Quantum tunneling of magnetization in Fe-substituted Mn_{12} studied by ac magnetic susceptibility

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Quantum tunneling of magnetization (QTM) in an Fe-substituted single molecular magnet Mn_{11}Fe has been studied by ac susceptibility measurements in $\text{Mn}_{11}\text{Fe}/\text{Mn}_{12}$ mixed crystal. Although the blocking temperature of the Mn_{11}Fe is lower than 2 K, a tunneling peak at a static magnetic field of 6 kOe was observed in the ac susceptibility with a suitable ac frequency (9873 Hz) at 5 K. This work also elucidates a way to choose the proper ac frequency to observe the QTM at a relatively higher temperature ($T > T_B$).

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I. INTRODUCTION

Mn_{12} is the one of the single-molecule magnets (SMMs) studied most widely and fruitfully since quantum tunneling of magnetization (QTM) was found in the experiments.^{1–3} It consists of an outer ring of eight ferromagnetic coupling Mn^{3+} ($S=2$) ions and an inner tetrahedron formed by four ferromagnetic coupling Mn^{4+} ($S=3/2$) ions. The antiferromagnetic coupling between the Mn^{3+} ions and the Mn^{4+} ions results in the ground state with a total spin $S=10$.^{4–7} The strong uniaxial magnetic anisotropy leads to a potential of 61 K between the up and down spin states, which is related to a blocking temperature $T_B=3$ K.⁷ At the temperature $T < T_B$, the measurements of the hysteresis loops and time relaxation are usually used to study the QTM.^{1–3,8} At the temperature $T > T_B$, the measurements of ac susceptibility can be employed to observe the thermally assisted QTM.⁹

Mn_{12} variations provide an opportunity to extensively study the QTM. One popular way is to replace the acetic acid or water molecules with other solvent molecules.^{10,11} In fact, due to changing interactions of the core ions, ion substitution for Mn ions is more direct and effective to modulate the QTM. Recently, the QTM of Mn_{12} with Cr substitution has been reported and quite different tunneling properties from that of Mn_{12} were found.^{12,13}

In our previous work,¹⁴ we have investigated the structure and some magnetic properties of Fe-substituted Mn_{12} : $[\text{Mn}_{11}\text{FeO}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}(\text{Mn}_{11}\text{Fe})$.¹⁴ Mn_{11}Fe has almost the same crystallographic structure as Mn_{12} except that one Mn^{3+} ion is replaced by one Fe^{3+} . But the QTM in Mn_{11}Fe was not found because of the inaccessible low blocking temperature ($T_B < 2$ K) in our measurements. In this paper, we elucidated an effective way to examine the QTM at the higher temperature ($T > T_B$) using ac susceptibility measurements and observed the QTM of Mn_{11}Fe in the $\text{Mn}_{11}\text{Fe}/\text{Mn}_{12}$ mixed crystal.

II. EXPERIMENT

The Fe-substituted Mn_{12} was synthesized through the reaction of $\text{Fe}(\text{CH}_3\text{COOH})_2$, $\text{Mn}(\text{CH}_3\text{COOH})_2$, and KMnO_4 at the temperature $T=60^\circ\text{C}$, which follows a modification of the procedure provided by Lis.¹⁵

The crystals from the same batch of the sample with the Fe ion content $6.00\% \pm 0.03\%$ among all metal ions were selected for our studies. The measured crystal has a size of about $1.5 \times 0.3 \times 0.3$ mm. Our previous work has shown that the sample consists of Mn_{11}Fe and Mn_{12} with a molar ratio of 2.58:1.¹⁴ In addition, the corresponding measurements were also carried out on the pure Mn_{12} single crystal with a size of $2.8 \times 0.5 \times 0.5$ mm for comparison.

The ac susceptibilities were measured as functions of temperature and magnetic field at the different frequencies using a Quantum Design physical property measurement system (PPMS-14T). The system has the highest dc magnetic field of 14 T and the operating temperature range from 1.8 to 400 K for magnetic measurements. The ac frequency and amplitude range from 10 to 10^4 Hz and from 1 to 16 Oe, respectively. The dc and ac magnetic field were both applied along the c axis of the crystal. The angle between the easy axis and the field direction was estimated to be less than 5° .

