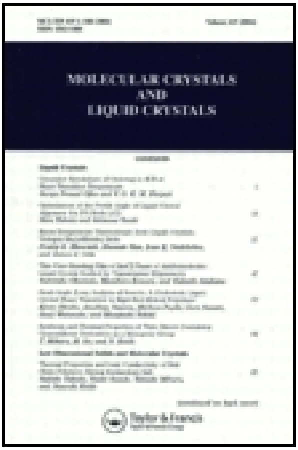

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High-Field Magnetization Process in Free Radical and Metal-Assembled Molecular Magnets

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High-Field Magnetization Process in Free Radical and Metal-Assembled Molecular Magnets

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We applied the high-field technique to study the magnetization process in model substances. Measurements have been performed on the powder samples under a pulsed magnetic field up to 50 T. A family of organic verdazyl radical is a candidate of an isotropic $S = 1/2$ antiferromagnetic linear chain model. The observed magnetization is practically zero up to a certain critical field around 40 T and steeply increases to the saturation value of 1 μ_B/molecule. The feature cannot be explained by the uniform chain model but agrees with the alternation linear chain model closed to the dimer model in which the ground state is a nonmagnetic singlet with an energy gap between the excited triplet state. Metal-assembled tetranuclear complexes $[Mn(MeOH)L(OH)M(bpy)]_2$ represent a prototype of geometrically frustrated spin systems. We observed a step-like magnetization process which clearly shows the successive transitions among quantum states with different total spins.

Keywords: high-field; magnetization; free-radical; quantum-spin; low-dimensional; alternating-bond

INTRODUCTION

Recently, a variety of newly designed magnets are synthesized in a well controlled manner, based on organic molecules and metal complexes. They often provide good model systems to study the quantum effects in low-dimensional magnets and in clustered molecular magnets, because of their structural flexibility. Among them, many free radical [1] and metal-assembled molecular magnets [2] were designed, and they have contributed to the progress in "low-dimensional quantum magnetism" field, because of a rich variety of their characteristics such as the difference of dimensionality, magnetic ions and magnetic interactions between neighboring ions.

We have performed magnetization measurements in some kinds of free radical and metal-assembled molecular magnets under a pulsed magnetic field. The measurement of magnetization process under a high magnetic field is a very powerful technique, because we can directly determine the magnitude of magnetic interaction between magnetic ions. Furthermore, we can imagine and expect the dimensionality and the spin-freedom of magnetic ion in magnetic compounds from the curvature of magnetization process. In addition, free radical compounds have the advantage of behaving as purely Heisenberg spin systems and, therefore, we can compare the experimental results with the numerical calculations in many kind of ideal model.

High-field magnetization measurements were carried out for powder samples by induction method using pulse magnets installed at ISSP in University of Tokyo and at KYOKUGEN in Osaka University.

FREE RADICAL

In the present work, we studied the magnetization process under a pulsed magnetic field up to 50 T in two kinds of 1,5-Dimethylverdazyl radical, i.e. p-CDOV and p-BDOV. Recently, Mukai *et al*. have done magnetic susceptibility measurements in p-CDOV and p-BDOV. [3] The alternating exchange couplings (J_1 and J_2) and alternating ratio ($\alpha = J_2/J_1$) are estimated as J_1/k_B = -24 K, J_2/k_B = -4.8 K and α = 0.2 and -28 K, -14 K and 0.5, respectively, by using an antiferromagnetic alternating linear chain model.

Figures 1(a) and (b) show magnetization curves in p-CDOV and p-BDOV at 1.5 K. As magnetic field increases, the magnetization is practically zero up to a certain critical field (H_c) and steeply increases to the saturation value of 1 μ_B/molecule. It is clear now that both compounds are in a nonmagnetic singlet state up to H_c and become to be magnetic due to the destruction of the energy gap between the ground singlet and excited magnetic states. From the result of magnetization curve at 1.5 K, we find H_c and the saturation field (H_s) for p-CDOV as H_c = 32.2 T and H_s = 39.5 T and for p-BDOV as H_c = 36.9 T and H_s = 43.2 T, respectively, and also determine the H_c/H_s ratio as 0.815 and 0.854, respectively. Figure 2(a) shows a theoretical prediction of the magnetization process for S = 1/2 Heisenberg antiferromagnetic chain with different values for the alternating ratio α.

