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Half-Step magnetization in the polyoxometalate family with \{Cu_3\}-type triangular spin ring

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Abstract. We report on pulsed field magnetization and ESR measurements of the family of copper(II)-substituted polyoxotungstates \([\text{Cu}_3(\text{H}_2\text{O})_3(\alpha-\text{XW}_9\text{O}_{33})_2]^{12-}\) (X=As, Sb) where the three Cu\textsuperscript{2+} ions form an antiferromagnetically-coupled triangle. The distinct features are the observation of half step magnetization and hysteresis loops as well as asymmetric/symmetric magnetization between a positive and negative field, depending on the diamagnetic heteroatom X. This is attributed to the interplay between an adiabatic magnetization and Dzyaloshinskii-Moriya interactions. Moreover, the more symmetric magnetization curve of X=Sb is discussed in terms of dynamical mixing of a S=1/2 state via a phonon mode.

In recent years, molecular clusters consisting of a finite number of interacting paramagnetic ions have attracted considerable interest. As zero-dimensional, nano-sized magnets these systems provide an opportunity for a better understanding of the basic principles of magnetism [1, 2]; for example, the crossover between quantum and classical behavior, the effect of geometrical frustration, quantum spin dynamics and tunneling.

A unique advantage of investigating molecular magnets lies in the flexibility of synthesizing compounds with various magnetic parameters: (i) the size of magnetic spin, (ii) the sign and magnitude of exchange interaction, and (iii) the spin topology. Among them S=1/2 antiferromagnetic triangle spin rings belong to the simplest class of a frustrated spin system. In spite of a simple spin topology, however, quantum magnetization behavior is expected to be rich due to the presence of two doublets with a different spin chirality [3, 4, 5].

The prototypical example of an S=1/2 triangle spin ring is found in the copper(II)-substituted polyoxotungstates \([\text{Cu}_3(\text{H}_2\text{O})_3(\alpha-\text{XW}_9\text{O}_{33})_2]^{12-}\) (X=As, Sb) (hereafter shortened as \{Cu\textsubscript{3}-X\}) [6, 7]. The \{Cu\textsubscript{3}-X\} compounds possess a sandwich-type structure with D\textsubscript{3h} symmetry, in which the central belt consisting of three Cu\textsuperscript{2+} ions is separated by two \((\alpha-\text{XW}_9\text{O}_{33})\) subunits. A spin triangle is formed by three CuO\textsubscript{4}(H\textsubscript{2}O) square pyramids linked by Na\textsuperscript{+} ions. The spin triangle with Cu \cdots Cu distances is sketched in the inset of Figure 1.

In the following, we will address a quantum magnetization process in the family of the \{Cu\textsubscript{3}-X\} compounds using fast-sweeping pulsed field magnetization and ESR [8].
Figure 1. (a) Magnetization curve vs pulsed magnetic field for \{\text{Cu}_3\text{-As}\} at 0.4 K for H $||$ plane. The saturated magnetization is normalized by $gS$. Arrows denote sweep directions ($A \rightarrow B \rightarrow C \rightarrow D$). Inset: a sketch of a spin triangle of \{\text{Cu}_3\text{-As}\} with Cu $\cdots$ Cu distance. (b) Magnetization of \{\text{Cu}_3\text{-Sb}\} in a fast sweeping pulsed field. Inset: a sketch of a spin triangle of \{\text{Cu}_3\text{-As}\} with Cu $\cdots$ Cu distance. The inset between two panels shows time dependence of a pulsed magnetic field.

Figure 1 shows the magnetization versus magnetic field plot for \{\text{Cu}_3\text{-X}\} at 0.4 K for H $||$ plane containing the spin triangle. Here note that the saturation magnetization is normalized by $gS$. The remarkable feature is the observation of hysteresis loops and asymmetric magnetization between a positive and negative field. This is totally unexpected for an antiferromagnetically coupled $S=1/2$ spin cluster without any single ion anisotropy.

