Butterfly hysteresis curve is a signature of adiabatic Landau-Zener transition

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We stress that the so-called butterfly hysteresis curves observed in dynamical magnetization measurements on systems of low-spin magnetic molecules such as V\textsubscript{15} and V\textsubscript{6} are a signature of adiabatic Landau-Zener transitions rather than that of a phonon bottleneck. We investigate the magnetization dynamics analytically with the help of a simple relaxation theory in the basis of the adiabatic energy levels of the spin 1/2, to a qualitative accordance with experimental observations. In particular, reversible behavior is found near zero field, the corresponding susceptibility being bounded by the equilibrium and adiabatic susceptibilities from below and above, respectively.

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Magnetic hysteresis curves in crystals of molecular magnets with an effective spin \( S = 1/2 \) such as V\textsubscript{15} (Refs. \[1\] and \[2\]) have under some conditions the so-called butterfly form that is conventionally considered as a signature of the phonon bottleneck. Similar phenomenon has been observed on ferric wheels NaFe\textsubscript{2}O\textsubscript{4}, where the ground state changes from \( S = 0 \) to \( S = 1 \) at some magnetic field.

We shall demonstrate that butterfly hysteresis curves can qualitatively be explained already by a simple relaxational model taking into account adiabatic Landau-Zener transitions at avoided level crossing. Using the additional equation for nonequilibrium phonons does not change the butterfly hysteresis curves qualitatively. While bad thermal contact between the crystal and the holder can apparently lead to the bottleneck and thus to smaller experimentally observed effective relaxation rates for the spin, these rates could be reduced for other reasons, too. In this case butterfly hysteresis curves arise without the bottleneck. Although this fact is known (see, e.g., Ref. \[3\]), an appropriate quantitative theory is still lacking.

In V\textsubscript{15} the zero-field splitting \( \Delta \) between the two low-lying spin levels is about \( \Delta/k_B \approx 50 \pm 80 \) mK (Refs. \[1\] and \[2\]), and for the experimental sweep rate \( dB_z/dt = 0.1 \) T/s the Landau-Zener parameter \( \varepsilon = \pi \Delta^2/(2hv) \) with \( v = 2Sg\mu_B dB_z/dt \) is about 10\(^9\). This means that, in the absence of relaxation, the system follows the lowest adiabatic energy level \( E_\downarrow \) (see Fig. 1), the probability to remain in the original spin-down state \( P = e^{-\varepsilon} \) being negligibly small.

In the opposite limit of very fast relaxation between the adiabatic levels \( E_- \) and \( E_+ \) the system relaxes up the energy, \( E_- \rightarrow E_+ \), before crossing the resonance and down the energy, \( E_+ \rightarrow E_- \), after crossing the resonance, the level populations \( n_{\pm} \) satisfying the equilibrium condition
\[
n_{\downarrow}^{\text{eq}} - n_{\uparrow}^{\text{eq}} = \tanh \left( \frac{\hbar \omega_0}{2k_B T} \right),
\]
where
\[
\hbar \omega_0 = E_+ - E_- = \sqrt{W^2 + \Delta^2}
\]
and \( W = 2Sg\mu_B B_z \) is the energy bias that in the field-sweep experiments is a linear function of time: \( W = vt = 2Sg\mu_B (dB_z/dt) t \).

Changing to the spin-up/down basis allows to calculate the reduced magnetization
\[
m_z = \frac{W}{\sqrt{W^2 + \Delta^2}} (n_+ - n_-),
\]
where \( n_- = 1 \) and \( n_+ = 0 \) far before crossing the resonance. In the absence of relaxation (adiabatic case) one has \( n_- \cong 1 \) and \( n_+ \cong 0 \) at any moment of time, while at equilibrium \( n_{\pm} \) satisfy Eq. (1) and the magnetization is given by
\[
m_z^{\text{eq}} = \frac{W}{\sqrt{W^2 + \Delta^2}} \tanh \left( \frac{\sqrt{W^2 + \Delta^2}}{2k_B T} \right).
\]

In the case \( k_B T \gg \Delta \) the equilibrium magnetization simplifies to \( m_z^{\text{eq}} \approx \tanh \left[ W/(2k_B T) \right] \), independently of \( \Delta \). Note that, whatever the relaxation processes, one has \( m_z = 0 \) at resonance, \( W = 0 \).

