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Non-exponential relaxation and the distribution of the second-order transverse anisotropic parameters in Mn_{12}

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Abstract. The Landau-Zener multi-crossing relaxation in Mn_{12} molecule is studied based on the tunnel splitting obtained from the spin-coherent-state path integral including the local stray field. It is found that the spins with larger second-order transverse anisotropic parameters will finish the relaxation before the higher resonance is reached. Such a pre-relaxation seriously modifies the relaxation behavior at higher resonance and makes the distributions of the second-order transverse anisotropic parameters extracted from different resonances un-scaled. Our analysis shows that scaled distributions can be found from the relaxation curves of $k = 6$ and $k = 7$ resonance by including the effect of pre-relaxation.

PACS. 75.45.+j Macroscopic quantum phenomena in magnetic systems – 75.50.Xx Molecular magnets

Since the first signature of quantum effect (i.e., the so-called quantum steps) was observed in the hysteresis loop of single-molecule magnet(SMM) Mn_{12} acetate [1,2], such a SMM has raised intense interesting in the field of molecular magnetism. However, the origin of the tunnel splitting in Mn_{12} acetate is still far from being absolutely clear. The main controversy comes from the origin of the second-order transverse anisotropy which plays an important role in quantum tunnelling in Mn_{12} acetate. Chudnovsky and Garanin have suggested a distribution of the second-order transverse anisotropy due to the crystal dislocations [3], and gained experimental support from the electronic paramagnetic resonance (EPR) and other experimental measurements [9–11]. Recently, Cornia et al. suggested that the disorder of solvent molecules in Mn_{12} acetate is the origin of the second-order transverse anisotropy [4] and del Barco et al. shown there is not strict tetragonal symmetry in Mn_{12} acetate [7]. The solvent-disorder theory was confirmed by some recent experiments using the higher quality of the deuterated crystal [5,6,8] and also some further theoretical works were done [12]. The first evidence of the distribution of the second-order transverse anisotropic parameters in magnetic relaxation is the non-exponential behavior which comes from a distribution of tunnel splitting. As a matter of fact, it has been shown that the random local stray field raising from the environmental spins can lead to a distribution of tunnel splitting and non-exponential relaxation in Fe_8 [15], but in Mn_{12} acetate, the distribution of tunnel splitting is much broader [6,9] and hence should come mainly from the distribution of second-order transverse anisotropic parameters, but the random local stray field as well. In a recent experimental analysis [6], the distribution of the second-order transverse anisotropic parameters $P(E)$ is extracted from the relaxation curve based on the tunnel splitting obtained from the perturbation theory [3]. However, the extracted distributions $P(E)$ for different resonances (say, $k = 6$ and $k = 8$) *do not* overlap (scale). The result looks physically unreasonable since the distribution $P(E)$ should be independent of the resonance index. This is the motivation of the present paper. We present a detail analysis on the way of extracting $P(E)$ from the relaxation curve basing on the result obtained from the spin-coherent-state path integral with the random local stray field. It is shown that the spins with larger second-order transverse anisotropic parameters will finish relaxation before the higher order resonance is reached. This pre-relaxation makes both the distribution center and width of $P(E)$ become smaller for higher order resonance. By including the effect of pre-relaxation, the extracted distributions of the second-order transverse anisotropic parameters for $k = 6$ and $k = 7$ do overlap (scale) very well.

Up to the second-order anisotropy, the Hamiltonian of the Mn_{12} acetate molecule is given by

$$H = -DS_z^2 + E(S_x^2 - S_y^2) - g\mu_B \mathbf{S} \cdot (\mathbf{B} + \mathbf{h}), \qquad (1)$$

where $D = 0.5483$ K [6,8,9], $\mathbf{B}$ is the applied magnetic field, and $\mathbf{h}$ is the local stray field which may originate from the interactions between the giant spin and the environmental spins (including other giant spins or nuclear spins) [17] and also the misalignment (or the tilt) of the easy axis in Mn_{12} acetate molecule as the longitudinal field

