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# Adiabatic Landau-Zener-Stückelberg transition with or without dissipation in the low-spin molecular system $V_{15}$

I. Chiorescu,<sup>1,\*</sup> W. Wernsdorfer,<sup>1</sup> A. Müller,<sup>2</sup> S. Miyashita,<sup>3</sup> and B. Barbara<sup>1</sup>

<sup>1</sup>*Laboratoire Louis Néel, CNRS, Boîte Postale 166, 38042 Grenoble, France*

<sup>2</sup>*Fakultät für Chemie, Universität Bielefeld, D-33501 Bielefeld, Germany*

<sup>3</sup>*Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan*

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The spin- $\frac{1}{2}$  molecular system  $V_{15}$  shows no barrier against spin reversal. This makes possible direct phonon activation between the two levels. By tuning the field sweeping rate and the thermal coupling between the sample and the thermal reservoir we have control over the phonon-bottleneck phenomena previously reported in this system. We demonstrate adiabatic motion of molecule spins in time dependent magnetic fields and with different thermal coupling to the cryostat bath. We also discuss the origin of the zero-field tunneling splitting for a half-integer spin.

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Research on quantum-mechanical behavior in large systems is of fundamental interest and also of major importance in quantum computation related applications (Ref. 1 and references therein). A special class are the magnetic two-level systems, realized in mesoscopic molecular crystals at millikelvin temperatures.<sup>2</sup> Here, one scales up the quantum properties of one molecule in its local environment to large enough signals generated by the whole crystal. Any coupling between the *spin-up* and *spin-down* orientations of the molecular spin results in tunneling splittings whose magnitudes control the quantum dynamics of the spin. Quantum tunneling of the magnetization across the anisotropy barrier was observed in  $Mn_{12}$  or  $Fe_8$  high-spin molecules,<sup>3</sup> and the quantum interference of tunneling paths was demonstrated in  $Fe_8$ .<sup>4</sup> In these molecules splittings are very small ( $\lesssim 10^{-6}$  K). Large splittings ( $\gtrsim 10^{-3}$  K) are usually found in low spin molecules or high- and intermediate spin molecules in large transverse fields.<sup>2,4,5</sup> In such systems, the archetype of which is the low-spin molecule  $V_{15}$ ,<sup>6-8</sup> the Landau-Zener-Stückelberg (LZS) tunneling probability<sup>9</sup> is very close to 1 and, in the absence of environment, the transitions should be adiabatic. At finite temperature, dynamics of the magnetic moment depend on direct spin-phonon transitions fed by the energy exchange with the cryostat. The  $S = 1/2$   $V_{15}$  molecule shows an intrinsic phonon-bottleneck (PB) effect with characteristic “butterfly” hysteresis loops. Such systems are experimental realizations of dissipative two-level systems.<sup>10</sup> Similar results were reproduced since then in other low-spin systems.<sup>11</sup> The PB phenomena belong to a general class of almost adiabatic transitions in which only a small fraction of heat inflows during the process of approach to equilibrium (which remains in complete). A similar example of almost adiabatic transition is found in the Foehn effect in meteorology and similar effects (“magnetic Foehn” effect<sup>12</sup>) have been found in the magnetization processes of some Fe rings.<sup>13</sup>

In this communication we present results on mechanisms involved in the quantum dynamics of the  $V_{15}$  molecular spin. We prove fully adiabatic motion of this molecular multi-spin system in time-dependent magnetic fields and give more

insight on the PB effect in showing ways to control dissipation in regions close to tunneling gaps. This provides a possibility of increasing both relaxation and decoherence times. Furthermore, we discuss the origin of the zero-field splitting  $\Delta_0$  for half-integer spin.

The  $V_{15}$  complex ( $K_6[V_{15}As_6O_{42}(H_2O)]8H_2O$ ) forms a lattice with trigonal symmetry ( $a = 14.029$  Å,  $\alpha = 79.26^\circ$ ,  $V = 2632$  Å<sup>3</sup>) with two  $V_{15}$  molecules per cell.<sup>14</sup> All the fifteen  $V^{IV}$  ions of spin  $S = 1/2$  are placed in a quasispherical layered structure formed of a triangle sandwiched between two nonplanar hexagons. The exchange couplings between the V ions are antiferromagnetic making of  $V_{15}$  a typical example of a frustrated molecule. After the PB study given in Ref. 6, the next step, presented here, was to control the relaxation process by tuning the coupling between the spin-phonon system and the thermal reservoir. In order to reach a regime where the spin dynamics is independent of the thermal bath, thus entering a pure quantum regime, we minimized the coupling to the sample reservoir. This first limit of fast field variations and weak coupling to the cryostat was reached by inserting a thermal isolator between the sample (a single crystal of few tens of microns) and the sample holder, and restricting the temperature to lowest values. We optimized the other limit with best thermal coupling using a mixture of silver powder with grease.