In the intermediate-relaxation regime the time-dependent values of \( n_{\pm} \) can be obtained from the master
The population difference \( n_-(t) - n_+(t) \) obtained by numerical integration in Eq. (9) vs the energy bias \( W \) for the linear sweep from \( t = -\infty \) to \( \infty \) in the limit \( \Delta/k_B T \to 0 \) for different values of the reduced sweep rate \( A \) of Eq. (15) is lagging behind the transition frequency \( \omega_0 \). Whereas the equilibrium solution of Eq. (5) for \( n_-(t) - n_+(t) \) that is attained in the fast-relaxation limit is even in \( W \) with a minimum at \( W = 0 \), the general nonequilibrium solution for \( n_-(t) - n_+(t) \) is lagging behind \( n_-(eq) - n_+(eq) \) (see Fig. 2). For crossing the resonance in the positive direction, it has a minimum at some \( W_{bc} > 0 \). For \( W < W_{bc} \) one has \( n_- - n_+ > n_-(eq) - n_+(eq) \), whereas for \( W > W_{bc} \) one has \( n_- - n_+ < n_-(eq) - n_+(eq) \). This overshoot leads to the butterfly hysteresis curves for \( m_z(t) \) defined by Eq. (6). At \( W = W_{bc} \) the dynamic magnetization \( m_z(t) \) crosses the equilibrium magnetization curve, \( m_z(t_{bc}) = m_z(eq)(t_{bc}) \), that is the definition of the butterfly crossing.

The relaxation rate \( \Gamma \) in Eq. (5) is mainly due to the direct phonon processes and, in the absence of the phonon bottleneck, it has the form

\[
\Gamma = \Gamma_0 \coth \left( \frac{\hbar \omega_0}{2k_B T} \right). \tag{7}
\]

Here \( \Gamma_0 \) depends on the details of the spin-phonon coupling (for \( V_{15} \) and \( V_6 \) one of the candidates is Dzialoshinskii-Moriya interaction). We are not going to discuss the details of the spin-phonon interactions here as the butterfly curve is quite a general phenomenon. One has only to take into account that \( \Gamma \) depends on time via the transition frequency \( \omega_0 \). We set

\[
\Gamma_0 = \Gamma_{00} \left( \frac{\hbar \omega_0}{\Delta} \right)^\alpha, \tag{8}
\]

where in most cases \( \alpha = 3 \). For a better fit to experiments, one can include an \( \omega_0 \)-independent relaxation rate in Eq. (7), as was done in Ref. [3]. The solution of Eq. (5) has the form

\[
n_-(t) - n_+(t) = e^{-\tilde{\Gamma} t} \int_0^t dt' \Gamma(t') \coth \left( \frac{\hbar \omega_0(t')}{2k_B T} \right), \tag{9}
\]

where

\[
\tilde{\Gamma}(t) = \frac{1}{t} \int_0^t dt' \Gamma(t'). \tag{10}
\]

it is easy to check that \( \lim_{t \to \pm \infty} [n_-(t) - n_+(t)] = 1 \). The strongest deviation of \( n_-(t) - n_+(t) \) from 1 originates from such \( t \) for which \( \tanh [\hbar \omega_0(t)/(2k_B T)] \) in Eq. (9) is small enough compared to one. It is the range where thermal transitions become significant.

