

Tunneling and EPR linewidths due to dislocations in Mn₁₂ acetate

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Abstract. We compute the width and shape of the EPR and tunneling resonances due to dislocations in Mn₁₂ acetate crystals. Uncorrelated dislocations produce the Gaussian shape of resonances while dislocations bound in pairs produce the Lorentzian shape. We stress that the uniaxial spin Hamiltonian together with crystal defects can explain the totality of experimental data on Mn₁₂.

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The discovery of resonant spin tunneling in Mn₁₂ acetate [1,2] has triggered an avalanche of theoretical and experimental works on molecular nanomagnets (see Ref. [3] for references). Despite of a significant progress made in understanding Mn₁₂ and later discovered Fe₈ spin-10 systems, a number of key questions remains unanswered. One of them is the width and shape of the tunneling resonance. Recently, we have suggested that quantum magnetic relaxation in molecular nanomagnets can be explained by dislocations in the crystal lattice [3,4]. Recent experimental works give evidence of the effect of defects on tunneling and EPR in single crystals of Mn₁₂ and Fe₈ [5–7,9–12], in accordance with our suggestions (see also Ref. [8] on EPR in Mn₁₂). The analysis of these experiments requires computation of the width and shape of EPR and tunneling resonances due to dislocations, which is done in this paper. We argue that dislocations at common concentrations provide the observed width of tunneling resonances and the observed width of the EPR in Mn₁₂ and Fe₈.

Qualitatively, the importance of dislocations is clear from the fact that they give rise to long-ranged elastic strains which modulate crystal fields and thus create spatial dependence of the magnetic anisotropy. In spin tunneling and EPR experiments the resonant values of the magnetic field are determined by the anisotropy constants. For Mn₁₂ crystals in the field parallel to the easy axis, with the Hamiltonian $\mathcal{H} = -DS_z^2 - H_z S_z + \mathcal{H}'$ (\mathcal{H}' being a small tunneling term), the resonant spin tunneling occurs at

$$H_z = kD, \quad k = 0, \pm 1, \pm 2, \dots, \pm(2S - 1), \quad (1)$$

while the EPR between the levels m and $m - 1$ at frequency ω occurs at

$$H_z = \omega - D(2m - 1). \quad (2)$$

In our two recent works [3,4] we computed \mathcal{H}' due to dislocations and neglected the effect of dislocations on the resonance condition. Meantime, the spatial dependence of the magnetic anisotropy D due to dislocations causes resonances to spread over a certain field range. This range depends on the magnetoelastic coupling, the type, and concentration of dislocations.

The terms in the magnetoelastic coupling that are responsible for the modulation of the uniaxial anisotropy constant D can be written as

$$\mathcal{H}_{me} = -D' S_z^2, \quad D' = D[g_0(\varepsilon_{xx} + \varepsilon_{yy}) - g'_0 \varepsilon_{zz}], \quad (3)$$

where

$$\varepsilon_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \quad (4)$$

is the linear deformation tensor and $\alpha, \beta = x, y, z$. The coupling constants g_0 and g'_0 must be of order one, see reference [13] and references therein. For illustrations, we will use $g_0 = g'_0 = 1$.

For screw dislocations, one has $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = 0$ so this type of dislocations does not contribute into the EPR and tunneling resonance linewidths. For edge dislocations with the axis along the z axis of the crystal and the extra plane z, y inserted at $y > 0$ (see Fig. 1) one has $u_z = 0$, whereas other displacement components are given by [14]

$$u_x = \frac{b}{2\pi} \left[\arctan \frac{y}{x} + \frac{1}{2(1-\sigma)} \frac{xy}{x^2 + y^2} \right] \quad (5)$$

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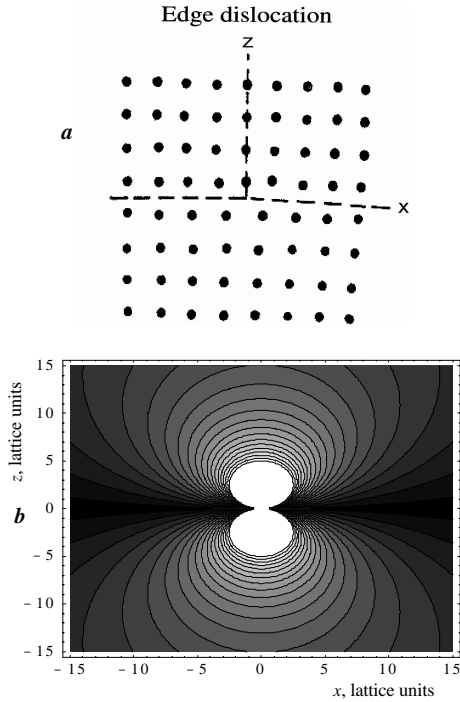


Fig. 1. (a): Edge dislocation running along the y axis with the extra plane y, z inserted at $z > 0$; (b): The magnitude of the dislocation-induced contribution into the uniaxial anisotropy constant D .

