Temperature dependence of the resonant tunneling fields in high-spin molecules

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Herein we have made two Mn-based high spin molecule samples, $S=10$ and $S=9$. Both samples show step hysteresis below 3 K, and their resonant fields are regularly spaced. Changes in temperature shift the resonant fields. The temperature dependence of the observed resonant fields can be fitted well with only a single-state tunneling if the mean-field interaction is taken into account. We also find that both the upward shift of the small step-index resonant fields and the downward shift of the large step-index resonant fields are due to mutual interactions. © 2004 American Institute of Physics. [DOI: 10.1063/1.1669359]

High-spin molecules are embedded in solids to form molecular complexes, and each molecule is separated from the others by disordered acetic acid molecules and the water of crystallization. An effective uniaxial anisotropy spin Hamiltonian in a zero field is

$$H_{an} = -D\hat{S}_Z^2,$$

where $D$ is the anisotropy parameter. A dipolar field among the molecules is around 40 mT for $S=10^6$ and is usually neglected. However, the square-root decay of magnetization suggests that the influence of the mutual interactions on the Mn12 high-spin molecules is appreciable. To study the effect of mutual interactions among the molecules, we introduce a mean field term, which is proportional to the mean magnetization $\langle S_z \rangle$. Since the magnetization is a dynamic quantity, the mutual interaction is time dependent. A rigorous solution of this time-dependent quantum problem is nontrivial. Since the tunneling rate is usually several orders of magnitude faster than the variation of both the applied field and the interaction field, the mean value $\langle S_z \rangle$ may be treated as quasistatic during the tunneling process. Thus, we phenomenologically introduce the mutual interaction by way of a mean field term, $\beta \langle S_z \rangle S_z$, into the spin Hamiltonian of a single high-spin molecule. The equation becomes

$$H = -D\hat{S}_Z^2 - g\mu_B H Z S_Z - \beta \langle S_z \rangle S_z,$$

where the first two terms are relative to the effective uniaxial anisotropy and the Zeeman energy. The third term, $\beta \langle S_z \rangle S_z$, describes the mutual interactions with the other high-spin molecules, and in which $\beta$ is a mean field parameter. The mean magnetization is $\langle S_z \rangle$, where $\langle S_z \rangle = \sum_n \langle S_z | n \rangle \rho_n$ and $\rho_n$ is the population of the state $|S_z=n\rangle$ per unit volume. From the degenerate levels, it is easy to derive the $n$th step-index resonant field from Eq. (2):

$$H_{nm} = H_n - \frac{\beta \langle S_z \rangle}{g\mu_B}.$$

The term of $H_n$ is the customary $n$th step-index resonant field, where

$$H_n = n \frac{D}{g\mu_B}.$$

The second term of Eq. (3) is a corrective one for $H_n$. It represents the mean field interactions and shifts $H_{nm}$ either upward or downward depending on the evolving magnetization.

If we consider both the quartic anisotropy and mean field terms, then there is an extra quartic term, $-BS_z^4$, that should be included into Eq. (2) as well. Eq. (3) should therefore be modified as

$$H_{nq} = H_n + n \frac{2B}{g\mu_B} \left[ \left( u - \frac{n}{2} \right)^2 + \frac{n^2}{4} \right] - \frac{\beta \langle S_z \rangle}{g\mu_B},$$

where $B$ is the quartic anisotropy parameter. The levels $u$ and $v$ are degenerate and the step index $u = u + v$. It is obvious that the first correction term in Eq. (5) is always positive and the second term can be either positive or negative. The relative magnitude of the correction terms is
The molecular crystal.\textsuperscript{10,11} The mean field term can possibly be estimated from the shape of experimental data\textsuperscript{~}. Therefore, at least the order of magnitude of the hyperfine interactions or dipolar interactions.\textsuperscript{9} It is quite reasonable that the geometric factor independently.\textsuperscript{2,12} However, since our sample is microcrystaline, we do observe that at the same temperature, both our 10 systems use a single value, implying that $\beta$ is a fixed parameter, e.g., the geometric factor of the sample. However, since our sample is microcrystalline, it is not easy to determine their crystal shape and thus the geometric factor independently.

In the measurement of the Mn12–Ac hysteresis loops, the resonant condition is usually considered to be only dependent on the external field.\textsuperscript{2,12} However, from both the experimental data (e.g., the square-root decay of the magnetization)\textsuperscript{7} and the mean field theory,\textsuperscript{9} we conclude that the time-dependent internal field may also play an important role in the resonance tunneling. Figures 1 and 2 display the experimental data of the resonant field with the same step-index gradual shifts down as the temperature increases; an interesting phenomenon. In Fig. 1, shaded regions exhibit the high spin theory with quartic anisotropy.\textsuperscript{13–15} Actually, a lot of fine structures from the tunneling of excited states are within the shaded regions. The temperature shift of resonant fields is considered as the transitions among the fine structures, which arise from the quartic anisotropy.\textsuperscript{13–15} As shown in Eq. (3), the mean field can also shift the resonant field values. We took the magnetization, i.e., $M_z$ or $\langle S_z \rangle$, from experimental data of the step hysteresis loops (e.g., Fig. 2) and used a $\beta$ as an adjustable parameter to fit the temperature dependence of the resonant fields. We found that the best fitting value of $\beta$ is 0.006 K for our molecules (Fig. 2). This value is rather small when compared with $D$ used in both systems, and the maximum of induced mutual interaction is about 40 mT which is the same order of magnitude as the dipolar interactions reported for the $S=10$ system.\textsuperscript{6} Since the expectation values of $\langle S_z \rangle$ can possibly vary from $-S$ to $S$, the largest shift of the resonant fields is about 0.072 T for the $S=9$ system. It about 1/6 of the interval of the resonant field, $\Delta H = 0.454$ T (Fig. 2). The precision of magnetization measurement in our system is around $10^{-5}$ emu and the uncertainty of the estimated mean field interaction is therefore less than $10^{-6}$ T. It is noteworthy that all the calculated data for both our $S=9$ and $S=10$ systems use a single $\beta$ value, implying that $\beta$ is a fixed parameter, e.g., the geometric factor of the sample. However, since our sample is microcrystalline, it is not easy to determine their crystal shape and thus the geometric factor independently.