In the case \( \Delta \approx k_B T \) that was realized in experiments on \( V_{15} \) in Refs. [1][2] (\( \Delta/k_B \approx 0.5 \) K, \( T = 0.1 \pm 0.2 \) K) the thermal transitions are important in the vicinity of the level crossing: \( W = vt \sim \Delta \). As the system spends the time \( t_{th} \sim \Delta/v \sim k_B T/v \) in this region, the case \( \Gamma_0 \approx v/\Delta \sim v/(k_B T) \) corresponds to the adiabatic limit, \( n_- \approx 1 \) and \( n_+ \approx 0 \), whereas the case \( \Gamma_0 \gg v/\Delta \sim v/(k_B T) \) corresponds to the equilibrium situation, \( n_- - n_+ \approx n_-(eq) - n_+(eq) \). In the intermediate case \( \Gamma_0 \sim v/\Delta \sim v/(k_B T) \) the dynamical relaxation effect is mostly pronounced, and the hysteresis curve has a butterfly shape with the crossing with the equilibrium magnetization curve at \( W_{bc} \sim k_B T \). Our numerical results obtained from Eq. (9) and shown in Fig. 3 are in a qualitative agreement with experimental and theoretical results of Ref. [1] except for the slowest-sweep curve \( dH_z/dt = 0.0044 \) T/s.

The low-temperature case \( \Delta \ll k_B T \) is trivial, since here there are no thermal transitions and the adiabatic solution \( n_- \approx 1 \) and \( n_+ \approx 0 \) is valid for all times, while the magnetization follows from Eq. (3).

In the high-temperature range \( \Delta \gg k_B T \) (in experiments on \( V_6 \) in Ref. [3] the estimated energy gap is \( \Delta/k_B \approx 0.4 \) K, whereas the maximal temperature was \( T = 4.2 \) K) thermal transitions take place in a much broader region \( |W| \sim W_0 \sim k_B T \) than the quantum-mechanical crossing \( |W| \sim \Delta \). The system spends the time

\[
t_{th} = k_B T/v, \tag{11}
\]

in the thermal-transition range. Neglecting the narrow region \( |W| \sim \Delta \) and approximating \( \hbar \omega_0 \approx |W| = v|t| \) one obtains from Eqs. (10) and (7)

\[
\tilde{\Gamma}(t) \approx \frac{\Gamma_{00} k_B T}{v} \left( \frac{v|t|}{\Delta} \right)^\alpha \Phi_\alpha \left( \frac{v|t|}{k_B T} \right) \text{sign}(t). \tag{12}
\]
in the nearly adiabatic limit \( A \gg 1 \) one obtains (for the increasing field)

\[
W_{bc} = vt_{bc} \cong k_B T \ln \left( \frac{A}{I_{\alpha}} \right)
\]

and

\[
n_-(t_{bc}) - n_+(t_{bc}) = \tan \frac{W_{bc}}{2k_B T} \cong 1 - \frac{2I_{\alpha}}{A},
\]

where

\[
I_{\alpha} \equiv \int_0^\infty dz \frac{z^\alpha}{\Phi_{\alpha}(1)} \left[ \coth \left( \frac{z}{2} \right) - 1 \right]
\]

\( I_1 = 1.60, I_2 = 4.62, I_3 = 18.6, I_4 = 94.4, I_5 = 576. \) One can see that, in fact, the apparent applicability condition of Eq. \( \text{[10]} \) and \( \text{[17]} \) is \( I_{\alpha}/A \ll 1 \) that results in rather large values of \( A \) for \( \alpha = 3 \) and higher. This is an essential correction to the \textit{a priori} estimation of Eq. \( \text{[13]} \).

With increasing \( \alpha \) the validity range of Eqs. \( \text{[10]} \) and \( \text{[17]} \) becomes narrower than \( I_{\alpha}/A \ll 1 \) since the former is the first term of the asymptotic expansion in powers of \( 1/A \) that becomes progressively bad with increasing \( \alpha \).