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is applied [6,8,9]. Due to the crystal dislocation or the solvent disorder, the second-order transverse anisotropic parameter E has a random distribution $P(E)$ which can be chosen as a Gaussian [6,8]

$$P(E) = (2\pi w^2)^{-1/2}\ e^{-(E-E_0)^2/2w^2}. \tag{2}$$

Our main interest is the Landau-Zener multi-crossing relaxation which is done by sweeping the longitudinal field at a constant rate $\alpha = dB_z/dt$ over a resonance for many times [8,9], a method firstly developed to measure the ground state tunnel splitting in Fe$_8$ [13,14]. For a given E, the relaxation equation is

$$\frac{dM}{dn} = -MP_{LZ}, \tag{3}$$

where n is the time crossing the resonance, P_{LZ} is the Landau-Zener transition rate and in low transition rate limit is given by

$$P_{LZ} = 1 - e^{-a_k \Delta_k^2(E,\mathbf{h})/\alpha} \simeq a_k \Delta_k^2(E,\mathbf{h})/\alpha, \tag{4}$$

where $a_k = \pi/[2\hbar g\mu_B(2S-k)]$, k is the index of the resonance (i.e., $|S_z = -S\rangle \leftrightarrow |S_z = S-k\rangle$), and $\Delta_k^2(E,\mathbf{h})$ is the tunnel splitting including the local transverse stray field

$$\Delta_k^2(E,\mathbf{h}) = \Delta_{k0}^2(E)\gamma_k(E,\mathbf{h}), \tag{5}$$

$\Delta_{k0}^2(E)$ can be found by the spin-coherent-state path integral with the instanton method [16,17] and the renormalization factor $\gamma_k(E,\mathbf{h}) = \left\{\cosh[2q(E)h_y] + (-1)^{2s-k}\times \cos[2d_k(E)h_x]\right\}/2$ with $\lambda = (D-E)/(D+E)$,

$$q(E) = g\mu_B\pi\sqrt{\lambda}/[2(D-E)(1-\lambda)^{1/2}], \tag{6}$$

$$d_k(E) = \frac{g\mu_B}{2(D+E)}\int_0^\pi \frac{d\phi}{1-\lambda\sin^2\phi - k\frac{D}{2(D-E)s^2}\cos\phi}. \tag{7}$$

By setting $M(n\to\infty) = M_{eq}$ and $M(n=0) = M_0$, the solution of equation (3) is

$$R_k = \frac{M_n - M_{eq}}{M_0 - M_{eq}} = \int P(E)dE \times \int W(\mathbf{h})d\mathbf{h}\exp\{-a_k(n/\alpha)\Delta_{k0}^2(E)\gamma_k(E,\mathbf{h})\}, \tag{8}$$

where $W(\mathbf{h}) = W(h_x)W(h_y)$ represents the distribution of the transverse local stray field. In the present case, since the amplitude of the sweeping field is much larger than the strength of the local stray field and n is much larger than 1 [8,14], we can approximately ignore the variation of the distribution center and width with the magnetization and $W(h_i)(i = x, y)$ will be chosen as a Gaussian with a fixed distribution center h_0 and width σ [15,18–21].

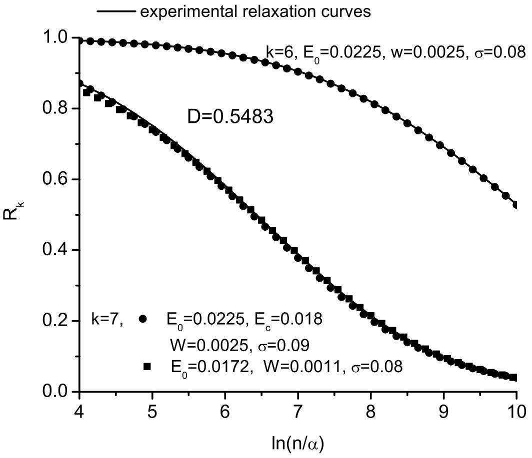

Fig. 1. Illustration of fitting the experimental relaxation curves for $k = 6$ and $k = 7$. The solid line is the experimental result from Figure 2a in reference [6], scatters are result from equation (8) using different schemes discussed in the text with distribution parameters of $P(E)$ and $W(\mathbf{h})$ shown in the figure.

