Quantum Level Structure of Molecular Magnets, Fe12 and V15

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Abstract

We review our recent work on molecular magnets, Fe12 and V15 with focusing on the determination of low-lying quantum energy levels which have permanent importance in understanding their unique quantum magnetism.

Key words: Molecular magnets; Fe12; V15; High-field magnetization; ESR

Recent synthesis technique has provided a variety of molecular magnets with a finite number of interacting paramagnetic ions. Interest inherent in a finite cluster is a quantum nature which manifests in well defined discrete energy levels. Due to the existence of discrete levels we can expect new quantum phenomena. Of particular interest is a situation of degeneracy of two magnetic levels, which easily comes from the level-crossing by an application of external field and raises fundamental problems of quantum dynamics. From this point of view, it is important to know the structure of energy levels of the systems.

(1) *Magnetization process of Fe12*

$[Fe(OCH_3)_2(dbm)]_{12}$ (Fe12) where dbm=dibenzoylmethane has a ring structure consisting of 12 paramagnetic Fe^{3+} (S=5/2) ions. Fig. 1 shows the magnetization $M(H)$ curve at 0.1 K for increasing pulse magnetic field H up to 55 T, together with dM/dH. Five distinct steps were observed with no hysteresis; $M(H)$ is practically zero up to 10 T and it rapidly increases by about 2 μ_B at each step with the field separation of 10 T, showing plateaus of 2, 4, 6, 8 and 10 μ_B. The behavior is characteristic of the system with discrete energy levels of different total spin states $|S_T$=0, 1, 2, ···, 30>, which is one important aspect of the quantum nature. With increasing H, each of the Zeeman level-crossings

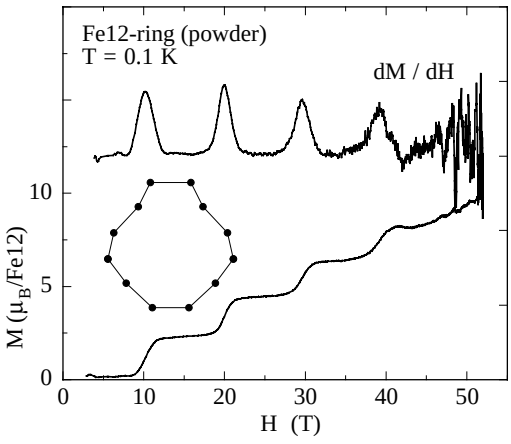

Fig. 1. Magnetization $M(H)$ curve at 0.1 K for increasing pulse magnetic field up to 55 T, together with dM/dH.

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raises the value of quantized magnetic moment in the ground state by one unit at regular interval, implying that the energy levels for every $S_{\rm T}$ states are given by a Landé interval rule. We can determine the energy gap $\Delta E/k_{\rm B}$=13.6 K between the $|S_{\rm T}=0>$ ground state and the $|S_{\rm T}=1>$ excited state, directly from the first transition field 10 T. Using the relation, $\Delta E = 4J/N$ with N=12, intraring interaction $J/k_{\rm B}$=40.7 K is determined. These values of $\Delta E/k_{\rm B}$ and $J/k_{\rm B}$ should be compared to 10.7 K and 31.9 K from the susceptibility data [1]. The $M(H)$ measurements at low temperature is a powerful direct method to determine the energy levels.

It should be noticed that the dM/dH curve is unusual; the second peak is higher and narrower than others. Besides, we found that the $M(H)$ curve at 1.3 K exhibits unusual features with an anomalous hysteresis for increasing and decreasing field; the magnetization change at each step occurs at two stages, leading to a characteristic wingled hysteresis loop with a plateau region. These anomalous behaviors around the level-crossing fields during the fast field passage are discussed elsewhere [2].

(2) *ESR of V15*

$K_6[V_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$ (V15) is characterized by a remarkable layer structure in an each quasispherical cluster, which has an overall trigonal symmetry with C_3 axis. A cluster containing 15 paramagnetic vanadium ions, V^{4+} (S=1/2), consists of two hexagons separated by a triangle.

The temperature dependence of the ESR intensity $I(T)$ is plotted in a log-log scale in Fig. 2, together with our own susceptibility $\chi(T)$ data normalized at 50 K. The straight lines represent the Curie law with the different effective number $N_{\rm eff}$ of S=1/2 paramagnetic ions. It is evident that $N_{\rm eff}$ which participates in the resonance decreases quite distinctly with decreasing temperature. The angular dependencies of g-value and linewidth also change quite drastically with temperature. A remarkable fact is that the anisotropy axis of g-value reverses between 300 K and 50 K, after showing the isotropic behavior at 200 K.

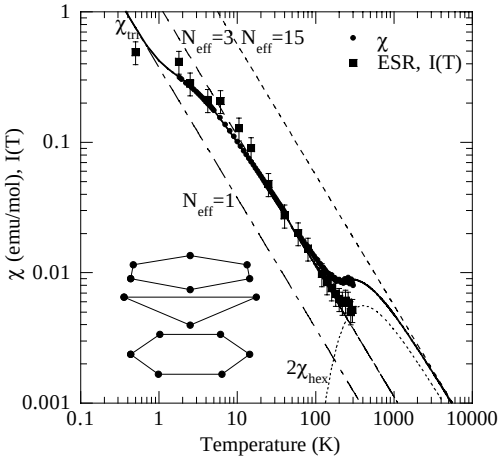

Fig. 2. Temperature dependence of the ESR intensity $I(T)$ in a log-log scale, together with susceptibility $\chi(T)$ normalized at 50 K.

All the peculiar behaviors are explained by a simplified model in terms of weakly coupled two subunits. One is a strongly dimerized hexagon, having the $S_{\rm hex}$=0 ground state and an $S_{\rm hex}$=1 excited state with the energy gap $\Delta_{\rm hex}$. The other is a weakly coupled triangle, having two degenerate Kramers doublets with $S_{\rm tri}$=1/2 as the ground state and a low-lying excited $S_{\rm tri}$=3/2 quartet state with the energy gap $\Delta_{\rm tri}$. We simply assume that the low-energy physics arises from additive contributions from two subunits. Indeed, from a geometrical reason, the spin frustration effectively decouples the triangle spin unit from the upper and lower hexagonal units. The calculated total susceptibility $\chi_{\rm tot}$ based on this model is in a reasonable agreement with the data as shown by the solid curve in Fig. 2, in which each contribution from $\chi_{\rm tri}$ and $2\chi_{\rm hex}$ are also shown. The fiting parameters $\Delta/k_{\rm B}$=3.74 K and $J/k_{\rm B}$=650 K should be compared with $\Delta/k_{\rm B}$=3.7K and $J/k_{\rm B}$=800 K from a more elaborate analysis of the susceptibility [3]. In short, V15 has two important energy scales, $\Delta_{\rm tri}$ between the doublet and quartet, $\Delta_{\rm hex}$ at which the singlets in the hexagon break and the molecules starts to behave as more than three spins.

At this stage, we have to introduce a weak coupling between two subunits to give rise to the collapsed single resonance. If the two subunits were decoupled completely, we would expect two signals having different g-values in contradiction to the observation. For the collapsed signal, $I(T)$ resembles very much $\chi(T)$ as observed and the T-dependent g-values are explained quantitatively by the averaging effect with the appropriate weight of two subunits, being proportional to $\chi_{\rm tri}$ and $\chi_{\rm hex}$. In such a way, we are now able to solve a puzzle of the anisotropy reversal between high and low temperatures. Details are discussed elsewhere [4].

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