

Butterfly Hysteresis Loop and Dissipative Spin Reversal in the $S = 1/2$, V_{15} Molecular Complex

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Time resolved magnetization measurements have been performed on a spin $1/2$ molecular complex, so-called V_{15} . Despite the absence of a barrier, magnetic hysteresis is observed over a time scale of several seconds. A detailed analysis in terms of a dissipative two-level model is given, in which fluctuations and splittings are of the same energy. Spin-phonon coupling leads to long relaxation times and to a particular “butterfly” hysteresis loop.

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In this Letter we study the dynamics of the magnetization reversal of a molecular crystal made of nanometric molecules with noninteracting $S = 1/2$ spins. Despite the absence of energy barrier against spin reversal, this system shows hysteresis. This result is interpreted in detail assuming spin rotation in a phonon bath, which is different from the situation of large-spin molecules where only the spin bath is believed to be relevant [1–4]. Resonant phonon transitions are irrelevant, unless between states at different energies [5] or in the presence of a transverse field large enough to create a tunnel splitting of the order of the temperature energy scale [6].

The molecular complex $K_6[V_{15}^{IV}As_6O_{42}(H_2O)] \cdot 8H_2O$ (so-called V_{15}) [7] is made of molecules with fifteen V^{IV} ions of spin $S = 1/2$, placed in a quasispherical layered structure formed of a triangle, sandwiched by two hexagons. The symmetry is trigonal (space group $R\bar{3}c$, $a = 14.029 \text{ \AA}$, $\alpha = 79.26^\circ$, $V = 2632 \text{ \AA}^3$). The unit cell contains two V_{15} clusters, and it is large enough that dipolar interactions between different molecules are negligible (a few mK). All intramolecular exchange interactions being antiferromagnetic, the total spin of this molecule is $S = 1/2$. Such a small spin has zero energy barrier and relatively large splitting in zero applied field ($\sim 10^{-2} \text{ K}$). Although spin entanglement results in 2^{15} eigenstates per molecule, the magnetization curves will be interpreted in terms of a dissipative two-level model [8–10].

Time resolved magnetization measurements were performed with the micro-SQUID technique (50–400 mK, 0–0.7 T/s) [11]. In order to maximize thermal contact with the bath, we choose a sample holder made with grease and silver powder and a small crystal of the V_{15} ($\sim 50 \mu\text{m}$). As an example we give a few hysteresis loops in Figs. 1a and 2a (only the positive parts are represented, the other ones being rigorously symmetrical). When the field increases, coming from the negative saturation, the magnetization curve passes through the origin of the coordinates, reaches a plateau, and then approaches saturation. This leads to a winged hysteresis loop characterized by the absence of irreversibility near zero field. Nevertheless, the initial susceptibilities are larger the faster the sweeping field, and the magnetization is out of equilibrium also near

zero field where it appears to be reversible. The wings depend sensitively on temperature T and field sweeping rate r . In Fig. 1a, where three hysteresis loops are presented at three different temperatures for a given sweeping rate, the plateau is higher and more pronounced at low temperature. The same tendency is observed at a given temperature and faster sweeping rates (Fig. 2a). When compared to its equilibrium limit (dotted curve in Fig. 2), each magnetization curve shows a striking feature: the plateau intersects the equilibrium curve and the magnetization becomes

