Chapter 1
Theory of deflagration and fronts of tunneling in molecular magnets

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Abstract Decay of metastable states in molecular magnets (MM) leads to energy release that results in temperature increase that, in turn, positively affects the decay rate. This is the mechanism of recently discovered magnetic deflagration that is similar to regular chemical burning and can propagate in a form of burning fronts in long MM crystals. Near spin-tunneling resonances the decay rate is also affected by the dipolar field (self-consistent with the switching magnetization) that can block or unblock tunneling. There are non-thermal fronts of tunneling in which the magnetization adjusts in such a way that the system is on resonance within the front core, so that the tunneling front can propagate. In general, both dipolar field and temperature control fronts of quantum deflagration. The front speed can reach sonic values if a strong transverse field is applied to boost tunneling.

1.1 Introduction

Deflagration or burning is decay of metastable states accelerated by the temperature rise due to the energy release in this process \( \text{[1,2]} \). In most cases the decay rate has the Arrhenius temperature dependence, \( \Gamma = \Gamma_0 \exp \left[ \frac{-U}{k_B T} \right] \), where \( U \) is the energy barrier. Because of the very strong positive feedback, burning can have a form of a thermal runaway: almost undetectably slow relaxation at the beginning followed by an explosion-like relaxation at the end (explosions at ammunition-storage sites, Bhopal disaster, etc.). In other cases there is a burning front propagating with a constant speed away from the ignition point. These fronts are driven by the heat con-
duction from the hot burned region to the cold unburned region before the front. Burning of a sheet of paper is a good example of a deflagration front.

Molecular magnets (MM), of which the most famous is Mn$_{12}$Ac [3], are burnable materials because of their bistability resulting from a strong uniaxial anisotropy that creates an energy barrier [4]. One can make magnetic state metastable by applying a magnetic field along the anisotropy axis. Burning, of course, should lead to a much faster relaxation than a regular relaxation at fixed low temperatures. Indeed, in early experiments on relaxation of large specimens of MM [5–7] an abrupt and nearly total relaxation of the metastable magnetization has been detected but not explained. The 2005 space-resolved experiments of the Sarachik group [8] on long crystals of Mn$_{12}$Ac have shown propagating fronts of relaxation. In this experiments, regularly-spaced Hall probes at the sides of the crystal detected the transverse magnetic field created by the non-uniformity of the magnetization [9]. Chudnovsky interpreted these propagating fronts of relaxation as fronts of deflagration [8]. Measurements of the time dependence of the total magnetization by the Tejada group, inspired by the above experiment, have shown a linear time dependence that was attributed to a deflagration front traveling through a Mn$_{12}$ crystal [10]. Here quantum maxima of the front speed vs the bias field have been detected, Fig. 4 of Ref. [10]. Discovery of magnetic deflagration opened an active field of experimental research, mainly on Mn$_{12}$Ac [11–14]. Experiments at high sweep rates [15,16] have shown spin avalanches propagating at a fast speed. In this region, deflagration can go over into detonation [17]. Magnetic deflagration (coupled to a structural phase transition) has also been observed on manganites [18] and intermetallic compounds [19,20]. To the contrast, it is problematic to observe deflagration fronts on another popular MM Fe$_8$ because of the pyramidal shape of its crystals.

One can ask if deflagration can exist in traditional magnetic systems, many having a strong uniaxial anisotropy. Unfortunately, the energy release in magnetic systems is much weaker than in the case of a regular (chemical) deflagration. Thus, at room temperatures, the ensuing temperature increase is too small to change the relaxation rate and support burning. Only at low temperatures the increase of the relaxation rate becomes large. A hallmark of magnetic deflagration is its non-destructive character. “Burned” MM can be recycled (put again into the metastable state) by simply reversing the longitudinal magnetic field.

A comprehensive theory of magnetic deflagration given in Ref. [21] includes calculations of the stationary speed of the burning front, ignition time due to local increase of temperature or change of the magnetic field, as well as the analysis of stability of the low-temperature state with respect to deflagration that depends on the heat contact of the MM crystal with the environment. However, up to now there is no complete accordance between the theory and experiment for several reasons. First, thermal diffusivity $\kappa$ of Mn$_{12}$ that plays a crucial role in deflagration has not been measured up to now. Second,
there is no completely satisfactory theory of relaxation in molecular magnets that takes into account important collective effects such as superradiance and phonon bottleneck.

Because of their not too large spin \( S = 10 \) for \( \text{Mn}_{12} \) and \( \text{Fe}_8 \), molecular magnets are famous exponents of spin tunneling \[22–25\] that has a resonance character and leads to the steps in dynamic hysteresis curves at the values of the longitudinal magnetic field where quantum levels of the spin at the two sides of the potential barrier match \[26–28\]. Since the discovery of magnetic deflagration there was a quest for quantum effects in it. The simplest approach \[10,21\] uses the fact that usually spin tunneling occurs via pairs of quantum levels just below the classical barrier. This tunneling is thermally assisted and can be described by an effective lowering of the energy barrier at resonance values of the bias field (Fig. 2 of Ref. \[7\]). Thus using the Arrhenius relaxation rate with such an effective barrier does incorporate spin tunneling. Experimentally it was found that spin tunneling strongly affects ignition of deflagration (Fig. 5 of Ref. \[11\]) and to a smaller extent the front speed (Fig. 5 of Ref. \[11\] and Fig. 4 of Ref. \[10\]).

Quantum effects in deflagration should be sensitive to the dipolar field created by the sample. In a long uniformly magnetized crystal of \( \text{Mn}_{12}\text{Ac} \) the dipolar field is \( B^{(D)} = 52.6 \text{ mT} \), as calculated microscopically in Ref. \[29\], while the measured value \[14\] is very close to it. This creates a dipolar energy bias \( W^{(D)} = g \mu_B B^{(D)} (m' - m) \) between the pair of resonant quantum levels \( m \) and \( m' \) (quantum numbers for \( S_z \) in the two energy wells). This energy bias typically largely exceeds the tunnel splitting \( \Delta \) that contributes to the resonance width. In the deflagration front the dipolar field typically changes between \( +B^{(D)} \) and \( -B^{(D)} \) and so does the energy bias. As the result, spin tunneling in the deflagration front does not occur at a fixed resonance condition. This can explain why the observed quantum maxima in the front speed can be not as strong as expected, compared to the effect of tunneling on the ignition of deflagration.

Further theoretical research led to the idea of the dipole-dipole interaction (DDI) playing an active role in deflagration by controlling the relaxation rate, as temperature does in the regular deflagration. Adding to the external bias field, the dipolar field can set particular magnetic molecules on or off resonance, facilitating or blocking their tunneling relaxation. The problem is self-consistent since tunneling of one magnetic molecule changes dipolar fields on the other ones. A numerical solution of this problem in a form of a moving front of tunneling at zero temperature (sometimes called “cold deflagration”) has been found in Ref. \[30\]. An analytical solution for the front of tunneling in the realistic strong-DDI case has been obtained in Ref. \[31\].

Pure non-thermal fronts of tunneling can occur in the case of a very good thermal contact of the MM crystal with the environment, so that its temperature does not increase and remains so low that tunneling takes place directly from the metastable ground state into a matching excited state on the other side of the barrier. This process can be efficient only if a strong transverse
field is applied and the corresponding tunnel splitting $\Delta$ is large enough. In this case the speed of fronts of tunneling can theoretically exceed the speed of a regular deflagration by a large margin. Indeed, the dipolar field in the crystal changes instantaneously, in contrast to the temperature changing via heat conduction. Second, the relaxation rate due to tunneling directly from the ground state can be much higher than the relaxation rate due to the barrier-climbing processes in the regular deflagration.

If the MM crystal is thermally insulated, its temperature is increasing as a result of a decay of the metastable state, so that there can be a mixture of both mechanisms of deflagration considered above. Whereas far from resonances a regular deflagration takes place, near resonances tunneling leads to a great increase of the front speed. A more detailed treatment of the quantum-thermal deflagration for a realistic model of Mn$_{12}$Ac with $S_4^z$ terms in the effective Hamiltonian is given in recent Ref. [33].

Theories of fronts of tunneling mentioned above are based on the model simplification considering it as one dimensional. In the regular deflagration, there is a mechanism that makes fronts flat and smooth (laminar), so that the deflagration problem in long crystals indeed becomes 1$d$. In the case of dipolar-driven fronts of tunneling, it is not immediately clear whether fronts are flat or not, and, moreover, there is a mechanism that favors non-laminar fronts. The full 3$d$ theory of fronts of tunneling that will be presented below, numerically yields non-flat and non-laminar fronts. The latter slows down the front speed in comparison to the simplified 1$d$ theory but, nevertheless, the speed can reach values comparable with the speed of sound in MM near tunneling resonances in strong transverse field.

In the main part of this contribution, first the regular (thermal) magnetic deflagration will be considered. Then calculation of the dipolar field in molecular magnets will be explained. The final part is devoted to the theory of fronts of tunneling.

1.2 Magnetic deflagration

For the generic model of a molecular magnet the energy has the form

$$\mathcal{H} = -DS_z^2 - g\mu_B B_z S_z + \mathcal{H'},$$  \hspace{1cm} (1.1)

where $D > 0$ is the uniaxial anisotropy constant and $\mathcal{H'}$ stands for all terms that do not commute with $S_z$ and thus cause spin tunneling. In Mn$_{12}$Ac there is an additional smaller longitudinal term $-AS_4^z$, the implications of which will be discussed later. In the biased case $B_z > 0$, the dependence of the energy on $\sigma_z \equiv S_z/S$ is sketched in Fig. [1.1] The energy barrier $U$ shown in Fig. [1.1] has the form
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\[ U = (1 - h)^2 U_0, \quad U_0 = D S^2, \quad h = g \mu_B B_z / (2 DS). \] (1.2)

With \( S = 10 \) the zero-field energy barrier \( U_0 \) has a large value of 67 K in Mn\(_{12}\)Ac. The energy of the metastable state is given by \( \Delta E = 2 S g \mu_B B_z \).