The physical origin of this difficulty is the following. For \( \Delta \ll k_B T \) in the nearly equilibrium limit \( A \ll 1 \) one obtains

\[
W_{bc} \cong k_B T (q_{\alpha} A)^{1/\alpha}
\]

and

\[
n_-(t_{bc}) - n_+(t_{bc}) \cong \frac{1}{2} (q_{\alpha} A)^{1/\alpha},
\]

where \( q_{\alpha} \equiv (\alpha/2) \Phi_{\alpha}(1) p_{\alpha} \) and \( p_{\alpha} \) is the solution of the transcendental equation

\[
p_{\alpha}^{1/\alpha} = e^{-p_{\alpha}} \Gamma \left( 1 + \frac{1}{\alpha} \right) + \int_0^{p_{\alpha}} dp \frac{p^{1/\alpha}}{e^{p_{\alpha}}}.
\]

One obtains \( p_1 = 0.693, p_2 = 0.535, p_3 = 0.482, p_4 = 0.455, p_5 = 0.438, \) and \( q_1 = 0.712, q_2 = 0.557, q_3 = 0.506, q_4 = 0.480, q_5 = 0.464. \) Note that the general applicability condition of our approximation replacing \( h\omega_{\text{th}} \gg |W| \) is \( W_{bc} \gg \Delta \). This yields the applicability condition for Eqs. \( \text{[10]} \) and \( \text{[20]} \)

\[
\left( \frac{\Delta}{k_B T} \right)^{\alpha} \ll A \ll 1.
\]

The full dependence of \( W_{bc} \) on the reduced relaxation time \( A \) of Eq. \( \text{[13]} \) can be found numerically from Eq. \( \text{[2]} \). The results for \( W_{bc}/(k_B T) \) for different \( \alpha \) in the limit \( \Delta \ll k_B T \) are shown in Fig. \( \text{[4]} \). Note that at the butterfly crossing the difference \( n_-(t) - n_+(t) \) attains a minimum, according to Eq. \( \text{[1]} \). The magnetization value at the butterfly crossing \( m_z^{(\text{eq})}(t_{bc}) \) can be obtained from Eq. \( \text{[4]} \) and it is given by

\[
m_z(t_{bc}) = \frac{W_{bc}}{\sqrt{W_{bc}^2 + \Delta^2}} \tanh \sqrt{\frac{W_{bc}^2 + \Delta^2}{2k_B T}}.
\]
reversible near zero field, in full agreement with the experimental finding. Note that the theoretical approach of Ref. 3 is not applicable in the vicinity of the Landau-Zener crossing. Using Eqs. (19) and (24), one can express $\tilde{\chi}$ as

$$\tilde{\chi} = \int_{-\infty}^{0} dt \Gamma(t) e^{\tilde{\Gamma}(t)t}\tanh\left(\frac{\hbar\omega_0(t)}{2k_B T}\right)$$  

(26)

that is plotted vs $A/I_\alpha$ for different values of $\Delta/(k_B T)$ in Fig. 5. In the nearly adiabatic limit $A \gg 1$ the asymptote of Eq. (26) is

$$\tilde{\chi} \approx 1 - 2\Gamma(\alpha + 1) \frac{\Phi_\alpha(1)}{A}$$  

(27)

In the nearly equilibrium limit $A \ll 1$, the most interesting is the asymptote corresponding to $\Delta/(k_B T) \rightarrow 0$:

$$\tilde{\chi} \approx (\alpha \Phi_\alpha(1) A)^{1/\alpha} 2^{-1+1/\alpha)} \Gamma(1 + 1/\alpha) .$$  

(28)

Summarizing, we gave a detailed analytical consideration of the adiabatic Landau-Zener effect with relaxation and we have shown that this is a minimal model to describe experimentally observed butterfly hysteresis curves. More complicated relaxation models including an additional kinetic equation for nonequilibrium phonons in the case of the phonon bottleneck seem to be nonessential to describe the butterfly hysteresis curves. One can interpret the latter in the framework of the simplest relaxation theory described above by choosing an appropriate relaxation rate $\Gamma$ that can be effectively reduced because of a poor thermal contact of the crystal with the holder. If the details of the phonon dynamics related to the phonon bottleneck are the subject of investigation, a special care should be taken to single out their effect on the magnetization hysteresis curves.

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