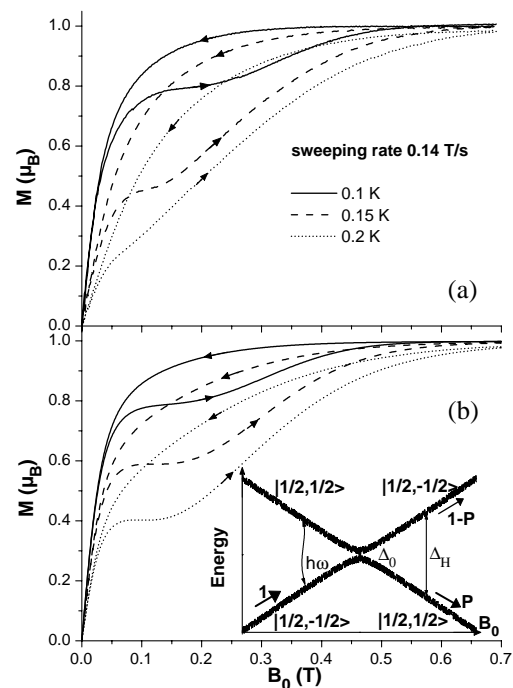


FIG. 1. (a) Measured and (b) calculated hysteresis loops for three temperatures and for a given field sweeping rate 0.14 T/s. The plateau is more pronounced at low T . The inset is a schematic representation of a two-level system $S_Z = \pm 1/2$ with repulsion due to nondiagonal matrix elements. In a swept field the switching probability P is given by the Landau-Zener formulas (see text). The two levels are broadened by the hyperfine fields and the absorption or the emission of phonons can switch the polarization state of spins.

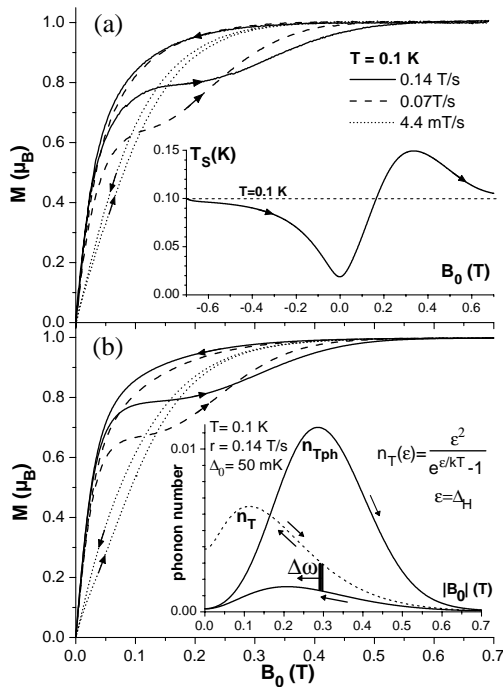


FIG. 2. (a) Measured and (b) calculated hysteresis loops for three field sweeping rates at $T = 0.1$ K. The observed plateau is more pronounced at high sweeping rate. The equilibrium curve can be approximated by the median of the two branches of the low sweeping rate hysteresis loop (dotted curve). In the inset of (a) is plotted the spin and phonon temperature $T_S = T_{ph}$ for $T = 0.1$ K and $r = 0.14$ T/s, when the field is swept from negative values. T_S decreases until zero field and then increases linearly within the plateau region. Then it overpasses the bath temperature to finally reach the equilibrium. In the inset of (b) the calculated number of phonons with $\hbar\omega = \Delta_H$ is plotted vs the sweeping field modulus (note the arrows) at equilibrium ($T_{ph} = T_S = T$, dashed line) and out-of-equilibrium ($n_{T_{ph}} = n_{T=T_S}$, $r = 0.14$ T/s, solid line). The difference between the two curves (thick segment $\Delta\omega$) suggests the moving hole in the phonon distribution, while their intersection gives the plateau intercept of the equilibrium magnetization curve.

smaller than at equilibrium. Equilibrium is then reached in higher fields near saturation.

In order to interpret this magnetic behavior of the V_{15} molecules, we will analyze how the level occupation numbers vary in this two-level system (see Fig. 1b, inset) when sweeping an external field. In the absence of dissipation, a two-level model is well described by the bare Landau-Zener model, in the adiabatic or nonadiabatic case (low or high sweeping rates). The probability for the $|1/2, -1/2\rangle \leftrightarrow |1/2, 1/2\rangle$ transition is $P = 1 - \exp(-\pi\Delta_0^2/4\hbar\mu_B r)$. In such a Landau-Zener transition, the plateaus of Fig. 2 should decrease if the sweeping rate increases, which is contrary to the experiments. Taking the typical value $r = 0.1$ T/s and the zero-field splitting $\Delta_0 \cong 0.05$ K [12–15], one gets a ground state switching probability very close to unity: in the absence of dissipation the spin 1/2 must adiabatically follow the field changes. Extremely large sweeping rates