In the absence of spin tunneling at low temperatures, \( U / (k_B T) \gg 1 \), the rate equation describing relaxation of the metastable population \( n \) (the fraction of magnetic molecules in the left well) has the form

\[ \dot{n} = -\Gamma \left( n - n^{(eq)} \right), \] (1.3)

where the relaxation rate is given by

\[ \Gamma = \Gamma_0 \exp \left( -\frac{U}{k_B T} \right) \left[ 1 + \exp \left( -\frac{\Delta E}{k_B T} \right) \right]. \] (1.4)

Here the second term in the square brackets describes back transitions from the stable well to the metastable well. In the strong-bias case, \( \Delta E \gg k_B T \), this term can be omitted. The equilibrium metastable population \( n^{(eq)} \) is given by

\[ n^{(eq)} = 1 / \left[ \exp \left( \frac{\Delta E}{k_B T} \right) + 1 \right]. \] (1.5)

In the strong-bias case it can be neglected.

The second equation describing deflagration is the heat conduction equation

\[ C \dot{T} = \nabla \cdot k \nabla T - \dot{n} \Delta E, \] (1.6)
where $k$ is thermal conductivity and $C$ is heat capacity. The second term on the right is the energy release due to decay of the metastable state. The heat capacity is mainly due to phonons, whereas the magnetic contribution is relatively small. At low temperatures only acoustic phonons are excited, whereas high-energy optical phonons are frozen out, thus $C$ has the form \cite{34}

$$C = Ak_B \left( \frac{T}{\Theta_D} \right)^\alpha,$$

(1.7)

where $\alpha = 3$ in three dimensions, $A = 12\pi^4/5 \simeq 234$ is a numerical factor and $\Theta_D$ is the Debye temperature, $\Theta_D \simeq 40$ K for Mn$_{12}$Ac. Although at low temperatures this expression is in a reasonable accordance with measurements on Mn$_{12}$Ac \cite{35}, its applicability range is very narrow, $T \lesssim 5$ K. On the other hand, the temperature generated in the deflagration (the so-called flame temperature) is typically above 10 K. The heat capacity of Mn$_{12}$Ac can be well described within a broad temperature range with the help of the extended Debye model (EDM) \cite{36} that comprises three different acoustic phonon modes as well as optical modes. Practically, one can use measured values of $C$ \cite{35}.

It is convenient to use the relation $C = d\mathcal{E}/dT$ to rewrite Eq. (1.6) in terms of the energy $\mathcal{E}$ as

$$\dot{\mathcal{E}} = \nabla \cdot \kappa \nabla \mathcal{E} - \dot{n} \Delta \mathcal{E},$$

(1.8)

where $\kappa = k/C$ is thermal diffusivity. The latter has not yet been measured, although a crude estimate $\kappa \simeq 10^{-5}$ m$^2$/s was deduced from experiments \cite{8, 13}. This value is comparable with that of metals. Temperature dependence of $\kappa$ that could be substantial at low temperatures remains unknown.

Equations (1.3) and (1.8), together with Eq. (1.4) and the relation

$$E(T) = \int_0^T C(T')dT',$$

(1.9)

is a strongly-nonlinear system of equations. It is easy to solve these equations numerically but it costs efforts to do it analytically. The two main problems to solve are (i) stability of the low-temperature state with respect to thermal runaway or ignition of a deflagration front and (ii) the shape and speed of the stationary deflagration front in long crystal.

\subsection*{1.2.1 Ignition of deflagration}

If the sample is perfectly thermally insulated, the whole released energy remains inside and the temperature monotonically increases. This leads to a thermal instability that can take a considerable time to develop, the ignition time. If there is a thermal contact with the environment, maintained at a
constant low temperature $T_0$, there are two possible cases. In the subcritical case, the temperature rise in the sample due to slow decay leads to temperature gradients and heat flow toward the sample boundaries that ensures a stationary low-temperature state (proper conditions of explosives’ storage). In the supercritical case, heat loss through the boundaries is insufficient to balance the increase of the heat release due to rise of temperature. This leads to ignition of a self-supporting burning process. In small crystals of MM, temperature gradients are higher and heat loss to the environment is more efficient. In larger crystals, temperature gradients are lower and thermal instability is more likely. This is why deflagration was observed in larger crystals.

Thermal instability occurs because of a stronger temperature dependence of the relaxation rate, Eq. (1.4), than that of the heat exchange with the environment. The essence of the problem is contained in the old model of explosive instability by Semenov described by a single equation

$$ \dot{T} = Q_{\text{reaction}} - Q_{\text{cooling}}, \quad (1.10) $$

where $Q_{\text{reaction}} \sim \Gamma(T)$ and $Q_{\text{cooling}} = \alpha(T - T_0)$. In the case B in Fig. 1.2, the thermal contact to the bath is too weak, $Q_{\text{cooling}} < Q_{\text{reaction}}$ at all $T$, so that the system is absolutely unstable. In the case A, the thermal contact is stronger and there is a stability range $T < T_2$, where the stationary state $T = T_1$ is an attractor. However, heating the system above $T_2$ leads to thermal explosion.

Semenov’s model is zero-dimensional, whereas in MM crystals the problem is at least one-dimensional and more complicated. There are different cases of thermal instability, mainly instability of a large crystal initially at uniform
temperature (that begins at the center), instability due to heating one end of a long crystal, and the instability due to a magnetic field gradient that makes the barrier lower at one side of the crystal. Analysis of all these cases has been done in Ref. [21]. In particular, when the magnetic field and temperature of the sample boundary \( T_0 \) are independent of coordinates, the crystal loses stability against formation and propagation of the flame (magnetic avalanche) when the rate of the spin flip for an individual molecule, \( \Gamma(H, T_0) \), exceeds

\[
\Gamma_c = \frac{k_B T_0}{U} \frac{8kT_0}{l^2 n_i \Delta E}.
\]

Here \( k \) is thermal conductivity at \( T_0 \) and the length parameter \( l \) is uniquely determined by geometry, being of the order of the smallest dimension of the crystal, whereas \( n_i \) is the metastable population in the initial state.

Experimentally magnetic deflagration can be initiated either by heating one end of the crystal [11–13] or by sweeping the magnetic field in the positive direction, that reduces the energy barrier and makes the condition in Eq. (1.11) satisfied [8]. In Ref. [10] deflagration was ignited by surface acoustic waves (SAW), instead of heating.

### 1.2.2 Deflagration fronts

Fronts of magnetic burning propagating in long crystals of molecular magnets are flat and smooth, i.e., the problem of deflagration is one-dimensional. The stability of flat fronts can be immediately seen. Indeed, if a fraction of a front gets ahead of neighboring fractions, the heat released at this place will be propagating not exactly straight ahead (as in a flat front) but also sideways. This will slow down this leading fraction of the front and speed up the lagging fractions surrounding it. Thus any local deviation from a flat front will disappear with time.

In a stationary-moving front, all physical quantities depend only on the combined variable that can be chosen, e.g., in the time-like form \( u \equiv t - z/v \), where \( v \) is the front speed. In terms of \( u \) the deflagration equations have the form

\[
\frac{dn}{du} = -\Gamma(T) \left( n - n^{(eq)}(T) \right)
\]

\[
\frac{d\mathcal{E}}{du} = \frac{1}{v^2} \frac{d}{du} \kappa \frac{d\mathcal{E}}{du} - \frac{dn}{du} \Delta E
\]

plus Eq. (1.9). Integrating the energy equation one obtains

\[
\mathcal{E} + n \Delta E - \frac{\kappa}{v^2} \frac{d\mathcal{E}}{du} = \text{const.}
\]
Far before and far behind the front, the term with the derivative vanishes. Thus one obtains the energy conservation law in the form

\[ E_i + n_i \Delta E = E_f + n^{(eq)}_f(T_f) \Delta E, \quad (1.14) \]

where \( i \) stands for "initial" (before the front) and \( f \) stands for "final" or "flame". This is a transcendental equation for the flame temperature \( T_f \) that has to be solved together with Eq. (1.9). If \( E_i \approx 0 \) (low initial temperature) and \( n^{(eq)}_f(T_f) \) is negligible (full-burning case realised at a strong bias, see Eq. (74) of Ref. [21]) one immediately finds the flame energy from \( n_i \Delta E \approx E_f \), and then \( T_f \) follows by inverting Eq. (1.9). In the incomplete-burning regime at small bias, a pulsating instability of stationary deflagration fronts [37] was found. The operations above assume that the heat is not exchanged via the sides of the crystal. In the opposite case, the energy conservation becomes invalid and the theory has to be extended.

One can immediately get an idea of the front speed by rewriting the deflagration equations (1.12) in the dimensionless form. In terms of the reduced variables

\[ \tilde{n} \equiv n/n_i, \quad \tilde{\mathcal{E}} \equiv \mathcal{E}/(n_i \Delta E), \quad \tilde{u} \equiv u \Gamma_f \quad (1.15) \]

and parameters

\[ \tilde{\Gamma} \equiv \Gamma/\Gamma_f, \quad \tilde{\kappa} \equiv \kappa/\kappa_f \quad (1.16) \]

equations (1.12) become

\[ \frac{d\tilde{n}}{d\tilde{u}} = -\tilde{\Gamma} \left( \tilde{n} - \tilde{n}^{(eq)} \right) \]
\[ \frac{d\tilde{\mathcal{E}}}{d\tilde{u}} = \frac{1}{\tilde{v}^2} \frac{d^2 \tilde{\mathcal{E}}}{d\tilde{u}^2} - \frac{d\tilde{n}}{d\tilde{u}} \quad (1.17) \]

where the reduced front speed \( \tilde{v} \) is related to the actual front speed \( v \) by

\[ v = \tilde{v} \sqrt{\kappa_f \Gamma_f}. \quad (1.18) \]

Refs. [2,8] give the expression above without \( \tilde{v} \) for the front speed.