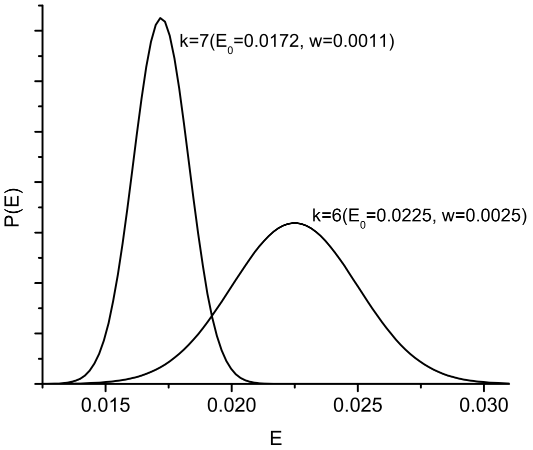

Fig. 2. The unscaled distribution of the second-order transverse anisotropic parameters extracted from the relaxation curves using a complete Gaussian distribution.

Using equation (8), the experimental relaxation curves for $k = 6$ and $k = 7$ resonance can be fitted by choosing appropriate distribution center and width of $P(E)$ and $W(\mathbf{h})$. It is found that, for $k = 6$ resonance, the relaxation curve can be best fitted by taking $E_0 = 0.0225$ K, $w = 0.0025$ K, $\sigma = 0.08$ T and $h_0 = 0$ [22], while for $k = 7$, the corresponding parameters are: $E_0 = 0.0172$ K, $w = 0.0011$ K, $\sigma = 0.08$ T and $h_0 = 0$. The fitted relaxation curves and the extracted $P(E)$ are shown in Figures 1 and 2. Here we get the same problem as that of the experimental analysis [6] based on the result from the perturbation theory, that is, the $P(E)$ extracted from $k = 6$ and $k = 7$ relaxation curve do not overlap (scale). It is seen that both the distribution center E_0 and width w decrease as k increases. del Barco et al. attributed this problem to "*the origin of the tunnel splitting cannot only be due to a second-order transverse anisotropy*" [6]. We have checked this point by comparing the tunnel splitting obtained from numerical diagonalization with the distribution center of tunnel splitting extracted from the experimental relaxation curves for $k = 6$ and $k = 8$ resonance (see Fig. 2b in Ref. [6]). It is found that the inclusion of the higher order term like $C(S_+^4 + S_-^4)$ does not help to solve the problem, for example, by omitting the local stray field, numerical diagonalization of the Hamiltonian

$H + C(S_+^4 + S_-^4)$ with $D = 0.5483$ K, $E = 0.0045$ K and $C = 2.2 \times 10^{-5}$ K [23] tells that $\Delta_6 \simeq 4.654 \times 10^{-8}$ K which is very closed to the experimentally extracted distribution center of $k = 6$ (i.e., 4.571×10^{-8} K), while the corresponding $\Delta_8 \simeq 4.632 \times 10^{-5}$ K is nearly 2 orders larger than the extracted distribution center of $k = 8$ (i.e., 8.511×10^{-7} K). On the other hand, recent experiment suggested that the second-order transverse anisotropy should be the main contribution to quantum tunnelling in Mn_{12} acetate molecule [7]. Consequently some important elements must have been ignored in extracting $P(E)$ from the relaxation curve for $k > 6$ resonance.

The physical origin is that the initial state of the $k = 7$ resonance is different from that of $k = 6$ resonance. Let us scrutinize the experimental process [6,8], starting from the negative saturated magnetization, the system is brought to the resonance by sweeping the field to the positive resonant field and relaxation under a sweeping field is measured. Experimental data shows there is not observable magnetization relaxation before $k = 6$ resonance is reached [6,8], approximately the relaxation due to the quantum tunnelling of $k < 6$ resonances can be omitted, hence the relaxation of $k = 6$ resonance can be considered as contributed by the complete $P(E)$. For $k = 7$ resonance, however, the relaxation due to quantum tunnelling as the field swept over the $k = 6$ resonance leads to an obvious magnetization step (see Fig. 16 in Ref. [8]) which has important sequence. It is known that the spins with larger E have larger tunnel splitting and thus higher Landau-Zener transition rate. This implies that some spins with larger E have finished quantum tunnelling before the measurement of relaxation for $k = 7$ resonance begins. In other words, the measured relaxation curve of $k = 7$ resonance is not contributed by the complete $P(E)$, but by an in-complete $P(E)$ with some larger E being cut. Accordingly, the $P(E)$ contributed to the relaxation of $k = 7$ resonance can be expressed as