III. RESULTS AND DISCUSSION

The temperature-dependent magnetization was measured on the mixed crystal at the applied magnetic field $H=100$ Oe. The results are displayed in Fig. 1. The zero-field-cooled (ZFC) curve shows a peak at temperature $T=3$ K,

FIG. 1. Magnetization of the $\text{Mn}_{11}\text{Fe}/\text{Mn}_{12}$ mixed crystal as a function of temperature at applied magnetic field $H=100$ Oe. Closed and open circles represent the ZFC curve and the field-cooled (FC) curve, respectively. The inset shows experimental (open circles) and fitted (solid line) hysteresis loop at $T=2$ K.

which agrees well with the blocking temperature of Mn_{12} . The magnetization does not decrease monotonously at $T < 3$ K for the existence of the other phase Mn_{11}Fe . We know that the blocking temperature of Mn_{11}Fe is lower than 1.8 K from Fig. 1. At an accessible temperature, only the QTM of Mn_{12}^* (represents the Mn_{12} in the mixed crystal) could be observed. Consequently the hysteresis loop of the Fe-substituted Mn_{12} at $T=2$ K includes a hysteresis loop of Mn_{12}^* and a superparamagnetic magnetization curve of Mn_{11}Fe , which is shown by the inset in Fig. 1. It is obvious that the fitted curve coincides well with the experimental measurement.

Since Mn_{11}Fe shows the superparamagnetism at the accessible temperature, the observation of the QTM needs to employ ac susceptibility measurements. Pohjola and Schoeller calculated the dynamic susceptibility $\chi_{ac}(H, T, \omega)$ in detail.¹⁶ Considering the high frequency limit, the frequency-dependent ac susceptibility can be written as follows:

$$\chi_{ac}(H, T, \omega) = \chi_{hf}(H, T) + \frac{\chi_0(H, T) - \chi_{hf}(H, T)}{1 - i\omega\tau(H, T)}, \quad (1)$$

where ω is the angular frequency with the relation to the frequency ν as $\omega = 2\pi\nu$. Arrhenius' law suggests the relaxation time

$$\tau = \tau_0 \exp\left[\frac{U(H)}{K_B T}\right], \quad (2)$$

where $U(H)$ is the potential barrier for thermal activation. For uniaxial magnetic anisotropy, it is given by⁹

$$U(H) = U_0 \left[1 - \frac{H}{H_0}\right]^2. \quad (3)$$

Here U_0 is the magnitude of the classical potential barrier in zero field and H_0 is the critical field at which the potential barrier becomes zero.

At the low-frequency limit $\omega\tau \ll 1$ the ac susceptibility χ_{ac} tends to be the isothermal equilibrium susceptibility χ_0 . The χ_0 can be obtained by differentiating the magnetization curve. At the high frequency limit $\omega\tau \gg 1$ the χ_{ac} tends to be the χ_{hf} .

For practical purposes, the χ_{ac} is usually divided into the real and imaginary components as

$$\chi' = \chi_{hf} + (\chi_0 - \chi_{hf}) \frac{1}{1 + (\omega\tau)^2}, \quad (4)$$

and

$$\chi'' = (\chi_0 - \chi_{hf}) \frac{\omega\tau}{1 + (\omega\tau)^2}, \quad (5)$$

respectively.

According to Eq. (5), the χ'' approaches its maximum when the relaxation time τ is equal to the inverse of the angular frequency ω . Thus the temperature-dependent χ'' can give a series of maxima at the different frequencies. The temperature at the maximum and the corresponding relaxation time ($\tau = \omega^{-1}$) satisfy the Arrhenius' law [see Eq. (2)],

FIG. 2. Real part (a) and imaginary part (b) of susceptibility of the mixed crystal as a function of temperature. Squares, circles, and triangles correspond to the frequencies 34, 500, and 9000 Hz, respectively. The inset displays the results fitted by Arrhenius' law. Open and closed squares correspond to Mn_{12}^* and Mn_{11}Fe , respectively.

which can be used to determine the potential barrier U and the relaxation time prefactor τ_0 .