It turns out that \( \tilde{v} \) in Eq. (1.18) is not merely a number but rather it is a function of dimensionless parameters such as

\[ W_f \equiv U/(k_BT_f). \quad (1.19) \]

Because of the non-linearity of Eq. (1.17), their general analytical solution that defines \( \tilde{v} \) does not exist. There are two parameter ranges in the problem: Slow-burning high-barrier range \( W_f \gg 1 \) and fast-burning low-barrier range \( W_f \ll 1 \).

In the former, burning occurs in the front region where the temperature is already close to \( T_f \). Assuming that \( \kappa \) is temperature independent, \( \tilde{\kappa} = 1 \), and linearizing \( \Gamma(T) \) near \( T_f \), one can solve the problem analytically. Within
the full-burning approximation \((n^\text{eq} \Rightarrow 0)\) the reduced front speed is given by \[ \tilde{v} = \sqrt{\frac{C_f T_f k_b T_f}{n_i \Delta E U}}. \] (1.20)

With the help of Eq. (1.7) (that is not accurate, however!) this result simplifies to
\[ \tilde{v} = \sqrt{\frac{(\alpha + 1)}{W_f}}. \] (1.21)

The applicability range of these expressions is \(\tilde{v} \ll 1\).

The corresponding profile of the metastable population \(n\) in the front has the form
\[ \tilde{n} = \frac{1}{1 + e^u} = \frac{1}{2} \left( 1 - \tanh \frac{\tilde{u}}{2} \right) \] (1.22)
that corresponds to the symmetric \(\tanh\) magnetization profile \(\sigma_z = 1 - 2n = \tanh(\tilde{u}/2)\). In real units the result reads
\[ n = \frac{n_i}{2} \left[ 1 + \tanh \left( \frac{z}{2\tilde{v}_l} - \frac{T_f t}{2} \right) \right], \] (1.23)
where \(l_d = \sqrt{\kappa_f / T_f}\) is the \(a\)-\textit{priori} with of the deflagration front. Magnetization profile of this kind can be seen in Fig. 11 of Ref. \[21\] and in the upper panel of Fig. 10 of Ref. \[33\]. The reduced energy in the front is given by
\[ \tilde{E} = (1 - e^{-u})^{-\tilde{v}^2} = (1 - \tilde{n})\tilde{v}^2. \] (1.24)

Since in the high-barrier approximation \(\tilde{v} \ll 1\), the formula above yields \(\tilde{E} \approx 1\) in the active burning region and actually everywhere except for the region far ahead of the front where \(\tilde{n}\) is very close to 1. This justifies the approximation made.

It should be noted that the full-burning approximation used above requires a bias high enough thus the barrier low enough, \(W_f \lesssim 6\), according to Eq. (79) of Ref. \[21\]. Thus the applicability range of the slow-burning high-barrier approximation is rather limited. The theory can be improved by taking into account incomplete burning. However, this makes analytics cumbersome because of the transcendental equation (1.13) defining \(T_f\). Numerical solution for the deflagration front poses no problems, nevertheless. Because of incomplete burning, \(T_f\) and thus the front speed decrease below the values given above.

In the low-barrier fast-burning regime \(W_f \lesssim 1\) there is no rigorous analytical solution to the problem. Additionally, the Arrhenius form of the relaxation rate, Eq. (1.4), becomes invalid. In this regime the magnetization profile is asymmetric, as can be seen in the upper panel of Fig. 12 of Ref. \[33\].

Making the symplifying approximation for the relaxation rate
\[ \tilde{\Gamma}(\tilde{E}) = \begin{cases} 0, & \tilde{E} < \tilde{E}_0 \\ 1, & \tilde{E} > \tilde{E}_0 \end{cases}, \] (1.25)
where $\tilde{E}_0$ will be defined below, one can solve the problem of a stationary deflagration front in the whole parameter range. Let us search for the front in which $\tilde{E} = \tilde{E}_0$ at $u = 0$. In the reduced form of the energy equation (1.13),

$$\frac{d\tilde{E}}{d\tilde{u}} = \tilde{v}^2 (\tilde{E} + \tilde{n} - 1),$$

one has $\tilde{n} = 1$ before the front, $u < 0$. Thus here the energy equation solves to

$$\tilde{E} = \tilde{E}_0 e^{\tilde{v}^2 \tilde{u}}.$$  \hfill (1.27)

On the other hand, for $u > 0$ the solution of the population equation $d\tilde{n}/d\tilde{u} = -\tilde{F} \tilde{n} = -\tilde{n}$ reads $\tilde{n} = e^{\tilde{v} \tilde{u}}$. Inserting this into Eq. (1.26), and integrating the differential equation, one obtains the solution

$$\tilde{E} = \left( \tilde{E}_0 - \frac{1}{1 + \tilde{v}^2} \right) e^{\tilde{v}^2 \tilde{u}} + 1 - \frac{\tilde{v}^2}{1 + \tilde{v}^2} e^{-\tilde{u}}.$$  \hfill (1.28)

The first term of this expression must vanish because of the boundary condition $\tilde{E}(\infty) = 1$. This defines the reduced front speed,

$$\tilde{v} = \sqrt{\frac{1}{\tilde{E}_0} - 1}.$$  \hfill (1.29)

To define $\tilde{E}_0$, consider the reduced Arrhenius relaxation rate
\[ \tilde{\Gamma} = \exp\left[ W_f \left( 1 - \frac{1}{\tilde{T}} \right) \right] \]  

and require

\[ W_f \left( 1 - \frac{1}{\tilde{T}_0} \right) = -1 \]  

as the switching point between \( \tilde{\Gamma} = 0 \) and \( \tilde{\Gamma} = 1 \). This yields

\[ \tilde{T}_0 = \frac{W_f}{1 + W_f}. \]  

Using Eq. (1.7), one obtains

\[ \tilde{\xi}_0 = \tilde{T}_0^{\alpha+1} = \left( \frac{W_f}{1 + W_f} \right)^{\alpha+1}. \]  

Substituting this into Eq. (1.29), one finally obtains

\[ \tilde{\nu} = \sqrt{\left( \frac{1 + W_f}{W_f} \right)^{\alpha+1}} - 1. \]  

Limiting cases of this formula are

\[ \tilde{\nu} \approx \begin{cases} \sqrt{(\alpha + 1)/W_f}, & W_f \gg 1 \\ 1/W_f^{\alpha+1/2}, & W_f \ll 1. \end{cases} \]  

It is remarkable that the rigorously obtained high-barrier slow-burning result of Eq. (1.21) is recovered exactly. In the low-barrier fast-burning case the reduced front speed becomes large, as well as the actual front speed of Eq. (1.18). One can see that Eq. (1.34) is in a good accordance with the numerical solution shown in Fig. 1.3.

The high-speed regime of the deflagration should be superceded by detonation when the front speed approaches the speed of sound. In detonation, thermal expansion resulting from burning sends a shock wave into the cold region before the front. As a consequence, the temperature before the front rises as a result of compression, initiating burning. Such a mechanism was recently considered for Mn_{12}Ac in Ref. [17].
1.3 Fronts of tunneling

1.3.1 Tunneling effects in the relaxation rate

The relaxation rate $\Gamma$ including spin tunneling is at the foundation of the quantum theory of deflagration in molecular magnets. In the generic model of MM, Eq. (1.1), tunneling resonances occur at the values of the total bias field $B_{\text{tot},z}$ (including the self-produced dipolar field) equal to

$$B_k = kD/(g\mu_B), \quad k = 0, \pm 1, \pm 2, \ldots$$

(1.36)

for all the resonances. Spins tunneling leads to the famous steps in the dynamic hysteresis curves [26–28]. In the real Mn$_{12}$Ac there is an additional term $-AS_z^4$ that makes higher-energy resonances be achieved at smaller $B_z$ than low-energy resonances. The resulting tunneling multiplets

$$g\mu_BB_{km} = k \left[ D + (m^2 + (m + k)^2) A \right]$$

(1.37)

were used to experimentally monitor [38,39] the transition between thermally assisted and ground-state tunneling [40] in Mn$_{12}$Ac. Below $B_k$ will stand for the resonance field $B_{km}$, for simplicity of notations.