The magnetization curves vs applied field  $B_0$  ( $= \mu_0 H$ ) of Fig. 1 show either a weak hysteresis or no hysteresis at all, depending on the competition between two field-dependent parameters: relaxation rate  $\tau_H$  and  $\Delta_H/v_{\Delta_H}$ , the time spent by the system at a given two-level energy separation [ $\Delta_H = \sqrt{\Delta_0^2 + (2\mu_B B_0)^2}$ ,  $v_{\Delta_H} = d\Delta_H/dt$ ]. In our experimental setup one may tune the ratio  $\tau_H v_{\Delta_H}/\Delta_H$  roughly between  $10^{-3}$ – $10^4$  by adjusting the field sweeping rate and sample thermal coupling, which makes it possible to study both regimes, spin system isolated [continuous line, Fig. 1(a)] or in thermal equilibrium with the cryostat [dashed line, Fig. 1(b)]. The PB model accounts for the interpretation<sup>6</sup> of such hysteresis curves (for clarity, only half cycles are shown in Figs. 1, negative field half cycles being symmetric to the positive

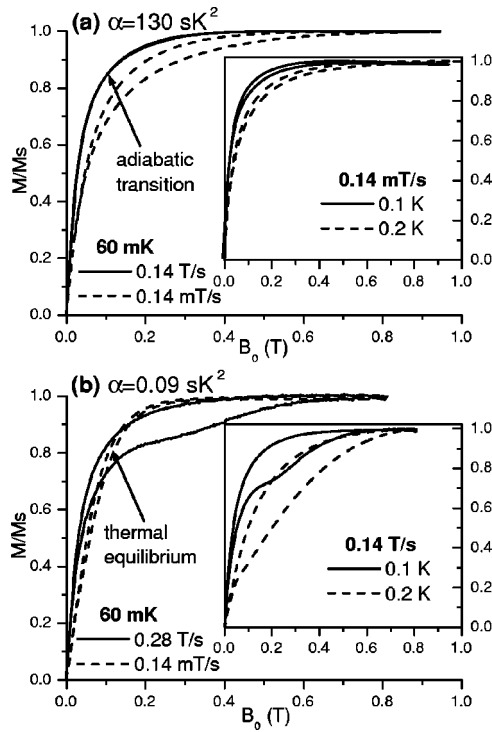


FIG. 1. (a) Hysteresis loops for a sample rather well isolated from the cryostat ( $\alpha = 130 \text{ s K}^2$ ). The curve at 60 mK and 0.14 T/s shows an adiabatic LZS spin transition, well fitted by Eq. (2). (b) Hysteresis loops measured in the case of a sample rather well coupled to the cryostat ( $\alpha = 0.09 \text{ s K}^2$ ).

field ones). The spin temperature  $T_S$  is such that  $n_1/n_2 = \exp(\Delta_H/k_B T_S)$ , where  $n_{1,2}$  ( $n_{1,2eq}$ ) are occupations numbers for levels out of equilibrium (in equilibrium). Most molecules are out of equilibrium at a temperature  $T_S$  different from the cryostat temperature  $T$ . Even for a good thermal contact between the sample and the cryostat, the energy flow from the latter is not sufficient to compensate the lack of phonons at energies  $\hbar\omega = \Delta_H \pm \Delta\omega$ , if the field is swept fast enough. The phonon-bottleneck model presented in Refs. 6 and 15 gives a relaxation law  $-t/\tau_H = x(t) - x(0) + \ln([x(t) - 1]/[x(0) - 1])$ , where  $x = (n_1 - n_2)/(n_{1eq} - n_{2eq})$  and