($\approx 10^9$ T/s) would be needed to get into the quantum nonadiabatic regime $P < 1$. The mark of the V_{15} system is that the dissipative spin-phonon coupling is acting also near zero applied field because $\hbar\omega \approx \Delta_0$ is of the order of the bath temperature, which is not the case for large-spin molecules where $\Delta_0 \ll k_B T$. The spin temperature T_S is such that $n_1/n_2 = \exp(\Delta_H/k_B T_S)$, where $\Delta_H = \sqrt{\Delta_0^2 + (2\mu_B B_0)^2}$ is the two-level field-dependent separation, and $n_{1,2}$ ($n_{1,2eq}$) the out of equilibrium (equilibrium) level occupation numbers. In the magnetization curves at 0.1 K (Figs. 1 and 2a), the spin temperature is significantly lower than the bath temperature T ($n_1 > n_{1eq}$, $T_S < T$) between -0.3 T (when the magnetization curve departs from the equilibrium one) and 0.15 T (the field at which the magnetization curve intersects the equilibrium one). After this intercept T_S is larger than the bath temperature ($n_1 < n_{1eq}$, $T_S > T$), and at sufficiently high fields (about 0.5 T) it reaches the equilibrium value ($n_1 = n_{1eq}$, $T_S = T$).

In a direct process, the spins at the temperature T_S should relax to the phonons temperature within a time scale τ_1 , the phonons being at the bath temperature. However, even with a silver sample holder, it is not possible to maintain the phonon temperature equal to the temperature of the bath. This is because in V_{15} below 0.5 K, the heat capacity of the phonons C_{ph} is very much smaller than that of the spins C_S , so that the energy exchanged between spins and phonons will very rapidly adjust the phonons temperature T_{ph} to the spin one T_S . Furthermore, the energy is transferred from the spins to only those phonon modes with $\hbar\omega = \Delta_H$ (within the resonance linewidth). The number of such lattice modes being much smaller than the number of spins, energy transfer between the phonons and the sample holder must be very difficult, a phenomenon known as the phonon bottleneck [16]. Following [17], the number of phonons per molecule available for such resonant transitions is $n_T = \int_{\Delta\omega} \sigma(\omega) d\omega / [\exp(\hbar\omega/kT) - 1]$, where $\sigma(\omega) d\omega = 3V\omega^2 d\omega / (2\pi^2 v^3)$ = number of phonon modes between ω and $\omega + d\omega$ per molecule of volume V , v is the phonon velocity, and $\Delta\omega$ is the transition linewidth due to fast hyperfine field fluctuations (they broaden both energy levels) [18]. Taking the typical values $v \approx 3000$ m/s, $T \approx 10^{-1}$ K, and $\Delta\omega \approx 5 \times 10^2$ MHz, we find n_T of the order of $\approx 10^{-6}$ to 10^{-8} phonons/molecule. Such a small number of phonons is very rapidly absorbed, burning a hole of width $\Delta\omega$ in the phonon density of states at the energy $\hbar\omega = \Delta_H$ [16]. If this phonon density of states does not equilibrate fast enough, the hole must persist and move with the sweeping field, leading to a phonon bottleneck.