In the case of an isolated magnetic molecule, the probability of a spin to be in one of the resonant quantum states is oscillating with time with the frequency $\Delta/\hbar$, where $\Delta$ is the tunnel splitting. However, coupling to the environment, e.g., to phonons, introduces damping to these oscillations. If the decay rate of at least one of the resonance states, $\Gamma_m$ or $\Gamma_{m'}$, exceeds $\Delta/\hbar$, tunneling oscillations of the spin are overdamped. This can be illustrated in the case of a resonance between the metastable ground state $|-S\rangle$ and the matching excited state at the other side of the barrier $|m\rangle$ of a biased MM at zero temperature. Ignoring all other levels, that is justified at $T = 0$, one can write down the Schrödinger equation in the form [31]

$$\dot{c}_{-S} = -\frac{i}{\hbar} \frac{\Delta}{2} c_{m'}$$

$$\dot{c}_{m'} = \left( \frac{iW}{\hbar} - \frac{1}{2} \Gamma_{m'} \right) c_{m'} - \frac{i}{\hbar} \frac{\Delta}{2} c_{-S},$$

(1.38)

where

$$W \equiv \varepsilon_{-S} - \varepsilon_{m'} = (S + m')g\mu_B(B_{\text{tot},z} - B_k)$$

(1.39)

is the energy bias between the two levels. Whereas the level $|-S\rangle$ is undamped, the level $|m\rangle$ can decay into lower-lying levels in the same well via phonon-emission processes. At $T = 0$ there are no incoming relaxation processes for $|m\rangle$. In this case the damped Schrödinger equation above is accurate, as it can be shown to follow from the density matrix equation. In the underdamped case $\Gamma_{m'} \lesssim \Delta/\hbar$ the solution of these equations is oscillat-
ing. The first choice for studying tunneling dynamics in molecular magnets is the overdamped case \( \Gamma_m' \gg \Delta/\hbar \), since for not too strong transverse fields \( B_\perp \) the tunnel splitting \( \Delta \) is a high power of \( B_\perp \) (Ref. [41]) and typically it is much smaller than \( \Gamma_m' \). In the overdamped case the variable \( c_{m'} \) in Eq. (1.38) adiabatically adjusts to the instantaneous value of \( c_{-S} \) and the solution greatly simplifies. Setting \( \dot{c}_{m'} = 0 \) in the second of these equations, one obtains

\[
c_{m'} = \frac{\Delta}{2\hbar} \frac{c_{-S}}{W/\hbar + i\Gamma_m'/2}.
\]

(1.40)

Inserting this into the first of equations (1.38) yields a closed differential equation for \( c_{-S} \). Using \( n = |c_{-S}|^2 \) for the metastable occupation number, one arrives at the rate equation

\[
\dot{n} = -\Gamma n,
\]

(1.41)

where the dissipative resonance-tunneling rate \( \Gamma \) is given by [42]

\[
\Gamma = \frac{\Delta^2}{2\hbar^2} \frac{\Gamma_m'/2}{(W/\hbar)^2 + (\Gamma_m'/2)^2}.
\]

(1.42)

This is a Lorentzian function with the maximum at the resonance, \( W = 0 \). Eqs. (1.41) and (1.42) were used in Refs. [30,31] to study dipolar-controlled fronts of tunneling at \( T = 0 \), or “cold deflagration”. The full system of equations (1.38) could also be used to this purpose but nothing had been published up to date.

At nonzero temperatures, tunneling transitions via higher energy level pairs become possible (thermally-assisted tunneling) and one has to take into account non-resonant thermal transitions over the top of the barrier. This makes the problem more complicated, and one needs to use the density matrix equation (DME) taking into account spin-phonon interactions explicitly. One of the first works using DME for Mn_{12}Ac was Ref. [42] in which spin tunneling was considered with the help of the high-order perturbation theory [41] for a small transverse field \( B_\perp \). The spin-phonon processes taken into account were due to dynamic tilting of the anisotropy axis by transverse phonons. Ref. [42] could qualitatively explain thermally-assisted tunneling via the level pairs just below the classical barrier. However, tunneling via low-lying resonant level pairs or tunneling directly out of the metastable ground state are inaccessible by this method because large enough splitting requires non-perturbatively large transverse field that can only be dealt with numerically.

Further work on spin-phonon relaxation in MM lead to elucidation of the universal relaxation mechanism [43,44]. This mechanism consists in distortionless rotation of the crystal field acting on a magnetic molecule, actually the same mechanism as used in Ref. [42]. It was, however, understood that this mechanism does not require any poorly-known spin-lattice coupling constants
and everything can be expressed through much easier accessible crystal-field parameters. This mechanism was overlooked in older theories of spin-lattice relaxation based on energy contributions responsible for the coupling. Rotations, to the contrary, cost no energy and the effect has a purely inertial origin.

**Fig. 1.4** Relaxation rate of Mn$_{12}$Ac vs temperature and longitudinal magnetic field in a small transverse field. Resonance multiplets with $k = 2, 3$ are seen.

**Fig. 1.5** Relaxation rate of Mn$_{12}$Ac vs temperature and longitudinal magnetic field in the transverse field $B_\perp = 3.5$ T. One can see the ground-state resonance at $B_z = 0.522$T and the first-excited-state resonance at $B_z = 0.490$T for $k = 1$ multiplet.
The universal relaxation mechanism allows a general numerical implementation of the DME fully based on the crystal field parameters, recently accomplished in Ref. [45] that summarizes the current state of the problem. Another important feature of Ref. [45] is using the so-called semi-secular approach capable of dealing with resonant pairs of levels and thus describe spin tunneling. Conventional implementations of the DME (see, e.g., Ref. [46]) use the secular approach that crashes on tunneling resonances. In Ref. [45] the relaxation rate $\Gamma$ is extracted from the time-dependent numerical solution of the DME (expressed in terms of eigenvalues and eigenfunctions of the density matrix) as the inverse of the integral relaxation time $\Gamma$ [47, 48]. Unlike using the lowest eigenvalue of the density matrix, this method also works at elevated temperatures.

The temperature and field dependence of $\Gamma$ in Mn$_{12}$Ac at a small transverse field ($B_\bot = 0.04$T that typically arises due to a 1º misalignment of the easy axis and the applied longitudinal field) is shown in Fig. 1.4. One can see very narrow and high maxima of $\Gamma$ (note that log $\Gamma$ is plotted) due to spin tunneling. Maxima corresponding to the ground-state tunneling, for which the maximum in $\Gamma$ does not disappear at $T = 0$, correspond to the highest value of $B_z$ in the multiplet. There are $k = 2$ and $k = 3$ tunneling multiplets seen in Fig. 1.4. Note that tunneling via low-lying resonances is relatively weak and it is eclipsed by the thermal activation contribution at higher temperatures.

At stronger transverse field such as $B_\bot = 3.5$T in Fig. 1.5, the barrier is strongly reduced and high-lying tunneling resonances are broadened away. Here, one can see the ground-state resonance ($B_z = 0.522$T) and the first-excited-state resonance ($B_z = 0.490$T) for $k = 1$ multiplet. The ground-state resonance does not disappear at the highest temperature that has an important implication in the dynamics of fronts of tunneling. Note the much higher tunneling rate at $T = 0$, in comparison to the previous figure.

A puzzle in the theory of relaxation of molecular magnets is the prefactor $\Gamma_0$ in the Arrhenius relaxation rate, Eq. (1.4), being by two orders of magnitude too small. This was already recognized in the early work [42]. Using the standard spin-lattice relaxation model considering one spin in an infinite elastic matrix, it is impossible to arrive at $\Gamma_0 \approx 10^7 s^{-1}$ observed in experiments [35, 49] without introducing artificially strong spin-phonon interactions [50]. For a strongly diluted molecular magnet, considering a single spin could be justified, but in the regular case it can not. High density of magnetic molecules should lead to such collective effects as superradiance [51–53] and phonon bottleneck [54–56]. Possibility of superradiance in fast avalanches triggered by a fast field sweep has been discussed in Ref. [15]. References [57, 58] report microwave emission from MM that can be interpreted as superradiance. However, it would be difficult to address these complicated issues while dealing with the quantum deflagration problem, so that the calculated relaxation rate will be simply multiplied by 100 to approximately match the experiment, as was done in Ref. [33].
Very sharp resonance peaks in the relaxation rate $\Gamma$ seen in Figs. 1.4 and 1.5 require an accurate calculation of the dipolar field in the crystal that can self-consistently control tunneling by setting individual molecules on or off resonance. The equations describing this are the same relaxational equation (1.3) and thermal equation (1.8), as before, only with $\Gamma$ depending on the total magnetic field

$$B_{\text{tot},z}(r) = B_z + B_z^{(D)}(r),$$

(1.43)

where $B_z$ is the external bias field and $B_z^{(D)}$ is the self-consistently calculated dipolar field. In the case of cold deflagration, the thermal equation can be discarded and one has to solve only the relaxational equation (1.41). Since the dipolar field depends on the magnetization everywhere in the crystal, the equations of quantum deflagration are integro-differential equations. Note that the transverse component of the dipolar field can be discarded because its effect is small.

For the purpose of calculating the dipolar field, conventional magneto-statics (see, e.g., Ref. [59]) is unsuitable because it provides an irrelevant magnetic field formally averaged over the microscopic scale that ignores the lattice structure. The physically relevant dipolar field is the field created at positions of magnetic molecules by all other molecules. It is a microscopic quantity that depends on the lattice structure. To illustrate this point, magnetostatic field in a uniformly magnetized long sample is $B^{(D)} = 4\pi M$, where $M$ is the magnetization. However, microscopically calculated dipolar field in a long uniformly magnetized crystal of Mn$_{12}$Ac is much smaller, $B_z^{(D)} = 5.26 M$.

It is convenient to express the $z$ component of dipolar field at site $i$ (i.e., at a particular magnetic molecule) in the form

$$B_z^{(D)} = (S g \mu_B / v_0) D_{zz},$$

(1.44)

where $v_0$ is the unit-cell volume. For Mn$_{12}$Ac one has $S g \mu_B / v_0 = 5.0$ mT. The reduced dipolar field $D_{zz}$, created by all other molecular spins polarized along the $z$ axis is given by

$$D_{i,zz} = \sum_j \phi_{ij} \sigma_{jz}, \quad \phi_{ij} = v_0 \frac{3 (\mathbf{e}_z \cdot \mathbf{n}_{ij})^2 - 1}{r_{ij}^3}, \quad \mathbf{n}_{ij} \equiv \frac{\mathbf{r}_{ij}}{r_{ij}},$$

(1.45)

where $\sigma_z \equiv S_z / S$. To calculate the sum over the lattice for the site $i$, one can introduce a small sphere of radius $r_0$ around $i$ satisfying $v_0^{1/3} \ll r_0 \ll L$, where $L$ is the (macroscopic) size of the sample. The field from the spins at sites $j$ inside this sphere can be calculated by direct summation over the lattice, whereas the field from the spins outside the sphere can be obtained by integration. The sum of the two contributions does not depend of $r_0$. If the magnetization in the crystal depends only on the coordinate $z$ along the
symmetry axis of the crystal that coincides with the magnetic easy axis $z$ (that is the case for a flat deflagration front), the integral over the volume can be expressed via the integral over the crystal surfaces. The corresponding contribution can be interpreted as that of molecular currents flowing on the surface. The details are given in the Appendix to Ref. [29].