$$\tau_H = \alpha \frac{\tanh^2(\Delta_H/2k_B T)}{\Delta_H^2} \quad (1)$$

is the relaxation time. The  $\alpha$  parameter reflects the thermal coupling sample cryostat (a large value indicates weak coupling, a small value indicates strong coupling);  $\alpha$  is proportional to the molecule density, phonon velocity, and phonon-bath relaxation time and inversely proportional to the level's width  $[\Delta\omega]$ , directly related to nuclear spin bath fluctuations,<sup>16</sup> of the order of 50 mK (Ref. 17)]. To compare measured and calculated hysteresis curves, one has to find the best set of parameters ( $\alpha, \Delta_0$ ). The experimental curves in Figs. 1(a,b) are best fitted by sets of parameters ( $\alpha \approx 130 \text{ s K}^2$ ,  $\Delta_0 \approx 80 \text{ mK}$ ) and ( $\alpha \approx 0.09 \text{ s K}^2$ ,  $\Delta_0 \approx 80 \text{ mK}$ ), respectively. As expected, ( $\alpha \approx 0.15 \text{ s K}^2$ ,  $\Delta_0$

$\approx 50 \text{ mK}$ ) obtained in Ref. 6 shows a comparable  $\Delta_0$  and  $\alpha$  between the present ones, meaning that the coupling with the cryostat was intermediate compared with those of Fig. 1. It is interesting to mention that recent neutron-scattering experiments done on  $V_{15}$  powder<sup>18</sup> obtained a value of  $\Delta_0$  comparable to our first determinations.

In Fig. 1(b) one can see that the magnetization curve becomes almost reversible if the field change is slow enough (dashed line). This is a natural consequence of the Boltzmann thermal equilibrium when spin-phonon transitions are highly probable. When the sweeping rate  $v_H$  or thermal isolation  $\alpha$  are increasing, the PB phenomena becomes more present and manifests itself through an opening in the hysteresis loops. In very low fields ( $\lesssim 0.1 \text{ T}$ ), the spin temperature is lower than the bath temperature ( $T_S < T$ ). Then a PB plateau of almost constant magnetization develops and  $T_S$  overpasses  $T$ . At sufficiently high fields ( $\sim 0.5 \text{ T}$ ) the system reaches its equilibrium ( $T_S = T$ ) by a small phonon avalanche. Of particular interest is the case  $\alpha = 130 \text{ s K}^2$  when the sample is thermally isolated from the sample holder. The reversibility of Fig. 1(a) (continuous line) is very different from the equilibrium reversibility. Here, the sweeping rate and isolation to the cryostat are large enough to drive the PB plateau near the saturation level: the PB phenomena is so important that the sample is completely isolated during our experimental time. The spin-phonon transitions have such a small probability that the system keeps its initial state (here, the ground state), allowing precise measurements of slow (free of spin-phonon transitions) relaxations. The multispin motion can therefore be considered as adiabatic with an excellent approximation, and the magnetization curve should be given by

$$M = \frac{1}{2} \frac{d\Delta_H}{dB_0} = \mu_B / \sqrt{1 + \left( \frac{\Delta_0}{2\mu_B B_0} \right)^2}. \quad (2)$$

Indeed, the adiabatic curve of Fig. 1(a) is nicely fitted by Eq. 2 with  $\Delta_0 \approx 80 \text{ mK}$ .

Magnetic relaxation experiments were performed in the same conditions as in Fig. 1(a), for different values of the applied field. As an example, we show in Fig. 2 the results obtained for  $T = 0.05, 0.15 \text{ K}$  and two fields especially chosen outside and inside the degeneracy zone [where  $\Delta_H(B_0)$  is nonlinear]. The corresponding  $\tau_H$  values, obtained by fitting the relaxation curves or simply calculated from Eq. (1) (with  $\alpha = 130 \text{ s K}^2$ ,  $\Delta_0 = 80 \text{ mK}$ ), are given in Table I. The fit using the relaxation law mentioned above [see Eq. (1)] is in remarkably good agreement with the data when the relaxation experiment is performed relatively far from the degeneracy point. The fit does not perform well for the faster relaxations developing inside the degeneracy zone and the obtained value for  $\tau_H$  is three to five times smaller than the expected value (deduced from the general shape of the hysteresis curve). This shows that in this case, i.e., within the mixing region, the phonon bath is no longer sufficient to explain the dissipation in this two-level system. An excess relaxation comes from the Dzyaloshinsky-Moriya (DM) interactions, allowed by molecule symmetry and the spin bath; in particular, from the fast fluctuations of the  $^{51}\text{V}$  nuclear