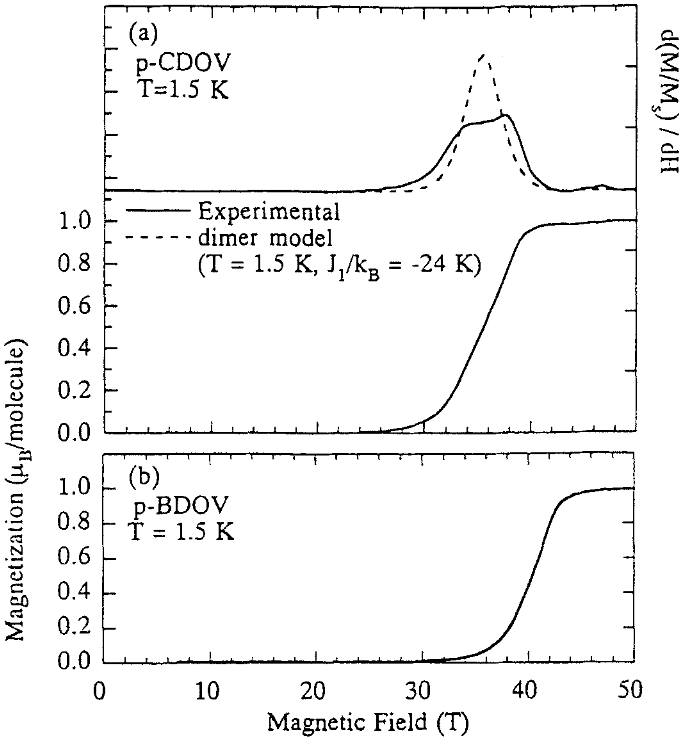

FIGURE 1 Magnetization curves for 1,5-Dimethylverdazyl radicals. (a) p-CDOV Field-derivative magnetization curves of p-CDOV and dimer model at 1.5 K for $J_1/k_B = -24$ K are also shown. (b) p-BDOV at 1.5 K.

Figure 2(b) shows the predicted critical fields H_c and H_s, and their ratio H_c/H_s in the magnetization process as a function of α at an absolute zero temperature. To determine α in p-CDOV and p-BDOV, each H_c/H_s is compared with the theoretical one as shown in Fig. 2(b). As a result, each α is estimated as $\alpha = 0.2$ and 0.1 in p-CDOV and p-BDOV, respectively. More recently, Suzuki *et al.* has calculated with the magnetization process for $S = 1/2$ alternating linear chain at finite temperatures by employing a quantum Monte Carlo (QMC) method as

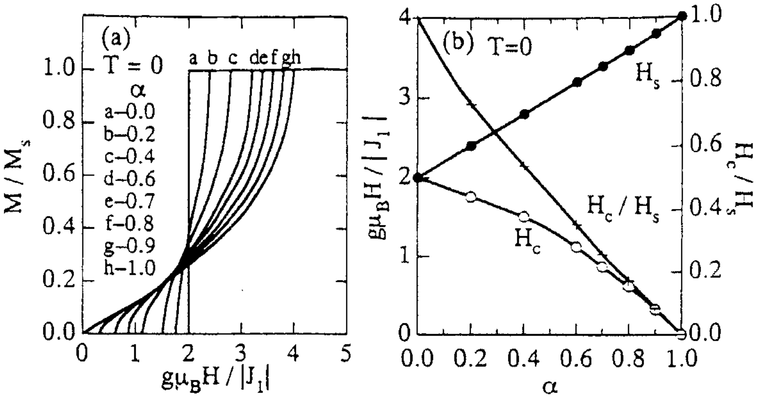

FIGURE 2 (a) Theoretical magnetization curves for the magnetization for alternating $S = 1/2$ Heisenberg antiferromangetic chains with different alternating ratio α. (b) The predicted critical fields H_c and H_s, and their ratio H_c/H_s of the magnetization as a function of α at $T = 0$.

shown in Fig. 3. Figure 3(a) shows the magnetization curves for $\alpha = 0.2$ and (b) the field-derivative curve of the magnetization at different temperatures. Consequently, we estimate J_1/k_B = -24 K for p-CDOV which agrees with the result by magnetic susceptibility measurement. Unfortunately, we cannot discuss about the alternating exchange couplings in p-BDOV that there is no calculation for $\alpha = 0.1$ at present.We hope that the magnetization process in p-BDOV stimulates further theoretical calculations for different α. In particular, we are very interested in the curvature of the field-derivative magnetization process at different temperatures as shown in Fig. 3(b). The present method using a pulsed magnetic field is very sensitive to the field-derivative magnetization, therefore, we can detect negligibly small anomalies as a jump or kink of magnetizations. The characteristic shape with two sharp peaks corresponding to the H_c and H_s for $k_BT/|J_1| = 0$ fades out with increasing temperature. As the temperature is increased further, the shape becomes featureless, that is, the magnetization curve as a function of magnetic field follows a straight line as seen in Fig. 3(a). It should be noted that the field-derivative magnetization curve of p-CDOV for $k_BT/|J_1| = 0.0625$, shown in Fig. 1(a), resembles the theoretical curve for $k_BT/|J_1| = 0.1$ in Fig. 3(b), but is quite different from the dimer model with J_1/k_B = -24 K, $J_2 = 0$ at T = 1.5 K. In other words, the comparison makes it clear that there is a remarkable