In particular, for a uniformly magnetized ellipsoid the total result has the form

$$D_{zz} \equiv \sigma_z \sum_j \phi_{ij} = \bar{D}_{zz} \sigma_z,$$

(1.46)

independently of $i$, where

$$\bar{D}_{zz} = \bar{D}_{zz}^{(sph)} + 4\pi \nu \left(1/3 - n(z)\right)$$

(1.47)

and $\nu$ is the number of molecules per unit cell ($\nu = 2$ for Mn$_{12}$Ac having a body-centered tetragonal lattice). Here $\bar{D}_{zz}^{(sph)}$ comes from the summation over a small sphere and the remaining terms come from the integration. For the demagnetizing factor one has $n(z) = 0, 1/3,$ and $1$ for a cylinder, sphere, and disc, respectively. One obtains $\bar{D}_{zz}^{(sph)} = 0$ for a simple cubic lattice, $\bar{D}_{zz}^{(sph)} < 0$ for a tetragonal lattice with $a = b < c$, and $\bar{D}_{zz}^{(sph)} > 0$ for that with $a = b > c$. The latter is the case for Mn$_{12}$Ac having $\bar{D}_{zz}^{(sph)} = 2.155$. For a long cylinder this results in $\bar{D}_{zz}^{(cyl)} = 10.53$ or, in real units [14,29],

$$B_D^{(cyl)} = 52.6 \text{ mT}.$$  

(1.48)

The dipolar energy per magnetic molecule can be written in the form $E_0 = -(1/2)\bar{D}_{zz} E_D$, where

$$E_D \equiv (S g\mu_B)^2 / v_0$$

(1.49)

is the characteristic dipolar energy, $E_D/k_B = 0.0671$ K for Mn$_{12}$Ac. The role of the DDI in spin tunneling is defined by the ratio of the typical dipolar bias $W^{(D)} = 2S g\mu_B B_z^{(D)} = 2E_D \bar{D}_{zz}^{(cyl)}$ to the width of the overdamped tunneling resonance $\Gamma_m$ in Eq. (1.42). It is thus convenient to introduce the parameter

$$\bar{E}_D \equiv 2E_D/(\hbar \Gamma_m')$$

(1.50)

that is always large. For instance, using the experimental Arrhenius prefactor $\Gamma_0 \simeq 10^7 s^{-1}$ for $\Gamma_m'$, one obtains $\bar{E}_D \simeq 10^3$.

For a cylinder of length $L$ and radius $R$ with the symmetry axis $z$ along the easy axis, magnetized with $\sigma_z = \sigma_z(z)$, the reduced dipolar field along the symmetry axis has the form

$$D_{zz}(z) = \int_{-L/2}^{L/2} dz' \frac{2\pi \nu R^2 \sigma_z(z')}{(z' - z)^2 + R^2} - k_D \sigma_z(z),$$

(1.51)
where $\sigma_z = 1 - 2n$ is polarization of pseudospins representing spins of magnetic molecules ($\sigma_z = \pm 1$ in the ground and metastable states, respectively) and

$$k_D \equiv \frac{8\pi\nu}{3} - \bar{D}_{zz}^{(sph)} = 4\pi\nu - \bar{D}_{zz}^{(cycl)} > 0,$$

(1.52)

$k_D = 14.6$ for Mn$_{12}$Ac. In Eq. (1.51), the integral term is the contribution of the crystal surfaces, while the lattice-dependent local term is the contribution obtained by direct summation over lattice site within the small sphere $r_0$ minus the integral over this sphere that must be subtracted from the integral over the whole crystal's volume. For other shapes such as elongated rectangular, one obtains qualitatively similar expressions [31].

A striking feature of Eq. (1.51) is that the integral and local terms have different signs. The integral term changes at the scale of $R$ while the local term can change faster, that creates a non-monotonic dependence of $D_{zz}(z)$. In the case of a regular magnetic deflagration, the spatial magnetization profile in the slow-burning limit is of the type $\sigma_z(z) = -\tanh (|z - z_0|/l_d)$, where $l_d$ is the width of the deflagration front that satisfies $l_d \ll R$, c.f. Eq. (1.23).

The resulting dipolar field is shown in Fig. 1.6, where the line is the result of Eq. (1.51) and points represent the dipolar field along the symmetry axis of a long cylindrical crystal calculated by direct summation of microscopic dipolar fields over the Mn$_{12}$Ac lattice. One can see that Eq. (1.51) is pretty accurate, small discrepancies resulting from $l_d$ being not large enough in comparison to the lattice spacing $a$. The central region with the large positive slope is dominated by the local term of Eq. (1.51) that changes in the direction opposite to that of the magnetization. For $R \gg l_d$, $D_{zz}$ reaches the values $\pm 14.6$ due to the local term before it begins to slowly change in the opposite direction. In real units the dipolar field at the local maximum and minimum

Fig. 1.6 Reduced dipolar field in a deflagration front in the slow-burning limit, created by the magnetization profile $\sigma_z(z) = -\tanh (|z - z_0|/l_d)$. Analytical result: Eq. (1.51).

Points: Direct summation of dipolar fields over Mn$_{12}$Ac lattice.
is $\pm B^{(kD)}_z$, where

$$B^{(kD)}_z = 72.9 \text{ mT},$$

(1.53)

exceeding the dipolar field of the uniformly magnetized long cylinder Eq. (1.48). Also one can see from Fig. 1.51 that the dipolar field becomes opposite to the magnetization at the ends of the cylinder, that should lead to an instability of the uniformly-magnetized state in zero external field.

The 1d theory of fronts of tunneling [30–33] is based on the simplifying assumption that the deflagration front is flat, $\sigma_z = \sigma_z(z)$, and the dipolar field is given by Eq. (1.51) everywhere. Since, in fact, the dipolar field also depends on the distance from the crystal’s symmetry axis, it is likely that such a more complicated structure of $B_z$ will self-consistently affect the front structure, making it non-flat.

There is also a question of stability of a smooth front at a small scale. Whereas flat and smooth fronts of regular burning are stable, there is an instability mechanism for a flat front in the presence of tunneling controlled by dipolar fields that will be explained below. This is why it is important to develop a full 3d theory of fronts of tunneling.

If the magnetization $\sigma_z$ of a MM crystal depends on all the coordinates $x, y, z$ but this dependence still has a macroscopic scale, one can again use the method of calculating the dipolar field that combines summation over a small sphere (where $\sigma_z$ does not change) and integration over the remaining volume of the crystal. In this case the integral over the volume does not reduce to an integral over the surface and it has to be done numerically. In the solution of the deflagration problem, it is convenient to discretize the volume of the crystal and use the same grid to sample the magnetization variables and to calculate the dipolar field. A problem with this integral is that a small sphere of radius $r_0$ (around each point $r \equiv r_i$ where the dipolar field is calculated) has to be excluded from integration and the contribution of this excluded region is comparable with the total result because of the singularity of the DDI.

The solution to this problem is, for any point $r$, to add and subtract the dipolar field in a uniformly magnetized crystal with $\sigma_z = \sigma_z(r)$. The total reduced dipolar field can be thus represented as

$$D_{zz}(r) = \int d r' \phi(r' - r) (\sigma_z(r') - \sigma_z(r)) + \sigma_z(r) (\vec{D}_{zz}(r) - kD),$$

(1.54)

where $\phi$ is defined in Eq. (1.45). Because of the terms subtraction at $r' \rightarrow r$, the contribution of the excluded small sphere in the intergal is negligible and the integral can be extended to the whole volume of the crystal. Then the values of the integral for all points of a rectangular grid can be computed via a summation method based on the fast Fourier transform (FFT) that takes $\sim N \log(N)$ operations, where $N$ is the number of grid points. Straightforward calculation of the integral costs $\sim N^2$ operations and it has to be avoided.
The remainder of Eq. (1.54) corresponds to a uniformly magnetized crystal and its structure is similar to Eq. (1.51). Again, the term with $k_D$ is the local contribution, while $\bar{D}_{zz}(r)$ is the contribution of surface molecular currents, the result of conventional magnetostatics. For a crystal of a rectangular shape with dimensions $L_x \times L_y \times L_z$ the result can be obtained as a particular case of Eq. (88) of Ref. [60] and it has the form

\[
\bar{D}_{zz}(r) = \sum_{\eta_x, \eta_y, \eta_z = \pm 1} \arctan \left( \frac{(L_x + \eta_x x)^{-1} (L_y + \eta_y y)(L_z + \eta_z z)}{\sqrt{(L_x + \eta_x x)^2 + (L_y + \eta_y y)^2 + (L_z + \eta_z z)^2}} \right),
\]

in total 16 different $\arctan$ terms.

### 1.3.3 Fronts of tunneling at $T = 0$

The theory of dipolar-controlled fronts of tunneling at $T = 0$ ("cold deflagration") [30,31] uses the relaxational equation (1.41) with the resonance tunneling rate of Eq. (1.42), in which the energy bias $W$ is given by Eq. (1.39) with $B_{tot,z}$ of Eq. (1.43). Within the 1d approximation [30,31], the dipolar field is given by Eqs. (1.44) and (1.51) for a cylinder. The problem is thus an integro-differential equation.