Now this description will be made quantitative. For a given splitting Δ_H , the time evolution of the two-level populations $n_{1,2}$ and of the phonon numbers $n_{T_{ph}}$ at T_{ph} obeys the set of two differential equations [17]: (i) $-\dot{n}_1 = \dot{n}_2 = P_{12}n_1 - P_{21}n_2$ and (ii) $\dot{n}_{T_{ph}} = -(n_{T_{ph}} - n_T) / \tau_{ph} - P_{12}n_1 + P_{21}n_2$, where $P_{12,21}$ are the transition

probabilities between the two levels (they are themselves linear functions of $n_{T_{\text{ph}}}$) and $\tau_{\text{ph}} \approx L/2v$ is the phonon-bath relaxation time (L is the sample size). Using the notations $x = (n_1 - n_2)/(n_{1\text{eq}} - n_{2\text{eq}})$, $y = (n_{T_{\text{ph}}} - n_T)/(n_T + n/2)$ with $n = \int_{\Delta\omega} \sigma(\omega) d\omega$ we get (i) $\dot{x} = (1 - x - xy)/\tau_1$ and (ii) $\dot{y} = -y/\tau_{\text{ph}} + bx$, where $b = C_S/C_{\text{ph}}$ and $1/\tau_1 = P_{12} + P_{21}$ the direct spin-phonon relaxation time. By solving numerically this system for typical values, e.g., $\tau_1 = 10^{-2}$ s, $\tau_{\text{ph}} < 10^{-6}$ s, and $b > 10^5$, we can see that $T_{\text{ph}} \rightarrow T_S \neq T$ (phonon bottleneck) very rapidly, as expected. This leads to $y = 1/x - 1$, and the second equation of the differential system becomes $\dot{x} = (x - x^2)/(1 + bx^2)/\tau_{\text{ph}}$. In the limit $b \gg 1$ (in our case $b \approx 10^8 - 10^{10}$) this equation has the solution

$$-t/b\tau_{\text{ph}} = x - x_0 + \ln[(x - 1)/(x_0 - 1)], \quad (1)$$

where $x_0 = x(t = 0)$ and $b\tau_{\text{ph}}$ is the spin-phonon recovery relaxation time ($T_{\text{ph}} = T_S \rightarrow T$). When the system is not far from equilibrium ($x \sim 1$), we get an exponential decay of the magnetization, with the same time constant $\tau_H = b\tau_{\text{ph}}$. For a spin 1/2 system [17],

$$\tau_H = \alpha \frac{\tanh^2(\Delta_H/2k_B T)}{\Delta_H^2}, \quad (2)$$

with $\alpha = 2\pi^2 \hbar^2 v^3 N \tau_{\text{ph}} / 3\Delta\omega$ (N the molecule density).

The dynamical magnetization curves calculated in this model are given in Figs. 1b and 2b. We started from equilibrium ($x_0 = 1$) in large negative fields. Then we let the system relax for a very short time δt and we calculated $x(\delta t)$ using Eq. (1). This value was taken as the initial value for the next field (the field step is $r\delta t$). The parameters have been chosen to mimic the measured curves of Figs. 1a and 2a [19]. The obtained similarity supports the possibility of the phonon bottleneck effect at the time scale of a few 0.1 s. In the Fig. 2a inset, we show the variation of the calculated spin-phonon temperature T_S for $T = 0.1$ K and $r = 0.14$ T/s. We can note a linear variation in the plateau region (small positive fields, $n_1/n_2 \approx \text{const}$), after a cooling in negative fields. The slope of this quasi-adiabatic linear region varies with the bath temperature and sweeping rate and gives the plateau dependence on these two parameters (see Figs. 1 and 2).

In the Fig. 2b inset we show the calculated field evolution of the number of phonons at energy $\hbar\omega = \Delta_H$ at equilibrium ($T_{\text{ph}} = T_S = T$, dashed line) and out of equilibrium ($n_{T_{\text{ph}}} = n_{T=T_S}$, $r = 0.14$ T/s, solid line). The difference between the two curves (thick segment $\Delta\omega$) suggests the moving hole in the phonon distribution, while their intersection gives the plateau intercept of the equilibrium magnetization curve (above which the hole disappears and $T_{\text{ph}} = T_S > T$). Let us note that in zero field the system is out of equilibrium even if magnetization passes through the origin of coordinates (without a barrier, the switch between $+1/2$ and $-1/2$ follows the level structure shown in the Fig. 1 inset). At larger fields, in the

plateau region, $n_1/n_2 \approx \text{const}$ at time scales shorter than $\tau_H = b\tau_{\text{ph}}$ [Eq. (2)], even after the plateau crosses the equilibrium curve. Equilibrium is reached when τ_H becomes small enough.