In the up sweep ($A \rightarrow B$) the magnetization of \{\text{Cu}_3\text{-X}\} first saturates to $1gS\mu_B$ and then jumps to $2.3gS\mu_B$ and finally approaches to the value of $3gS\mu_B$ in a high magnetic field of 13 T. In the down sweep ($B \rightarrow C$), the magnetization jumps occur from $3gS\mu_B$ to $1gS\mu_B$ and then falls off to zero. Although the overall magnetization curve is similar, both compounds show the difference in (i) sharpness of the jump and (ii) negative side magnetization.

We recall that the magnetization plateau to $1gS\mu_B$ at lower field corresponds to the saturation of $S^T = 1/2$ state while the step to $3gS\mu_B$ at higher field arises from the level crossing between $S^T = 1/2$ and $S^T = 3/2$ states [see Figure 2 (b)]. This suggests that the magnetization jump to $2.3gS\mu_B$ which is seen only in the up sweep between $5 \sim 8$ T is not due to the equilibrium quantum magnetization behavior. Noticeably, it amounts to roughly half of the equilibrium magnetization. We stress that the so-called half step magnetization depends on an applied field direction as well as on a heteroatom X. This signifies a dynamical quantum magnetization process.

To elucidate the observed quantum magnetization behavior, we take a general Hamiltonian of a spin triangle ring as follows:

$$\mathcal{H} = \sum_{l=1}^{3} \sum_{\alpha=x,y,z} J_{l,l+1}^\alpha \mathbf{S}_l \cdot \mathbf{S}_{l+1} + \sum_{l=1}^{3} D_{l,l+1} \cdot [\mathbf{S}_l \times \mathbf{S}_{l+1}] + \mu_B \sum_{l=1}^{3} \mathbf{S}_l \cdot \tilde{g}_l \cdot \mathbf{H}_l,$$

where the exchange coupling constants, $J_{l,l+1}^\alpha$, the Dzyaloshinskii-Moriya (DM) vectors, $D_{l,l+1}$, and the $g$-tensors, $\tilde{g}_l$, are defined as a site-dependent quantity with a periodic boundary.
Figure 2. (a) Q-band ESR spectra of \{Cu_3-As\} at 8.8 K. The numbers are the ESR transitions between the energy levels marked in Figure 2 (b). Inset: Angular dependence of the ESR spectra. The solid lines are simulated curves using the magnetic parameters discussed in the text. (b) Energy level diagrams for the Hamiltonian of Eq. (1) for H || plane.

The magnetic parameters are determined by considering a crystal symmetry as well as by simulating the magnetization steps and angular dependence of ESR [see the inset of Figure 2(a)]. An extremely high sensitivity of ESR on anisotropic exchange interactions and a small Hilbert space enable us to fix all parameters uniquely. For \{Cu_3-As\} we obtain $J_{12}^x = J_{12}^y = 4.50(0)$ K, $J_{23}^x = J_{23}^y = 4.56(0)$ K, $J_{31}^x = J_{31}^y = 4.03(0)$ K, $J_{23}^z = J_{31}^z = 4.06(0)$ K; $D_{12}^x = D_{23}^x = D_{31}^x = 0.52(9)$ K, $(D_{23}^x, D_{23}^y) = R(2\pi/3)(D_{12}^x, D_{12}^y)$, $(D_{31}^x, D_{31}^y) = R(4\pi/3)(D_{12}^x, D_{12}^y)$ where $R(\theta)$ denotes a rotation of the triangle by $\theta$ and $D_{12}^z = D_{12}^y = 0.52(9)$ K; $g_{11}^{xx} = g_{11}^{yy} = 2.2(5)$, $g_{22}^{xx} = g_{22}^{yy} = 2.1(0)$, $g_{33}^{xx} = g_{33}^{yy} = 2.4(0)$ and $g_{ii}^{zz} = 2.0(6)$ $(i = 1, 2$ and 3). The exchange couplings of \{Cu_3-Sb\} are slightly smaller than those of \{Cu_3-As\} due to an increase of Cu \cdots Cu distance (see the insets of Figure 1).