It is convenient to use the reduced energy bias $\tilde{W} \equiv W/(2E_D)$ that has the form

\[
\tilde{W} = \tilde{W}_{ext} + D_{zz}, \quad \tilde{W}_{ext} = \frac{(S + m')g\mu B}{2E_D}(B_z - B_k),
\]

where $m' = S - k$ is close to $S$ for not too strong bias. Propagating dipolar-controlled fronts of tunneling have been found numerically [30,31] and analytically [31] within the dipolar window near the resonance

\[
0 \leq \tilde{W}_{ext} \leq \tilde{D}_{zz}^{(cyl)},
\]

where $\tilde{D}_{zz}^{(cyl)} = 10.53$. In real units this yields the dipolar window

\[
B_k \leq B_z \leq B_k + B_z^{(D)},
\]

where $B_z^{(D)}$ is given by Eq. (1.48) for Mn$_{12}$Ac.

The solution for the front of tunneling depends on several parameters such as the transverse size of the crystal $R$ and the resonant value of the relaxation rate of Eq. (1.42), $\Gamma_{res} = \Delta^2/(\hbar^2 \Gamma_{m'})$. Rewriting the equations in a reduced form [31], one immediately finds that the front speed is of order $\Gamma_{res}R$. The only non-trivial parameter is $\tilde{E}_D$, Eq. (1.50). An analytical solution of the problem is possible because of the large value of $\tilde{E}_D$. The front speed is given
within the dipolar window, independently of $\tilde{E}_D$. Above $B_k + B_z^{(D)}$ the front speed is zero. The reason for this is that for the external field above $B_k + B_z^{(D)}$, the total field well before the front (where all spins are directed in the metastable negative direction and produce the dipolar field $-B_z^{(D)}$) is above its resonance value $B_k$ (and spin tunneling would even increase the total field). Thus in this case resonance tunneling transitions cannot occur. To the contrast, just below $B_k + B_z^{(D)}$ the field well before the front is a little bit below the resonance and increases closer to the front where the magnetization is switching. In this case, there is a wide region where the system is close to the resonance, and the front speed becomes very high. Thus as $B_z$ crosses the value $B_k + B_z^{(D)}$ from below, the front speed diverges and then drops abruptly.

Let us compare the speed of fronts of tunneling $v \approx \Gamma_{\text{res}} R$ with the speed of regular deflagration, Eq. (1.18). With a sufficiently strong transverse field applied, one can have $\Delta/\hbar \sim \Gamma_m$ at the applicability limit of the overdamped approximation, and then $\Gamma_{\text{res}} \sim \Gamma_m \gg \Gamma_f$ because thermal activation goes over high levels of the magnetic molecule where the distances between the levels and thus the energies of phonons involved are much smaller than for the low-lying levels, and also because $\Gamma_f$ is exponentially small since $T_f \lesssim U$.

Additionally, estimation of $l_d$ with $\kappa_f = 10^{-5} \text{m}^2/\text{s}$ and the experimental value $\Gamma_0 = 10^7 \text{s}^{-1}$ yield $l_d \sim 3 \times 10^{-4} \text{ mm}$ for $B_z$ near the first tunneling resonance and even smaller for larger bias. As in the experiment the width of the crystal was much larger than $l_d$ (0.3 mm in Ref. [8], 0.2 mm in Ref. [11], and 1 mm in Ref. [10]), one can see that $\Gamma_{\text{res}} R \gg \Gamma_f l_d$ is quite possible in a strong transverse field, and then the front of spin tunneling is much faster than the front of spin burning. A very conservative estimation with $\Gamma_{\text{res}} \Rightarrow \Gamma_f$ and $v^* \Rightarrow 1$ for the crystal 0.2 mm thick yields $v \sim 1000 \text{ m/s}$. As said above, in a strong transverse field one can have $\Gamma_{\text{res}} \gg \Gamma_f$ so that the speed of a spin-tunneling front can easily surpass the speed of sound that is about 2000 m/s in molecular magnets (see analysis in Ref. [36]).

A hallmark of the cold deflagration is residual metastable population behind the front [31] that can be rewritten as

$$n_f = (B_z - B_k) / B_z^{(D)}$$

(here $n = n_i = 1$ before the front). One can see that the change of $n$ across the front $\Delta n = 1 - n_f$ goes to zero at the right border of the dipolar window, $B_z = B_k + B_z^{(D)}$. This reconciles the situation with the general requirement that the rate of change of the magnetization of the crystal $\dot{M}$, limited by the tunneling parameter $\Delta$, remains finite. Indeed,
Fig. 1.7 Spatial profiles of the metastable population $n$ and the reduced bias $\tilde{W}$ in the front for $\tilde{W}_{\text{ext}} = 2$ and $\tilde{E}_D = 20$. Everywhere in the front the system is near the resonance, $\tilde{W} \approx 0$. At this value of $\tilde{W}_{\text{ext}}$ the solution begins to lose stability and periodic structures behind the front begin to emerge.

$$\dot{M} \propto (1 - n_f)v = \Gamma_{\text{res}} R (B_z - B_k) / B_z^{(D)}$$

reaches only a finite value $\dot{M} \propto \Gamma_{\text{res}} R$ at the right border of the dipolar window before it drops to zero.

Fig. 1.8 Reduced front speed $v^*$ of Eq. (1.59) vs the reduced bias $\tilde{W}_{\text{ext}}$ of Eq. (1.56) for different number of grid points. For $\tilde{W}_{\text{ext}} \lesssim 1$ (the laminar regime) the numerical results are in a good accordance with Eq. (1.59) (straight line).
To obtain a numerical solution for the cold deflagration, the integro-differential equation was discretized to make the integral in Eq. (1.51) a sum and the whole problem a set of coupled non-linear first-order differential equations. The program was written in Wolfram Mathematica. A typical result for spatial profiles of the metastable population \( n \) and and total energy bias \( \tilde{W} \) are shown in Fig. 1.7. In the cold deflagration front, magnetization and dipolar field are self-consistently adjusting in such a way that inside the front core of the width \( R \) the spins are on resonance and can tunnel. To the contrary, before and after the front magnetic molecules are off resonance and tunneling is blocked. One of the reasons why fronts of tunneling can be so fast is that their width \( R \) entering the expression for the front speed, Eq. (1.59), is much larger than the width of the deflagration front \( l_d \), c.f. Eq. (1.18). The solution shown in Fig. 1.8 is an example of the laminar solution for the cold deflagration front that is realized for a not too strong bias, \( \tilde{W}_{\text{ext}} \lesssim 1-2 \) or \( B_z - B_k \lesssim 5-10 \) mT.

For a stronger bias, the laminar solution becomes unstable. The front of tunneling is moving with a non-constant speed, leaving spatially-nonuniform distribution of the unburned metastable population behind. The spatial dependence of the dipolar field becomes discontinuous and the resonance condition in the front is not fulfilled (see Fig. 6 of Ref. [31]). As a result, the front speed begins to decrease as the instability develops with the increase of the bias, Fig. 1.8. The instability of the solution is manifesting itself in the dependence on the discretization, absent in the laminar regime.

The only experimentally feasible method to ignite cold deflagration is the sweep of the bias field \( B_z \). When \( B_z \) is swept in the positive direction in a negatively magnetized MM crystal, the resonance condition is first achieved at the ends of the crystal where the (negative) dipolar field is weaker (see, e.g., the right side of Fig. 1.6). Spin tunneling at the ends of the crystal caused by field sweep leads to change of the dipolar field in this region that brings the system closer to the resonance in a region of the depth of order \( R \), the transverse size of the crystal. At some moment, a spatial structure close to a stationary front of tunneling is formed and it begins to propagate into the depth of the crystal, the field sweep playing no role anymore. This mechanism is illustrated in Fig. 9 of Ref. [31]. Numerical calculations show that front of tunneling is ignited at the “magic” value of the reduced bias \( \tilde{W}_{\text{ext}} \simeq 5 \), weakly dependent on \( \tilde{E}_D \). For this value of the bias, the front of tunneling is non-laminar.

Fronts propagating at other values of the bias, including laminar fronts, can be ignited by a modified procedure proposed in Ref. [31]. First, a global bias is being changed, as before, by a uniform field sweep until the desired value of \( W_{\text{ext}} \) is reached. After that, front of tunneling can be ignited by a local increase of the bias near the crystal’s end using a small coil producing a local magnetic field. This method works well in the numerical solution of the cold deflagration problem. However, such kind of experiment has not been performed yet.
Cold deflagration can be most likely observed on thinner crystals having a good thermal contact to the environment, so that the heat released inside the crystal gets quickly removed and the temperature does not increase. As said above, the effect only exists within dipolar windows near tunneling resonances.

It was shown that disorder in resonance fields of individual magnetic molecules is compensated for by adjustment of the dipolar field in the front, so that fronts of tunneling survive.

1.3.4 1d theory of quantum deflagration

Here we consider a more general situation in which the temperature of the crystal is increasing as the result of the decay of the metastable state, the case when the crystal is thermally insulated. The decay process is controlled by both the temperature (for any bias) and by the dipolar field (near tunneling resonances). The theory of the general quantum-thermal deflagration includes the relaxation equation and the heat conduction (energy diffusion) equation, as well as the expression for the dipolar field in the 1d approximation. The relaxation rate was calculated for the generic Mn$_{12}$Ac model in Ref. and for the realistic model of Mn$_{12}$Ac containing the term that splits tunneling resonances in Ref.

Whereas an analytical solution of this problem has not been found, its qualitative features can be well understood and the numerical solution based on discretization is available. In the case of a zero or weak transverse field, that was the case in all experiments up to date, spin tunneling is thermally assisted and it only modifies the main effect of regular deflagration, resulting in tunneling peaks in the field dependence of the front speed $v(B_z)$. As in the case of regular deflagration, ignition can be achieved by raising the temperature at an end of the crystal.