Figure 2 plots the temperature-dependent susceptibility at the ac magnetic field of 10 Oe applied along the c axis of the crystal. At the different frequencies $\nu = 34, 500$, and 9000 Hz, all the χ'' show two out-of-phase peaks. In fact, the double peaks correspond to different magnetic anisotropy related to two blocking temperatures. The out-of-phase peaks at the relatively higher temperature have the same positions with that of Mn_{12} at each corresponding frequency, and were concluded to be contributed by Mn_{12}^* . While the peaks at the lower temperature are speculated to origin from Mn_{11}Fe . Applying the Arrhenius law to fit for these two peaks, respectively, the relaxation time constants and the potential barriers were obtained [see the inset in Fig. 2]. Mn_{11}Fe has a lower potential barrier of 42.6 K than 68.6 K of Mn_{12}^* . Although the potential barrier of 68.6 K coincides well with that of pure Mn_{12} ,⁷ it was noted that Mn_{12}^* has a smaller relaxation time constant τ_0 than that of pure Mn_{12} ,⁷ which has also been seen in Mn_{12} with Cr substitution.¹²

For classical thermally activated relaxation, the potential barriers decrease monotonically with the applied magnetic field H_z increasing.⁹ For QTM systems, the tunneling leads to a series of potential barrier minima at the tuning field H_n , which correspond to the steps of the hysteresis loops. So these minima are also the evidence of the QTM. At the non-zero field H_z the temperature-dependent relaxation time still follows the Arrhenius law,⁹ and consequently the same methods could be used to examine the field-dependent potential barrier and relaxation time. The magnetic field was applied along the c axis of crystal at $T=10$ K to ensure that all the measurements would be carried out at the equilibrium state. The ac susceptibilities were measured at the temperature from 10 K down to 2 K. The field-dependent potential barrier curves $U(H)$ of Mn_{12}^* and Mn_{11}Fe were derived from the Arrhenius' law fitting [see Figs. 3(a) and 3(c)]. There are two minima at field $H_0=0$ kOe and $H_1=4$ kOe for Mn_{12}^*

FIG. 3. Field-dependent potential barriers and at $T=5$ K field-dependent relaxation time of Mn_{12}^* and Mn_{11}Fe .

[see Fig. 3(a)], which coincides with the tuning field interval $\Delta H=4.4$ kOe given by the hysteresis loops from the inset in Fig. 1 (the difference is caused by the different magnetization states of the sample).⁸ For Mn_{11}Fe , there exists a different field interval $\Delta H=6$ kOe [see Fig. 3(c)], which means that Mn_{11}Fe has a stronger magnetic anisotropy.

According to the experimental $U(H)$ and τ_0 , relaxation time τ could be determined at a given temperature by Eq. (2). Figures 3(b) and 3(d) show the field-dependent relaxation time of Mn_{12}^* and Mn_{11}Fe at $T=5$ K, respectively. The relaxation time also has a sharp drop at the tuning field H_n . From Eqs. (4) and (5), it can be found that the drops would lead to the maxima or minima of the field-dependent ac susceptibility. As the monotonous function of the relaxation time, the χ' approaches its maximum, which we denote as the tunneling peak, at the tuning field H_n . Although the χ'' is nonmonotonous, there still exists the tunneling peak when $\omega\tau > 1$ or $\omega\tau < 1$ for all values of τ . All the peaks are the same direct evidence of the QTM as the steps in the hysteresis loop. To observe these tunneling peaks, the QTM-induced change of susceptibility should be large enough.