Furthermore, we measured the relaxation of the magnetization of our crystal at different fields and temperatures along the plateau region. The relaxation curves compared well to exponential decay, and the obtained relaxation times are presented in Fig. 3a. The comparison with those calculated (Fig. 3b) is acceptable. But we noted that a direct fit to Eq. (1) would necessitate larger values for α and Δ_0 ($\approx 0.4 - 0.6$ sK² and $\approx 0.2 - 0.3$ K). Note that in V_{15} we have $b\tau_{\text{ph}} > \tau_1$ and this leads to the phonon bottleneck regime. However, in other systems one might have $b\tau_{\text{ph}} < \tau_1$ in which case the phonons would be at equilibrium but still with a butterfly hysteresis loop (τ_H is a linear combination of τ_1 and $b\tau_{\text{ph}}$ [17]). This type of hysteresis loop is general and characterizes dissipative spin reversal in the absence of barrier.

In conclusion, the V_{15} molecular complex constitutes an example of a dissipative two-level system [8] of mesoscopic size. The total spin 1/2 being formed of a large number of interacting spins, its splitting results from the structure itself of the molecule (intramolecular hyperfine and Dzyaloshinsky-Moriya couplings) and it is rather large (a fraction of Kelvin) [12]. In V_{15} and in other low-spin systems, splittings must be much larger than in large-spin molecules where the presence of energy barriers lowers them by orders of magnitude (e.g., 10^{-11} K in Mn_{12} [1,2]).

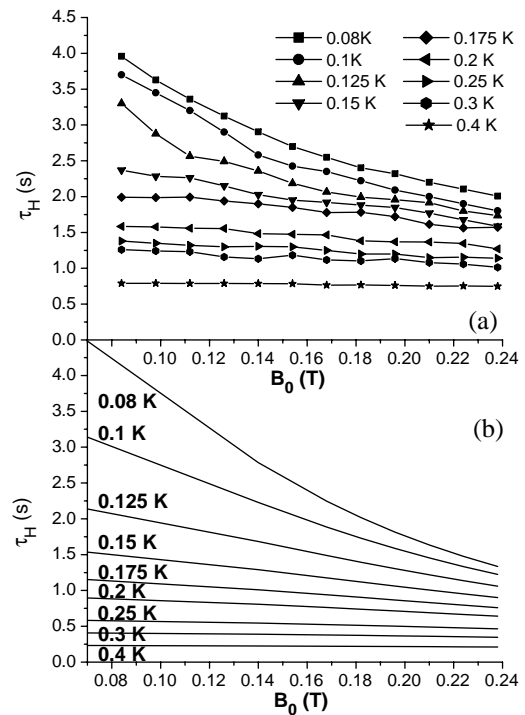


FIG. 3. The relaxation times τ_H , (a) measured and (b) calculated (same parameters as in Figs. 1 and 2b).

This is the reason why spin-phonon transitions within the tunneling gap are important in low-spin molecules and not relevant in high-spin ones, unless a large transverse field is applied [6] (it increases the tunnel splitting and probability) in which case we would also expect similar phenomena.

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- [18] The fast hyperfine fluctuations are characterized by the transverse nuclear relaxation time T_2 associated with the dipolar internuclear interactions, and the total spread of the energy is given by hyperfine couplings [4].
- [19] $\alpha = 0.15 \text{ s K}^2$ ($2.9 \times 10^{-47} \text{ s J}^2$), $\Delta_0 = 50$ mK within a precision range of $\approx 20\%$. Taking $L \sim 30\text{--}50 \text{ }\mu\text{m}$, $N \sim 10^{27} \text{ m}^{-3}$, $\Delta\omega \sim 5 \times 10^8 \text{ s}^{-1}$, one gets a phonon velocity $v \approx 2800\text{--}3600 \text{ m/s}$ which is quite a reasonable value.