Fig. 1.9 shows the front speed calculated for the bias and crystal size corresponding to the experiments in Refs. and using the relaxation rate shown in Fig. 3 of Ref. The tunneling peaks are quite pronounced, at variance with the results of these experiments. The latter can be due to a large ligand disorder in Mn$_{12}$Ac that leads to a substantial scatter of the anisotropy constant $D$ and thus of the positions of the resonances of individual molecules, especially for the bias as strong as here. Just above 3 T and just below 3.5 T there are regions where the speed is too high to be measured in this calculation, an effect of ground-state tunneling.

Spatial profiles of the magnetization, energy, and the total bias field in the deflagration front give an idea of the role played by spin tunneling. Fig. 1.10 shows the spatial profiles at the asymmetric peak of $v$ at $B_z = 2.852$ T in Fig. 1.9. Here the front speed is high because of tunneling at the face of the front, where in the lower panel the total bias field is flat at the level of the
Fig. 1.9 Numerically calculated speed of the deflagration front in a long Mn$_{12}$Ac crystal for a weak transverse field.

Fig. 1.10 Spatial profiles of the deflagration front in a small transverse field, $B_z = 0.05$ T at the peak of the front speed at $B_z = 2.852$ T. There is a resonance spin tunneling at the face of the front and burning in its central and rear parts. In the tunneling region, the total field $B_{z,tot}$ sticks to its resonance value.

tunneling resonance at $B_{z,tot} = 2.889$ T. Magnetization distribution adjusts so that the dipolar field ensures resonance for a sizable group of spins that can tunnel. Tunneling of these spins results in energy release, the temperature and relaxation rate increase, and tunneling gives way to burning in the central and rear areas of the front.

Formation of the asymmetric maxima of the front speed can be explained as follows. When $B_z$ increases, the peak of $B_{z,tot}$ that arises due to the local dipolar field (central part of Fig. [1.6]) reaches the resonant value. In thick
crystals ($R \gg l_d$) this happens if $B_z + B_z^{kD} = B_k$, where $B_z^{kD}$ is given by Eq. (1.53). This defines the left border of the dipolar window $B_z = B_k - B_z^{kD}$ (that differs from $B_z = B_k$ for the cold deflagration). At the left border of the dipolar window, a strong increase of $v(B_z)$ begins. The maximum of $B_{z,\text{tot}}$ sticks to the resonance value and becomes flat with progressively increasing width. Greater width of the resonance region results in a stronger tunneling and higher front speed. With further increase of $B_z$, the right edge of the tunneling region moves too far away from the front core into the region where the temperature is too low. As the tunneling resonance in question is thermally assisted, it disappears at low temperatures, thus the flat region of $B_{z,\text{tot}}$ cannot spread too far to the right. As a result, the flat configuration of $B_{z,\text{tot}}$ becomes unstable and suddenly $B_{z,\text{tot}}$ changes to the regular shape of the type shown in Fig. 1.6.

If a strong transverse field is applied, the barrier becomes lower and it can completely disappear at a ground-state tunneling resonance. In this case $\Gamma(T, B_k)$ is practically temperature independent and this maximum of the relaxation rate does not disappear at the highest temperatures achieved after burning, $T_f$. An example is the ground-state tunneling maximum at $B_z = 0.522$T in Fig. 1.5. Although at high temperatures this maximum is hardly visible in the log scale, it is clearly visible in the normal scale in Fig. 5 of Ref. [33]. In such strong transverse fields, the speed of the front becomes very high and spin tunneling plays the dominant role in the front propagation. Figure 1.11 shows a high front speed within a broad dipolar window

$$B_k - B_z^{(kD)} \leq B_z \leq B_k + B_z^{(D)}$$

\[ (1.62) \]
having the width of 125.5 mT. The front speed diverges towards the right edge of the dipolar window in accordance with Eq. (1.59) and becomes supersonic. A qualitatively similar behavior was observed earlier in calculations for the generic model of Mn$_{12}$Ac, see Fig. 4 of Ref. [32]. In contrast to thermally-assisted tunneling resonances, progressive flattening of $B_{z,\text{tot}}$ at its resonant value is not limited by the temperature before the front since ground-state tunneling occurs already at zero temperature. Thus the front speed diverges at the right edge of the dipolar window, Eq. (1.62), where the width of the tunneling region becomes very large.

Comparing the present results with the analytical and numerical results for the cold deflagration, one can see that thermal burning in the central and rear parts of the front are stabilizing the process, so that the laminar solution, Eq. (1.59), holds up to the right edge of the dipolar window. There is no breakdown of the laminar regime seen in Fig. 1.8 at $W_{\text{ext}} \simeq 1$.

Another feature of quantum deflagration is complete burning due to the temperature rise, in contrast to the incomplete burning in the cold deflagration, Eq. (1.60). Although the speed of the cold deflagration front diverges at $B_z \to B_k + B_z^{(D)}$ (in the laminar regime), the amount of burned metastable population goes to zero, so that the rate of burning remains finite, Eq. (1.61). In quantum deflagration burning is complete up to the equilibrium residual population $n^{(eq)}$ in Eq. (1.5) while the front speed is diverging, so that the rate of burning is diverging, too.

Accordingly, the width of the front becomes very large at $B_z \to B_k + B_z^{(D)}$, in contrast to the width of the cold-deflagration front that remains constant. The structure of the front of the quantum-thermal deflagration near the right border of the dipolar window has a two-tier structure. First goes a fast front of tunneling that reverts a small fraction of the magnetization. The latter leads to heat release that ignites a front of thermal burning that burns all. In the stationary case the speed of the second part of the front is the same but it takes time to develop, thus the width of the whole two-tier front is large. Note that the speed of the quantum deflagration front is not limited by the speed of sound, contrary to the case of detonation [17].

### 1.3.5 3d theory of quantum deflagration

As mentioned above, the 1d theory of fronts of tunneling assumes a flat front that is not well justified because the dipolar field is given by Eq. (1.51) only at the symmetry axis. Different values of $B_{z,\text{tot}}$ away from the symmetry axis should self-consistently result in the distribution of the magnetization that depends on all coordinates $x, y, z$, i.e., in a non-flat front.

On the top of this, there is an instability mechanism for a flat front at a smaller scale due to DDI. In Fig. 1.10 we have seen that, approaching a front of tunneling from before, $B_{z,\text{tot}}$ increases and reaches the resonance value,
then it becomes flat. Now, if a small fraction of the surface of a front (going from left to right and changing the magnetization in the positive direction) moves ahead of its neighbors, it produces a negative dipolar field on the lagging neighboring parts of the front, as any dipole, see Fig. 1.12. This brings the neighbors further from the resonance, so they tunnel later and their lagging increases. Conversely, lagging portions of the front produce a positive dipolar field on the leading part of the front that helps it to propagate faster. (The same mechanism leads to instability of flat domain walls considered in Ref. [29].)

The DDI instability mechanism can potentially destroy any initially flat front of tunneling, making it microscopically rough. The question is whether micro-random dipolar fields produced by a micro-random magnetization in the front are still compatible with resonance tunneling. It is clear that roughness of the front breaks the concept of the adjustment of the system to the resonance, so that the speed of the front should decrease. On the other hand, spins are crossing the resonance, although at random times, so that still there should be a speed-up of the deflagration front near tunneling resonances.

In 3d model of quantum deflagration the dipolar field was calculated using Eq. (1.54) for crystals of box shape with dimensions $L_x = L_y \ll L_z$ using the relaxation rate $\Gamma$ for $B_{\perp} = 3.5$T shown in Fig. 1.5. The crystal was discretized with about 1 million total grid points in all 3 dimensions. The resulting system of first-order nonlinear equations was implemented in Wolfram Mathematica in a vectorized form using a compiled Butcher’s 5th-order Runge-Kutta solver with a fixed step.

As expected, roughness of the front due to the dipolar instability has been detected within the dipolar window, Eq. (1.62), where the computed front
Fig. 1.13 Front speed within the $3d$ model for a strong transverse field ($B_\perp = 3.5$ T) in the vicinity of the ground-state tunneling resonance at $B_z = 0.522$ T.

Fig. 1.14 Profile of the metastable population $n$ in the $3d$ model of quantum deflagration for Mn$_{12}$Ac at $B_\perp = 3.5$ T and $B_z = 0.5$ T (upper) and 0.56 T (lower).

speed is lower than within $1d$ model, Fig. 1.11 Nevertheless, the front speedup due to spin tunneling is still huge, reaching sonic speeds in Mn$_{12}$Ac on the right of the dipolar window, see Fig. 1.13.

Outside the dipolar window, a regular deflagration with a flat front and front speed $v \simeq 50$ m/s has been found for this value of the transverse field.
With entering the dipolar window from the left, the front becomes progressively non-flat with its central part leading. Front roughness emerges and increases with the bias. Fig. 1.14 shows the profile of the metastable population $n$ for the crystal with $L_x = L_y = 0.2\text{mm}$, as in experiments of Refs. [11, 13], for $B_z = 0.5\text{T}$ and $0.56\text{T}$. The metastable population $n$ is represented as a 3d plot as a function of $x$ and $z$ with $y = 0$ at some moment of time. The unburned cold portion of the crystal on the right is shown in blue, while the burned hot part on the left is shown in red. In the upper part of the figure showing the result for $B_z = 0.5\text{T}$ the front is essentially non-flat and there is some roughness, especially strong near the symmetry axis. The speed of this front $v = 161\text{m/s}$ is already much greater than the speed of the regular deflagration, $50\text{m/s}$.

Numerical results for a larger bias $B_z = 0.56\text{T}$ and a longer crystal are shown in the lower part of Fig. 1.14. The front has a nearly sonic speed of $v = 1674\text{m/s}$ and is very rough, while becoming flat again. The animation of this process looks like precipitation. Ignition of this front occurs at some distance from the left end of the crystal where the resonance condition is fulfilled. From this point, a very fast tunneling front is propagating to the right while a regular slow burning front is propagating to the left.