We define the ratio of the classical relaxation τ_c to the QTM-induced relaxation minimum by γ , the change of the χ' and χ'' could be written as follows:

$$\Delta\chi' = \chi_T \frac{(\gamma^2 - 1)(\omega\tau_c)^2}{[\gamma^2 + (\omega\tau_c)^2][1 + (\omega\tau_c)^2]}, \quad (6)$$

and

$$\Delta\chi'' = \chi_T \frac{(\gamma - 1)(\omega\tau_c)[(\omega\tau_c)^2 - \gamma]}{[\gamma^2 + (\omega\tau_c)^2][1 + (\omega\tau_c)^2]}. \quad (7)$$

Here $\chi_T = (\chi_0 - \chi_{hf})$ is independent of the frequency. The χ_T only is the function of the field H at a certain temperature T . It can be easily deduced from Eqs. (6) and (7) that the $\Delta\chi'/\chi_T$ approaches its maximum when $(\omega\tau_c)^2 = \gamma$, which coincides with the condition for the zero point of the $\Delta\chi''/\chi_T$. We calculated the γ according to the field-dependent relaxation time in Fig. 3 at $T=5$ K and figured the $\Delta\chi'/\chi_T$ and

FIG. 4. Relative changes of real part $\Delta\chi'/\chi_T$ (a) and imaginary part $\Delta\chi''/\chi_T$ (b) as functions of $\omega\tau_c$ at $T=5$ K. Solid ($\gamma=16$) and dashed line ($\gamma=3$) correspond to Mn_{12}^* and Mn_{11}Fe , respectively.

$\Delta\chi''/\chi_T$ as the function of $\omega\tau_c$ in Fig. 4. For the zero-field tunneling of Mn_{12}^* , the τ_c with the $\gamma=16$ is about 0.16 s. This means that the most proper frequencies for the observation of the QTM are about 4 and 18 Hz, corresponding to the maximum of the $\Delta\chi'/\chi_T$ and $\Delta\chi''/\chi_T$, respectively. The frequency of 4 Hz exceeds the accessible frequency range ($10\text{--}10^4$ Hz) of the PPMS-14T, other observable frequencies were chosen for our measurements, which are shown in Fig. 5. We note that the field-dependent ac susceptibilities with the frequencies $\nu=18$ and 34 Hz both show two peaks near $H_0=0$ kOe and $H_1=4.0$ kOe. The peaks are more direct evidence of the QTM than the drops of the $U(H)$ obtained by the Arrhenius' law fitting. In addition, although the $\Delta\chi''/\chi_T$ approaches its maximum for Mn_{12}^* ($\gamma=16$) at $\nu=18$ Hz with a corresponding position labeled by line 2 in Fig. 4, it is less than the $\Delta\chi'/\chi_T$ at this frequency. For $\nu=34$ Hz marked by line 1 in Fig. 4, the $\Delta\chi''/\chi_T$ is larger than the $\Delta\chi'/\chi_T$. Experimental results in Figs. 5(a) and 5(b) surely prove that at $\nu=18$ Hz the zero-field tunneling peak of the $\chi''(H)$ is lower than the $\chi'(H)$, which is opposite to the situation at $\nu=34$ Hz. According to Fig. 4, the $\Delta\chi''/\chi_T$ decreases much more slowly than the $\Delta\chi'/\chi_T$ with the frequency increasing. The frequency $\nu=980$ Hz has been assumed as the limit frequency for the observation of QTM in Mn_{12}^* , but which is true only for the $\Delta\chi'/\chi_T$. At this frequency the $\Delta\chi'/\chi_T$ tends to be zero (about 2.6×10^{-4}), while the $\Delta\chi''/\chi_T$ is near 0.015, which is only about one order lower than that at $\nu=34$ Hz. As we expected, the experimental results present that although there is no tunneling peaks found in the $\chi'(H)$ curve with $\nu=987$ Hz, the $\chi''(H)$ still clearly reveals the QTM even at higher field $H_2=8.2$ kOe [see the inset in Fig. 5(c)]. Furthermore, the zero-field tunneling peak reduces by one order

FIG. 5. Field-dependent ac susceptibilities of Mn₁₂ at frequencies 17 (a), 34 (b), and 987 Hz (c). Closed and open circles represent real and imaginary part of susceptibility, respectively. The inset shows the details of imaginary part in (c) at higher field.

comparing to that at $\nu=34$ Hz, which agrees well with our former analyses.

