. 3 shows the magnetization curve measured by using one cycle of oscillating pulsed magnetic field and the enlarged curve in low field region are also shown in the inset. Magnetization curve is well fitted by the theoretical Brillouin curve for S=4 and no higher spin state is realized in field range under investigation. This fact limits the upper value of J_{13}/J to less than $6 - 27/|J|$. Small but not negligible anomaly like a hysteresis loop is seen in the field range lower than about 1T. This is discussed later.

X-band ESR measurements revealed a lot of fine structure, however it was difficult to assign the origin of each transition in the powder spectrum because of level mixing in low field. This complexity is removed when we measure the ESR spectrum at high field. Fig. 4 shows the field derivative spectrum of typical ESR transmission at high frequency and high field at 1.6 K. Note that the abscissa in the figure is the shifted value of the resonance field from the marker signal of DPPH. Frequency dependence of resonance field revealed isotropic g=2. The splitting of

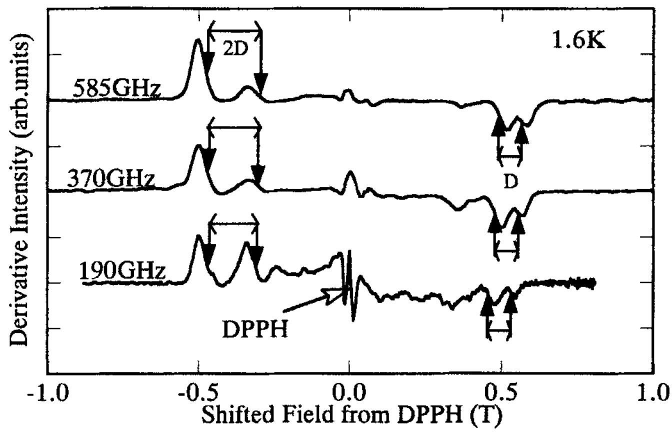

FIGURE 4 Field derivative of typical ESR spectrum at 1.6K.

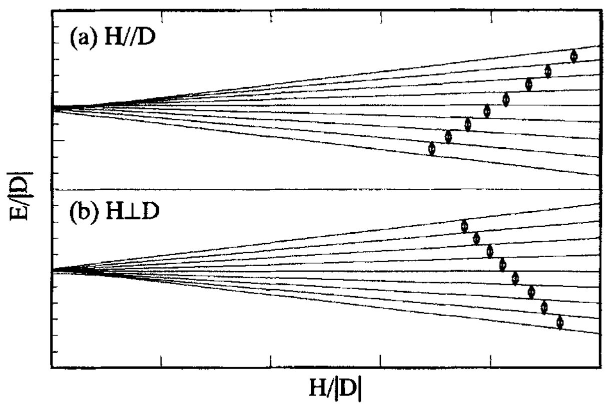

FIGURE 5 Energy level scheme as a function of field. (a) the case H parallel to D term principal axis. (b) the case H perpendicular to D term principal axis. Expected transitions are also shown by arrows.

the fine structure is almost frequency independent. Further, in any spectra shown in Fig. 4, the splitting in lower field is almost two times lager than that in higher field. These facts imply that the origin of fine structure is zero-field splitting due to the uniaxial single-ion anisotropy. Spin Hamiltonian with zero-field splitting term D is given by

$$H = \vec{S} \cdot \bar{\bar{g}} \cdot \vec{H} + \vec{S} \cdot \bar{\bar{D}} \cdot \vec{S}\,. \tag{3}$$

Assuming small E-term, that is, E=0 and isotropic g, energy level for S=4 manifold with D term of negative sign is calculated as shown in Fig. 5. Considering Boltzmann distribution for energy levels of Zeeman splittin at low temperature and at high field, we expect that ESR absorption is observed intensively at lower field and splitting of spectra is $2\,|D|$ in the case when H is parallel to the pricipal axis of D. Conversely, in $H \perp D$ configuration, it is easy to observe the ESR at higher field and its interval is $|D|$. From this analysis the value of D is estimated to be approximately -0.11K.

DISCUSSION

As a consequence of ESR measurements extended to the field 25T, it has become clear that there exists a small D term with negative sign. This leads to the existence of energy barrier, which is amount to be 1.76K, between spin up and down state. Therefore, it may be related to the anomalous hysteresis loop observed in the magnetization curve at 1.8K. Under ordinary condition, it is hard to think such irreversible phenomena because our temperature under investigation is not low enough to the energy barrier. In fact, there is no hysteresis in the magnetization measurement using static field by superconducting magnet. The origin of this anomaly may be attributable to the dynamical effects caused by a rapid field change in pulse field measurement. To make this ambiguity clear, we have started to study the AC susceptibility measurements down to very low temperature. And now it's under investigation.

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