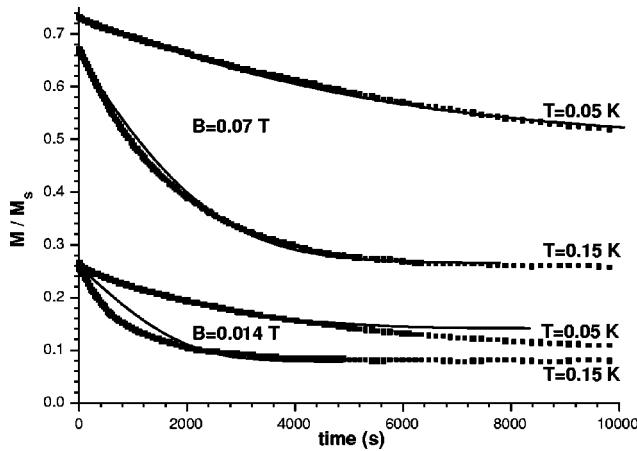


FIG. 2. Relaxation measurements at  $T=0.05$  and  $0.15$  K (dots) fitted with the PB model [lines, see Eq. (1)], outside ( $B=0.07$  T) and inside the degeneracy zone ( $B=0.014$  T).

spins. The DM interactions generate off-diagonal terms coupling the spin-up and spin-down states, whereas the spin bath gives a noticeable spread of energy levels almost touching each other near zero field, both effects enhancing the relaxation in this particular region. Also, they are at the origin of the large zero-field splitting  $\Delta_0$  in the  $V_{15}$  molecule as will be discussed below.

$V_{15}$  has an effective spin  $1/2$ , which is a half-integer. As well known as the Kramers's theorem, all the energy levels have to be at least doubly degenerate in the time-reversal symmetry. Therefore, if we consider the tunneling of the magnetization of the half-integer spins in a single-mode path-integral formula, the tunneling rate must be zero. This is due to zero tunnel splitting  $\Delta_0$ . The consequence is that magnetization reversals cannot be adiabatic with half-integer spins. However, as shown above, the  $V_{15}$  system shows very clear adiabatic spin reversal, with zero-field splitting of about almost  $0.1$  K. The most characteristic feature of  $V_{15}$  is its multispin character. We shall see that this character is a necessary but not sufficient condition for producing finite zero-field splittings with odd-integer spins. Note that  $\Delta_0$  cannot be due to internal dipolar fields that range in the millitesla scale. However, these fields together with nuclear spins certainly provide sources of decoherence.

Due to frustration on antiferromagnetic triangles in  $V_{15}$ , the energy structure of this system consists of one quartet ( $S=3/2$ ) and two doublets ( $S=1/2$ ) well separated from excited levels by a gap of the order  $10^2$  K. At zero field, the

TABLE I. Relaxation times obtained by the fit of curves in Fig. 2 (third column) and calculated (fourth column) for  $\alpha=130$  s K<sup>2</sup> and  $\Delta_0=80$  mK [obtained by fit of hysteresis loops in Fig. 1(a)].

$T$ (K)	$B_0$ (mT)	$\tau_H$ fit (s)	$\tau_H$ th. (s)
0.05	14	1507	8716
0.15	14	551	1323
0.05	70	3883	3675
0.15	70	970	997