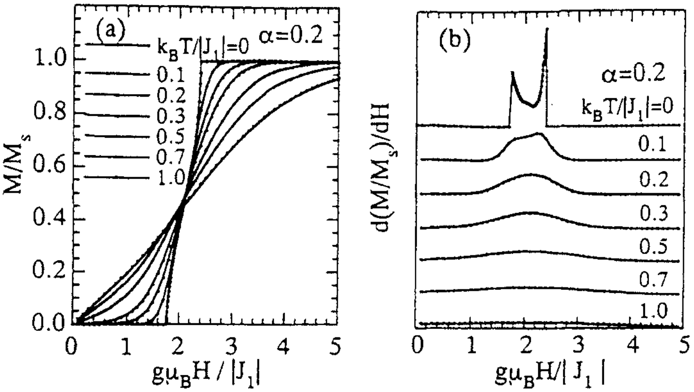

FIGURE 3 (a) Magnetization curves for $\alpha = 0.2$ at different temperatures. (b) Field-derivative magnetization for $\alpha = 0.2$.

difference of the field-derivative magnetization curve among the isolated antiferromagnetically-coupled dimer system and the weakly antiferromagnetically-coupled alternating chain system. A most important point is that when the temperature become sufficiently lower than the exchange coupling, we can reveal the real nature of these magnetic systems.

To conclude, two kinds of free radical, p-CDOV and p-BDOV, are representative of $S = 1/2$ Heisenberg antiferromagnetic chain with alternating exchange interaction in which the ground state is a nonmagnetic singlet with an energy gap between the excited triplet state.

METAL-ASSEMBLED MOLECULAR MAGNETS

Metal-assembled tetranuclear complexes $[Mn(MeOH)L(OH)M(bpy)]_2$ (M = Zn, Cu, Ni, Mn) with rhombus structure consisting of twin triangles, represent a prototype of geometrically frustrated spin systems. In these systems we expect many possible ground states with different total spins, depending on the relevant interactions and magnetic field. As an example, the magnetization curves of M = Cu up to 40 T at 1.8 and 4.2 K are shown in Fig. 4. The observed step-like magnetization clearly shows the successive transitions among different states with different quantum energy levels. From the absolute values of magnetization, the first plateau of the magnetization around 15 T

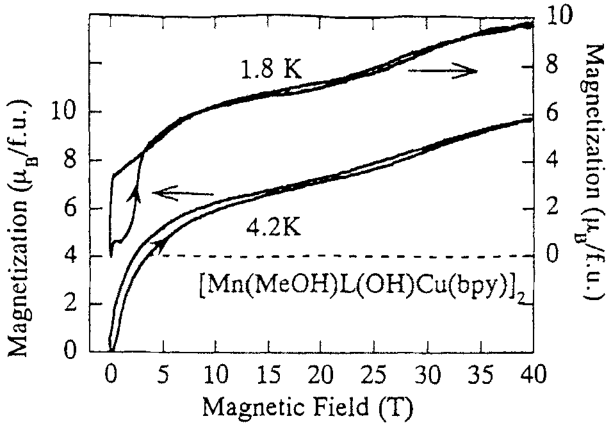

FIGURE 4 Magnetization curves in [Mn(MeOH)L(OH)Cu(bpy)]$_2$ at 1.8 K and 4.2 K.

(~ 7 μ_B/f.u.) and the second one around 40 T (~ 9.5 μ_B/f.u.) correspond to the states with the total spin of $S = 3$ and $S = 4$, respectively, assuming $g \sim 2.4$. In the present system compound of 4 spins ($S_{Mn(III)}$ = 2, 2 and $S_{Cu(II)}$ = 1/2, 1/2), a total of 18 spin states with the total spin S values ranging from 0 to 5 are possible. Therefore, we can expect one more transition into $S = 5$ state at much higher field around 65 T. There transition fields are not so far from the calculated values [5] using the reported exchange parameters, J_{Mn-Mn} = -4.5 cm^{-1} and J'_{Mn-Cu} = -8.1 cm^{-1}. We note that the predicted anomaly of magnetization is strongly observed in the measurement for powder sample due to the existence of rather large anisotropy $D \sim$ -4.9 cm^{-1}.

Acknowledgments

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[5] T. Tonegawa, private communiacation.