Figure 3 shows the fine structures in the $n=2$ resonant field with the quartic anisotropy and the mean-field interaction. While temperature increases, both the gradual decrease and the sudden change of the resonant fields had been previously attributed to the quartic anisotropy induced excited-states tunneling.\textsuperscript{13–15} Additionally in Fig. 3 the decrease could also be interpreted as magnetization relaxation with our mean field model. Indeed, from Eq. (6), with the appropriate material constants two different mechanisms both give the correct order of magnitude correction to explain the shift of resonant fields. However, several features can only be addressed within the mean field model related to the resonant fields. When the applied field is reversed then the high-spin molecules, initially at the state $\langle S_z \rangle = -S$, will transit to other states and the mean value $\langle S_z \rangle$ moves from $-S$ to $S$ at thermal equilibrium. Therefore, for a positive $\beta$ the resonant field shifts upward at negative $\langle S_z \rangle$ and shifts downward at positive $\langle S_z \rangle$. Indeed, we do observe that at the same tem-

\[ \Delta H_m = \frac{2B}{\beta(S_z^2)} \left( u - \frac{n^2}{2} + \frac{n^2}{4} \right), \]

so that at a small step-index, the mean field correction always dominates, especially at ground state, i.e., $n=0$.

Mutual interactions in high-spin molecules can be due to hyperfine interactions or dipolar interactions.\textsuperscript{9} It is quite reasonable to estimate the mean field strength from the demagnetization field which is

\[ H_d = -\vec{N} \cdot \vec{M}, \]

where $N$ is a tensor and $M$ is the total magnetic moment of the high-spin molecule. If we assume the molecules to be uniformly magnetized prolate spheroids, then the demagnetization field can be simplified as $H_d = -(N_e - N_z)M_z$. Therefore, at least the order of magnitude of the $\beta$ in our mean field term can possibly be estimated from the shape of the molecular crystal.\textsuperscript{10,11}

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temperature the resonant fields really move downward of large \( H_z \) (positive \( \langle S_z \rangle \)) and upward of small \( H_z \) (negative \( \langle S_z \rangle \)) (Fig. 2). Besides the shift of the resonant field at a specific temperature, we also note that the resonant fields deviate from the standard value of \( nD = g \mu_B \) in a quite different way as the temperature varies. The \( n \)th resonant field gradually decreases as the temperature increases (Fig. 3). This might be because the high temperature results in a large transition rate.\(^{16}\) Therefore, for the same \( n \)th resonant field, the mean value \( \langle S_z \rangle \) moves from \(-S\) to \( S\) rather quickly at a high temperature; the mutual interaction is larger for a low temperature at the same applied field sweep rate. In zero field, on the other hand, the resonance field only shifts upward for positive saturated magnetization. Even though the shift of the resonant field can also be attributed to the quartic anisotropy term,\(^{6}\) the reduction of the resonant fields is still unclear since it should always shift upward. The energy spectrum of the \( S = 10 \) system clearly shows that the resonant fields shift distinctly at different temperature for two mechanisms. A transverse field will produce similar results as the temperature increases. According to Eq. (3), a large change of \( \langle S_z \rangle \) yields a particularly significant shift in the resonant fields. Even though we do not observe the reported abrupt jump of the resonant fields at 2 K in \( n = 1,^{16} \) the reported jump of resonant fields above 2 K may be due to dramatic changes in mutual interactions and magnetization.

In summary, our analysis not only elucidates the origin of the temperature dependence of the resonant fields but also clarifies the respective roles of the high-order anisotropy and interaction fields. We have manufactured two different \( \text{Mn}_{12} \) based samples, and found that the temperature dependence on the shift of the fields in \( S = 9 \) and \( S = 10 \) system are quite similar. We do not observe a spin parity effect, i.e., whether \( S \) is even or odd, in the temperature shift of resonant fields. We have successfully explained the shift of the resonant fields in different step index and its temperature dependence from the mean field model. The abrupt change of the resonant field in the same step index can be understood from the tunneling nature of the magnetization when temperature changes. We have also successfully used the mean-field interaction model to explain the upward shift of small step-index resonant fields and downward shift of large step-index resonant fields at the same temperature. The best fitting of the experimental data gives a 40 mT mutual interaction strength which is in the same order of magnitude as the dipolar interaction strength reported for \( S = 10 \) molecules.\(^{5}\) This is strong evidence that mutual interactions play an important role during the tunneling process, the additional evidence being the phenomenon of square-root decay.\(^{7}\) It should be noted that the shift of the resonant fields due to the mean field can be observed at any temperature. This shift, due to the quartic anisotropy, can only be identified at a very low temperature with a small step index, since possible overlapping of a different resonant fields step index (Fig. 1). However, both the anisotropy shift and the mean-field shift of the resonant field are of the same order of magnitude, around 1 K, and further work therefore needs to be done to differentiate between them.

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