$$P(E) = \begin{cases} C(2\pi w^2)^{-1/2}\ e^{-(E-E_0)^2/2w^2}, & E \leq E_c, \\ 0, & E > E_c, \end{cases} \tag{9}$$

where C is the re-normalization factor to assure that $\int_{E \leq E_c} P(E)dE = 1$, E_0 and w are the same as extracted from relaxation curve of $k = 6$ resonance. In this way, it is found that the relaxation curve of $k = 7$ resonance can be best fitted by taking $E_0 = 0.0225$ K, $w = 0.0025$ K, $E_c = 0.018$ K, $\sigma = 0.09$ T and $h_0 = 0$. The result of fitting for $k = 7$ relaxation curve is shown in Figure 1 and the extracted $P(E)$ is shown in Figure 3. The increase of the distribution width of $W(\mathbf{h})$ is easy to understand since $\mathbf{h}$ includes contribution from the misalignment of the easy axis, which will increase as the applied longitudinal field increases.

By considering the pre-relaxation happened before the $k = 7$ resonance is reached, the extracted $P(E)$ from $k = 6$ and $k = 7$ resonance do overlap (scale) very well. However, as one can see form Figure 3, the value of E_c seems to be smaller than the expected one. Physically E_c can be determined from the pre-relaxation happened in $k = 6$ resonance. Suggest that the pre-relaxation can be *effectively* represented as sweeping over the $k = 6$ resonance for n_1 times, then E_c can be found approximately by [15]

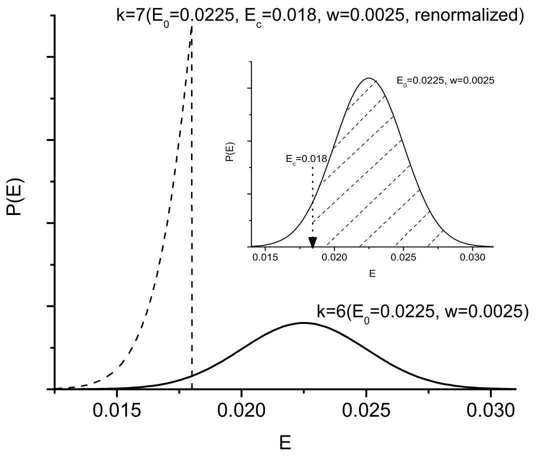

Fig. 3. The scaled distribution of the second-order transverse anisotropic parameters extracted from the relaxation curves using a complete Gaussian distribution ($k = 6$) and a cut-off Gaussian distribution ($k = 7$). The inset shows the scaled distributions in un-renormalized case and the shade area represents the pre-relaxation part.

$$P_{LZ}(E_c, k = 6, \alpha) \simeq \frac{a_6}{\alpha} \int W(\mathbf{h}) d\mathbf{h} \Delta_6^2(E_c, \mathbf{h}) = 1/n_1. \tag{10}$$

Now we show the way to find out n_1. According to equation (3), one can safely set $M_{eq} = 0$ [24] and we know that $M_i = 1$ for $k = 6$, this implies that $R_6 = M_n(k = 6)$, namely R_6 just represents the magnetization. Since the magnetization is continuous for crossing from $k = 6$ to $k = 7$, we have

$$M_i(k = 7) = M(n_1, k = 6), \tag{11}$$

alternatively speaking, n_1 can be found from the relaxation curve of $k = 6$ resonance provided that the initial magnetization of $k = 7$ resonance is known. Although the experimental data for $M_i(k = 7)$ is not available, one can approximately estimate it from the relaxation curve in the low transition rate limit. Low transition rate means that sweeping over the $k = 7$ resonance 1 time does not lead to observable change of the magnetization, this implies that $M_i(k = 7) \simeq M(k = 7, n = 1)$. For fitting the relaxation curve, this approximation is reasonable since the main contribution of the relaxation curve is from $n > 1$. As illustrated in Figure 4, if we take $\alpha = 3.33 \times 10^{-3}$ T/s, we have $n_1 \simeq 8$, then one can find out from equation (10) that $E_c \simeq 0.0207$ using the tunnel splitting formula in equation (5). However, if we take $\alpha = 1.33 \times 10^{-2}$ T/s, then $n_1 \simeq 148$, the estimated E_c is 0.01825 which is very closed to what we have found (i.e., $E_c = 0.018$). As a conclusion, we can say that the extracted $P(E)$ of $k = 7$ resonance shown in Figure 3 is reasonable.