Since the way is successful, similar measurements were used to study the characteristics of the QTM in the Mn₁₁Fe/Mn₁₂ mixed crystal. The ac susceptibilities of the mixed crystal are plotted versus the magnetic field in Fig. 6. We note that the $\chi'(H)$ and $\chi''(H)$ curves at $\nu=34$ Hz [see the inset in Fig. 6] shows the two tunneling peaks at the tuning field $H_0=0$ kOe and $H_1=4$ kOe, which agrees well with the characteristics of Mn₁₂ discussed above and confirms further the existence of Mn₁₂ in the mixed crystal. From Fig. 3 we know that the other phase Mn₁₁Fe, comparing to the Mn₁₂, has a much smaller classical relaxation time ($\tau_c=9.3 \times 10^{-5}$ s) and a smaller relaxation ratio $\gamma=3$, corresponding to the zero-field tunneling. Thus the frequency $\nu=2900$ Hz is most proper to observe the zero-field tunneling peaks for Mn₁₁Fe. Here it should be mentioned that for Mn₁₂, the tunneling peak shown by ac susceptibility with a frequency $\nu > 1000$ Hz decrease at least by two orders of magnitude comparing to that done at $\nu=34$ Hz. That is, the tunneling peaks of the mixed crystal at high frequency

FIG. 6. Field-dependent ac susceptibilities of the Mn₁₁Fe/Mn₁₂ mixed crystal at frequencies 2893 (a) and 9873 Hz (b). Closed and open circles represent real and imaginary part of susceptibility, respectively. The inset shows the characteristics of Mn₁₂* ($\nu=34$ Hz).

($\nu > 1000$ Hz) are mainly contributed by Mn₁₁Fe. Figure 6(a) displays the result with $\nu=2900$ Hz. At the field $H_0=0$ kOe, the χ' has a high tunneling peak, while the χ'' has a small drop near zero, which agrees with the theoretical expectation. The small drop means that the frequency of the measurement is a little smaller than the true most proper frequency. It is noted that the tunneling peaks at the other tuning field H_n are not distinct for $\nu=2900$ Hz. We used a high frequency of 9873 Hz that corresponds to the position labeled by line 3 in Fig. 4, and obtained a satisfying $\chi'(H)$ curve. As seen in Fig. 6(b), the expected tunneling peak is found at $H_z=6$ kOe. Besides the expected peak, we also note the other neighbor peak at $H_z=5$ kOe.

We attribute the neighbor peak to a sizable fourth-order term AS_Z^4 similar to Mn₁₂.^{8,16,17} So the spin Hamiltonian that describes Mn₁₁Fe can also similarly written as¹⁷

$$\hat{H} = -DS_Z^2 - AS_Z^4 - g\mu_B H_Z S_Z, \quad (8)$$

where D is the magnetic anisotropy constant and the AS_Z^4 is the high-order term in crystalline anisotropy, and the last term represents the Zeeman energy. The Hamiltonian determines the tuning field as follows:

$$H_z^{mm'} = \frac{n}{g\mu_B} [D + A(m^2 + m'^2)], \quad (9)$$

where $n=m+m'$ corresponds to the n th resonant tunneling. For the same n , there can be several sets of different magnetic quantum numbers m and m' , which corresponds to the field position H_n^m of the neighbor peak, i.e., the satellite peaks mentioned by Leuenberger and Loss.¹⁷ The height and line-width of the peaks are determined by the transverse field and

spin-phonon coupling. In addition, the similar satellite peaks have also been reported in Mn_{12} .⁸

IV. CONCLUSIONS

The single molecular magnet Mn_{11}Fe in the $\text{Mn}_{11}\text{Fe}/\text{Mn}_{12}$ mixed crystal has been studied by ac magnetic susceptibility measurements. Both the field-dependent potential barriers fitted by the Arrhenius' law and the tunneling peaks shown by ac susceptibility reveal the QTM in Mn_{11}Fe . The field interval of 6 kOe indicates that Mn_{11}Fe has a stronger magnetic anisotropy. The field-dependent ac susceptibility also

displays a satellite peak at $H=5$ kOe, which is attributed the quartic magnetic anisotropy AS_Z^4 . In addition, the way for checking the QTM by ac susceptibility measurements has been proved to be quite effective for studying the influence of quantum tunneling upon the magnetic relaxation in Mn_{12} and Mn_{11}Fe at $T > T_B$.

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