1.4 Discussion

Regular temperature-driven magnetic deflagration in long crystals of Mn$_{12}$ has been experimentally observed and is relatively well understood. The lack of a quantitative accordance between the theory and experiment can be attributed to still unknown temperature dependence of the thermal diffusivity $\kappa$, as well as to the absence of a microscopic theory of relaxation in MM taking into account collective effects such as phonon/photon superradiance and phonon bottleneck.

Effects of spin tunneling on ignition of deflagration and front speed near resonance values of the bias field have been experimentally detected in zero transverse field. However, these effects are due to thermally-assistent tunneling just below the top of the barrier and they are not strong.

To the contrast, spin tunneling directly out of the metastable ground state in strong transverse fields can lead to huge effects such as supersonic quantum deflagration within the dipolar window around tunneling resonances. Unfortunately, creating an initial state for this process is practically difficult. In a strong transverse field also non-resonant spin tunneling is rather fast. During the system is being biased to reach the initial state close to the resonance, it is already relaxing and a large portion of the metastable population gets lost before a front of tunneling could start. In addition, non-resonant tunneling in a biased MM leads to heat release that can result in self-ignition if the crystal is thermally insulated.
It would be desirable to employ a fast field sweep to bring the MM into starting position for quantum deflagration in a strong transverse field without deteriorating its state. To observe non-thermal fronts of tunneling, thinner crystals with a good thermal contact to the environment have to be used.

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References

1. I. Glassman, Combustion (Academic Press, 1996)
2. L.D. Landau, E.M. Lifshitz, Fluid Dynamics (Pergamon, London, 1987)
3. T. Lis, Acta Crystallogr. B 36, 2042 (1980)
4. R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature (London) 365, 141 (1993)
5. C. Paulsen, J.G. Park, in Quantum Tunneling of Magnetization – QTM’94, ed. by L. Gunther, B. Barbara (Kluwer, Dordrecht, 1995)
6. F. Fominaya, J. Villain, P. Gaudit, J. Chaussey, and A. Caneschi, Phys. Rev. Lett. 79, 1126 (1997)
7. E. del Barco, J.M. Hernández, M. Sales, J. Tejada, H. Rakoto, J.M. Broto, E.M. Chudnovsky, Phys. Rev. B 60, 11898 (1999)
8. Y. Suzuki, M.P. Sarachik, E.M. Chudnovsky, S. McHugh, R. Gonzalez-Rubio, N. Avraham, Y. Myasoedov, E. Zeldov, H. Shtrikman, N.E. Chakov, G. Christou, Phys. Rev. Lett. 95, 147201 (2005)
9. N. Avraham, A. Stern, Y. Suzuki, K.M. Mertes, M.P. Sarachik, E. Zeldov, Y. Myasoedov, H. Shtrikman, E.M. Rumberger, D.N. Hendrickson, N.E. Chakov, G. Christou, Phys. Rev. B 72, 144428 (2005)
10. A. Hernández-Minguez, J.M. Hernández, F. Macia, A. García-Santiago, J. Tejada, P.V. Santos, Phys. Rev. Lett. 95, 217205 (2005)
11. S. McHugh, R. Jaafar, M.P. Sarachik, Y. Myasoedov, A. Finkler, H. Shtrikman, E. Zeldov, R. Bagai, G. Christou, Phys. Rev. B 76(17), 172410 (2007)
12. S. McHugh, R. Jaafar, M.P. Sarachik, Y. Myasoedov, A. Finkler, E. Zeldov, R. Bagai, G. Christou, Phys. Rev. B 80(2), 024403 (2009)
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13. S. McHugh, B. Wen, X. Ma, M.P. Sarachik, Y. Myasoedov, E. Zeldov, R. Bagai, G. Christou, Phys. Rev. B 79(17), 174413 (2009)
14. S. McHugh, R. Jaafar, M.P. Sarachik, Y. Myasoedov, H. Shtrikman, E. Zeldov, R. Bagai, G. Christou, Phys. Rev. B 79, 052404 (2009)
15. J. Vanacken, S. Stroobants, M. Malfait, V.V. Moshchalkov, M. Jordi, J. Tejada, R. Amigo, E.M. Chudnovsky, D.A. Garanin, Phys. Rev. B 70, 220401R (2004)
16. W. Decelle, J. Vanacken, V.V. Moshchalkov, J. Tejada, J.M. Hernández, F. Maciá, Phys. Rev. Lett. 102(2), 027203 (2009)
17. M. Modestov, V. Bychkov, M. Marklund, Phys. Rev. Lett. 107, 20720 (2011)
18. F. Maciá, A. Hernández-Minguez, G. Abril, J.M. Hernandez, A. García-Santiago, J. Tejada, F. Parisi, P.V. Santos, Phys. Rev. B 76(17), 174424 (2007)
19. S. Velez, J.M. Hernandez, A. Fernandez, F. Maciá, C. Magen, P.A. Algarabel, J. Tejada, E.M. Chudnovsky, Phys. Rev. B 81, 064437 (2010)
20. S. Vélez, J.M. Hernandez, A. García-Santiago, J. Tejada, V.K. Pecharsky, K.A. Gschneidner, D.L. Schlagel, T.A. Lograsso, P.V. Santos, Phys. Rev. B 85, 054432 (2012)
21. D.A. Garanin, E.M. Chudnovsky, Phys. Rev. B 76, 054410 (2007)
22. E.M. Chudnovsky, JETP 50, 1035 (1979)
23. M. Enz, R. Schilling, J. Phys. C 19, L711 (1986)
24. E.M. Chudnovsky, L. Gunther, Phys. Rev. Lett. 60, 661 (1988)
25. E.M. Chudnovsky, L. Gunther, Phys. Rev. B 37, 9455 (1988)
26. J.R. Friedman, M.P. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996)
27. J.M. Hernández, X.X. Zhang, F. Luis, J. Bartolomé, J. Tejada, R. Ziolo, Europhys. Lett. 35, 301 (1996)
28. L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, Nature 383, 145 (1996)
29. D.A. Garanin, E.M. Chudnovsky, Phys. Rev. B 78, 174425 (2008)
30. D.A. Garanin, E.M. Chudnovsky, Phys. Rev. Lett. 102, 097206 (2009)
31. D.A. Garanin, Phys. Rev. B 80(1), 014406 (2009)
32. D.A. Garanin, R. Jaafar, Phys. Rev. B 81(18), 180401 (2010)
33. D.A. Garanin, S. Shoyeb, Phys. Rev. B 85, 094403 (2012)
34. C. Kittel, Quantum Theory of Solids (Wiley and Sons, New York – London, 1963)
35. A.M. Gomes, M.A. Novak, R. Sessoli, A. Caneschi, D. Gatteschi, Phys. Rev. B 57, 5021 (1998)
36. D.A. Garanin, Phys. Rev. B 78, 020405(R) (2008)
37. M. Modestov, V. Bychkov, M. Marklund, Phys. Rev. B 83, 214417 (2011)
38. L. Bokacheva, A.D. Kent, M.A. Walters, Phys. Rev. Lett. 85, 4803 (2000)
39. W. Wernsdorfer, M. Murugesu, G. Christou, Phys. Rev. Lett. 96(5), 057208 (2006)
40. E.M. Chudnovsky, D.A. Garanin, Phys. Rev. Lett. 79, 4469 (1997)
41. D.A. Garanin, J. Phys. A 24, L63 (1991)
42. D.A. Garanin, E.M. Chudnovsky, Phys. Rev. B 56, 11102 (1997)
43. E.M. Chudnovsky, Phys. Rev. Lett. 92, 120405 (2004)
44. E.M. Chudnovsky, D.A. Garanin, R. Schilling, Phys. Rev. B 72, 094426 (2005)
45. D.A. Garanin, in Advances in Chemical Physics, vol. 147, ed. by S.A. Rice, A.R. Dinner (John Wiley & Sons, Inc., Hoboken, NJ, USA, 2012)
46. F. Luis, J. Bartolomé, J.F. Fernández, Phys. Rev. B 57, 505 (1998)
47. D.A. Garanin, V.V. Ishchenko, L.V. Panina, Teor. Mat. Fiz. 82, 242 (1990)
48. D.A. Garanin, Phys. Rev. E 54, 3250 (1996)
49. F. Luis, J. Bartolomé, J.F. Fernández, J. Tejada, J.M. Hernández, X.X. Zhang, R. Ziolo, Phys. Rev. B 55, 11448 (1997)
50. M.N. Leuenberger, D. Loss, Europhys. Lett. 46, 692 (1999)
51. R. Dicke, Phys. Rev. 93, 99 (1954)
52. E.M. Chudnovsky, D.A. Garanin, Phys. Rev. Lett. 89, 157201 (2002)
53. E.M. Chudnovsky, D.A. Garanin, Phys. Rev. Lett. 93, 257205 (2004)
54. A. Abragam, A. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970)
55. D.A. Garanin, Phys. Rev. B 75, 094409 (2007)
56. D.A. Garanin, Phys. Rev. B 77, 024429 (2008)
57. A. Hernández-Minguez, A. Jordi, R. Amigo, A. García-Santiago, J.M. Hernández, J. Tejada, Europhys. Lett. 69, 270 (2005)
58. O. Shafir, A. Keren, Phys. Rev. B 79(18), 180404 (2009)
59. L.D. Landau, E.M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, London, 1960)
60. D.A. Garanin, R. Schilling, Phys. Rev. B 71, 184414 (2005)
61. K. Park, M.A. Novotny, N.S. Dalal, S. Hill, P.A. Rikvold, Phys. Rev. B 65, 014426 (2001)
62. S. Hill, S. Maccagnano, K. Park, R.M. Achey, J.M. North, N.S. Dalal, Phys. Rev. B 65, 224410 (2002)
63. K. Park, M.A. Novotny, N.S. Dalal, S. Hill, P.A. Rikvold, Phys. Rev. B 66, 144409 (2002)