We have presented a detail analysis on extracting the second-order transverse anisotropic parameters $P(E)$ from the relaxation curve in Mn_{12} acetate molecule. It is found that the pre-relaxation of the spins with larger E before the relevant resonance point is reached will lead to

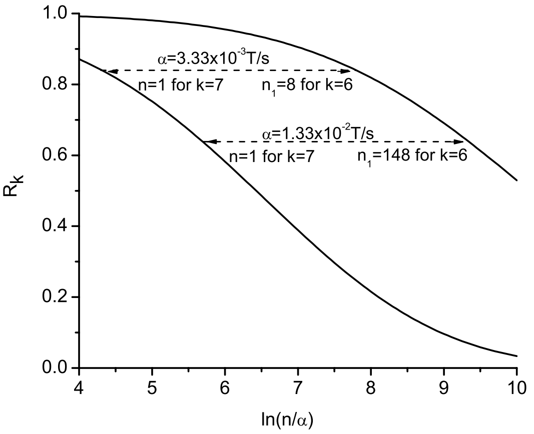

Fig. 4. Illustration of how to find n_1 from the relaxation curves under the low transition rate approximation.

so-called "E-cutting" effect, namely, the extracted $P(E)$ of higher resonance has lower distribution center and narrower distribution width. This result implies that, in a rigorous way, the exact $P(E)$ can only be extracted from the relaxation curve of the $k = 0$ resonance, which is almost impossible due to the extremely low transition rate in Mn_{12} acetate molecule. It should be noted that such an "E-cutting" effect is an important element when the relaxation of higher resonance is considered. As one can see from Figure 4, the "E-cutting" effect is so serious that the dynamical property of different resonances are controlled by qualitatively different distributions $P(E)$ though we are measuring the same sample. This implies that $P(E)$ extracted for $k > 6$ resonance is not reliable in Mn_{12} acetate molecule.

Although we are able to extract the scaled $P(E)$ from the relaxation curves of different resonances, the origin of the $P(E)$ is not very clear. The extracted distribution center of $k = 6$, $E_0 = 0.0225$ K, is very closed to $E = 22$ mK, the prediction of dislocation theory for a concentration of dislocation per unit cell of $c = 10^{-3}$ [10]. However, as pointed out in the experimental analysis [6], the relaxation curve cannot be fitted according to the dislocation theory which predicts $\langle E\rangle = 0$, we get the same conclusion using the scheme proposed in the present paper. We have also tried to fit the relaxation curve based on the solvent-disorder theory, i.e., by adapting a discrete distribution of E. To do this, equation (8) is re-written as

$$R_k = \sum_{i=1}^{3} b_i \int W(\mathbf{h}) d\mathbf{h} \exp\left\{-a_k(n/\alpha)\Delta_{k0}^2(E_i)\gamma_k\left(E_i, \mathbf{h}\right)\right\}, \tag{12}$$

where b_i is the weight factor which is taken to be proportional to the measured population of its corresponding isomers [4,6,12], i.e., $b_1 : b_2 : b_3 = 0.5 : 1 : 0.25$ with $E_1 < E_2 < E_3$. It is found that the relaxation curve of $k = 6$ can be fitted by taking $E_1 = 0.01$ K, $E_2 = 0.0239$ K, $E_3 = 0.0283$ K, $\sigma = 0.06$ T and $h_0 = 0$. By including the random local stray field, the relaxation curve can be fitted by 3 δ-functions. However, we find that it is impossible to fit the relaxation curve with the condition $E_3 = 2E_2$ which is the prediction of solvent-disorder theory and the extracted E's value are also larger than the prediction [4,12]. Probably the origin of the second-order transverse anisotropic parameters is a "mixed result", i.e., both dislocation and disorder contribute to the distribution [6], but further analysis is necessary for confirming this point.

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