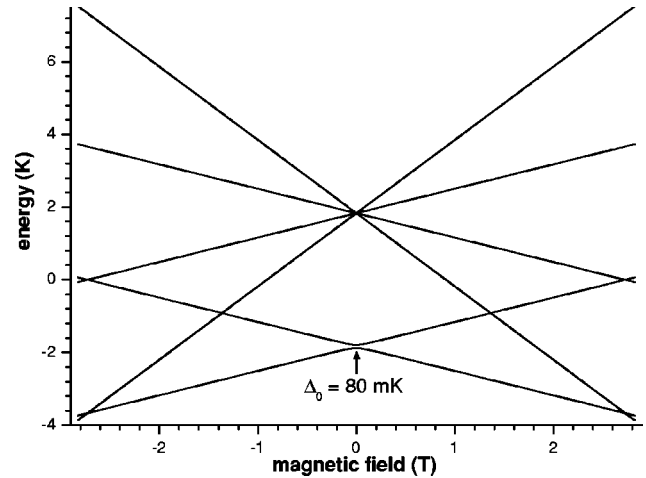


FIG. 3. Energy levels of three effective spins  $1/2$ , obtained from  $H = J \sum_{i<j} \vec{S}_i \cdot \vec{S}_j + D \sum_{i<j} (S_i^x S_j^x - S_i^y S_j^y) - g \mu_B B_0 \sum_i S_i^z$  (Ref. 19) with  $J=2.445$  K (Ref. 7) and  $D=50$  mK (for  $\Delta_0=80$  mK).

ground state is fourfold degenerated (although with a spin  $S=1/2$ ). By making use of this degree of freedom, one can generate level repulsion.<sup>19</sup> In order to mix the states whose magnetization differs by 1, we need the interactions to contain  $S^+$  and  $S^-$ . In the theoretical calculations the transverse field is often used for this purpose. However, in order to find the source of the avoided level crossing for the molecules in zero field, we have to find interactions with time-reversal symmetry, that is, products of even number of spin operators, such as  $S^z S^x$ , etc. Generally symmetric combinations of operators, e.g.,  $S_i^z S_j^x + S_i^x S_j^z$ , are rearranged into anisotropy and do not cause the avoided level structure. This is not the case with antisymmetric combinations of the form  $S_i^z S_j^x - S_i^x S_j^z$  for which it has been found that new avoided level structures are created (such terms were proposed to induce gaps otherwise forbidden in magnetic molecules.<sup>20</sup>) This is a sufficient condition for having a finite zero-field splitting with half-integer spins. The subsequent structure of the energy spectrum at low energy is generally like that depicted in Fig. 3 for the case of a frustrated triangle (the 15 spins  $1/2$  form three effective spins  $1/2$ , antiferromagnetically coupled.<sup>7</sup>) Here, we introduced the DM interaction ( $D=50$  mK) in a simple way to demonstrate that the gap actually opens with this type of perturbation. However, the real molecule consists of a more complicated structure, where a spin of the inner triangle connects to the spins of the upper and lower hexagons of the  $V_{15}$  molecule, and other DM interactions can exist and should be taken into account.<sup>21</sup> A more realistic energy structure will be investigated after the determination of the arrangement of DM interactions on the bonds.<sup>22</sup> For an effective triangle, there are two sets of avoided structures and they cross in zero field, allowing the Kramers's theorem to be satisfied. Depending on the details of DM interactions, two different situations may occur depending on whether or not the two sets of level repulsion structures are orthogonal to each other. In the first case the four states are classified into two sets of subspaces, and the LZS mechanism exactly holds because the LZS transition occurs independently in each branch of the avoided level crossing structure. In the second



case, the four states form an irreducible space, where one of the states scatters into all of the four states when the field is swept, and the LZS mechanism should not hold. However, even in this last case, the change of magnetization at the crossing point as a function of the sweeping velocity is almost perfectly expressed by the LZS formula.<sup>19</sup> As a consequence, one can say that the change of magnetization in multispin systems with DM interactions should follow the LZS model in a wide range of interaction parameters.

In short, previous studies of the “butterfly” hysteresis loop in the multispin  $V_{15}$  molecule<sup>6,7</sup> are now extended to the nondissipative LZS regime. First, we have shown that the crossover from the dissipative to the nondissipative LZS regime can easily be achieved by changing the coupling of the sample to the cryostat. This first demonstration of dissipation control in a two-level system has important implications for

further applications on quantum information and computers. The role of the spin bath becomes visible when experiments are performed near zero field, in the level mixing region. However, the associated relaxation times are still long enough to allow adiabatic magnetization experiments. Second, we directly verified the zero-field gap previously obtained in the dissipative regime and attributed it to the effect of the DM interactions of this multispin system. The third result is the clear comparison between experiments and theory, showing that the conditions for the existence of a gap in a half-integer multispin system with antisymmetric interactions (e.g., DM interaction) are fulfilled.

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\*Present address: Department of Applied Physics, Delft University of Technology, 2628 CJ, Delft, The Netherlands

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