The resulting energy level diagram is depicted in Figure 2 (b). At zero field, the energy gap of $\Delta = 1.0(6)$ K opens between the ground state manifolds of a total spin $S^T = 1/2$ with a degenerated chirality. The sizable DM interactions, amounting to 12% of $J_{ij}$, are responsible for a lifting of a degeneracy in addition to a small isosceles distortion. Note that the overall magnetization curve is sharper for X=As than for X=Sb. Since the deviation from the triangle becomes larger in X=Sb, larger distortion from equatorial triangle might be responsible for that.

Another effect of DM interactions is on a different behavior of level crossings between the $S^T = 1/2$ and $S^T = 3/2$ states; the ground state has an anti-level crossing with the $S^T = 3/2$ state while the second lowest state shows a tiny admixture to it. Based on this fact, we can figure out the origin of the nearly half step magnetization seen at high fields between 5-8 T in the up sweep. For the up sweep the lowest $S^T = 1/2$ state transits to the lowest $S^T = 3/2$ one. In contrast, the second lowest $S^T = 1/2$ state undergoes the successive transition of $S^T = 1/2 \rightarrow S^T = 3/2 \rightarrow S^T = 1/2$. Thus, the former process will contribute to the magnetization by $2g_S\mu_B$ while the latter magnetization change gives zero magnetization, that is, no increase of magnetization above 4.6 T. When the two processes are averaged, the half step
magnetization of $1gS\mu_B$ will result in at zero temperature. However, at 0.4 K the observed step of $1.3\ gS\mu_B$ is bigger than the zero temperature one. At finite temperature and finite sweeping speed, the spin in the level 2 will undergo the partial relaxation to the level 1. As a result, the population of the level 1 will increase with respect to the level 2. This gives the increase of the expected half magnetization to $1.3\mu_B$.

Remarkably, the half step magnetization is absent in the negative field for \{Cu$_3$-As\}. This can be understood in terms of the competition between the fast sweeping field and the thermal relaxation. The field sweep speed, $dH/dt$, follows a cosine type time dependence [see the middle inset of Figure 1]. Upon approaching to the point B, thus, $dH/dt$ goes to zero. In this situation, the sweep field period will slow down to the extent that the second lowest $S^T = 1/2$ state undergoes a relaxation to the lowest $S^T = 3/2$ one. This means that at the field top in the positive side, the magnetization is saturated and all spins are in the ground state [the level 1 in Figure 2 (b)]. In the down sweep, the thermal relaxation is quenched because of the fast sweeping rate of cosine function. As a result, the spins follow the level 1 all the time showing the change of magnetization $S^T = 3/2 \rightarrow S^T = 1/2 \rightarrow S^T = 1/2 \rightarrow S^T = 3/2$. We have to note that the reversal at the zero field is caused by the formation of the tunneling gap between the levels 1 and 2 by the intra-molecule hyperfine coupling of Cu$^{2+}$ ions. Since the spins are mostly confined to the ground state, the effective temperature of the spin system is much lower than the equilibrium one. Actually, the sharp drop of the magnetization with larger value than equilibrium state supports a decoupling of the spins from environments.

In contrast, for \{Cu$_3$-Sb\} the half step magnetization is appreciable in the negative field. We might think the mixing between the two $S^T = 1/2$ states as possible origin. If the compound contains a phonon mode where three copper atoms vibrate out of phase, it lowers C$_3$ symmetry. This dynamical distortion of the regular triangle via a phonon mode can lead to a mixing of the two chiral states. This causes the fast re-population of spins between the lowest and the second lowest $S^T = 1/2$. If such effect is lager in X=Sb, we can have the symmetric magnetization process between the positive and negative field. This is because the ground state and the excited states of $S^T = 1/2$ are mixed. In fact, such behavior is also found in the triangles made of V$^{4+}$ ions [4].

To summarize, we have reported the observation of half step magnetization and hysteresis loops as well as asymmetric/symmetric magnetization between a positive and negative field, depending on the heteratom X. This feature is characteristic for an adiabatic change of magnetization and DM interactions which induce a different mixing of the spin chirality of a total $S^T = 1/2$ Kramers’ doublet. Further, the different behavior of the half step magnetization between X=As and Sb suggests a dynamical mixing of a S=1/2 state via a phonon mode.

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References