and

$$u_y = -\frac{b}{2\pi} \left[\frac{1-2\sigma}{4(1-\sigma)} \ln(x^2 + y^2) + \frac{1}{2(1-\sigma)} \frac{x^2}{x^2 + y^2} \right], \quad (6)$$

where b is the Burgers vector coinciding with the lattice period and $0 < \sigma < 1/2$ is the Poisson elastic coefficient (we will use $\sigma = 0.25$ in the numerical work). The relevant components of the deformation tensor are $\varepsilon_{zz} = 0$ and

$$\varepsilon_{xx} + \varepsilon_{yy} = -\frac{b(1-2\sigma)}{2\pi(1-\sigma)} \frac{y}{x^2 + y^2}. \quad (7)$$

Displacements due to other types of edge dislocations can be obtained from equations (5, 6) by the change of variables. In particular, for edge dislocations with the axis along the y axis of the crystal and the extra plane z, y inserted at $z > 0$ one should make a replacement $y \Rightarrow z$. This yields $\varepsilon_{yy} = 0$,

$$\varepsilon_{xx} = -\frac{b}{4\pi(1-\sigma)} z \frac{(3-2\sigma)x^2 + (1-2\sigma)z^2}{(x^2 + z^2)^2}, \quad (8)$$

and

$$\varepsilon_{zz} = -\frac{b}{4\pi(1-\sigma)} z \frac{(1+2\sigma)x^2 - (1-2\sigma)z^2}{(x^2 + z^2)^2}. \quad (9)$$

Generally, the axis of an edge dislocation can be directed along the x , y , and z axes of the crystal, and in

each of these cases there are four possible orientations of the extra crystallographic plane. One can write

$$D' = D \frac{g_D(\varphi)}{r}. \quad (10)$$

Here r is the distance from the dislocation axis, measured in the lattice units, whereas $g_D(\varphi)$ is a function of the angle which is of order one if $g_0 \sim g'_0 \sim 1$. One can immediately see from equation (10) that the contribution of dislocations in the EPR and tunneling resonance linewidth must be large. Indeed, for $r \sim 1$ one has $D' \sim D$, whereas the spatial decay of D' is slow, so that each dislocation affects a large number of molecules in the crystal thus rendering each molecule a different value of the uniaxial anisotropy. This leads to a substantial inhomogeneous broadening of resonances which follows from equations (1, 2).

In a crystal with dislocations, the deformation tensor at any given point is a sum of contributions due to many different dislocations. The superposition principle for deformations follows from the linearity of the equations of the theory of elasticity [14] and it holds everywhere outside dislocation cores, *i.e.*, for the distances from the dislocation axes $r \gtrsim 1$. Statistical properties of deformations in a crystal depend on the spatial distribution of dislocations which is poorly known. Let us find analytically the distribution of the anisotropy constant D assuming that dislocations are distributed at random. The distribution function for D' in equation (3) can be defined as

$$f_{\tilde{D}'} = \left\langle \delta \left(\tilde{D}' - \sum_{i=1}^N \tilde{D}'(\mathbf{r} - \mathbf{r}_i) \right) \right\rangle, \quad \tilde{D}' \equiv \frac{D'}{D}, \quad (11)$$

where $N \gg 1$ is the number of dislocations in the crystal and the averaging is carried out over their positions \mathbf{r}_i in the plane perpendicular to the dislocation axis within a circular region of radius R . We choose the observation point in the middle of the crystal, $\mathbf{r} = 0$. One can define

$$c = \frac{N}{\pi R^2} = \frac{1}{\pi R_c^2}, \quad (12)$$

where c is the concentration of dislocations and R_c is the characteristic distance between dislocations.

Let us at first analyze the large- $|\tilde{D}'|$ asymptotes of $f_{\tilde{D}'}$, due to the regions with large deformations of both signs close to one of dislocations. In that case one can neglect the influence of all other dislocations and consider the one-dislocation model

$$f_{\tilde{D}'} = \frac{1}{\pi R_c^2} \int_0^{2\pi} d\varphi \int_0^{R_c} r dr \delta \left(\tilde{D}' - \frac{g_D(\varphi)}{r} \right). \quad (13)$$

Integration yields

$$f_{\tilde{D}'} = \frac{(\tilde{D}'_c)^2}{|\tilde{D}'|^3}, \quad |\tilde{D}'| \gtrsim \tilde{D}'_c \equiv \frac{\sqrt{\langle g_D(\varphi)^2 \rangle}}{R_c}, \quad (14)$$

where \tilde{D}'_c is the characteristic value of D' at the distance R_c and $\langle \dots \rangle$ is the angular average. This formula becomes

invalid for $\tilde{D}' \lesssim \tilde{D}'_c$, where the lines of constant \tilde{D}' in equation (13) cross the boundary of the region under consideration, $r = R_c$. In fact, for $\tilde{D}' \lesssim \tilde{D}'_c$ equation (13) becomes invalid and one has to take into account other dislocations. Equation (14) suggests that one should introduce the distribution function for the reduced quantity α

$$f_\alpha \equiv \tilde{D}'_c f_{\tilde{D}'}, \quad \alpha \equiv \tilde{D}' / \tilde{D}'_c, \quad (15)$$

which has the asymptote

$$f_\alpha = 1/|\alpha|^3, \quad \alpha \gtrsim 1. \quad (16)$$

In the general case, with the help of the identity $2\pi\delta(x) = \int_{-\infty}^{\infty} d\omega e^{i\omega x}$, the averaging over the coordinates of different dislocations in equation (11) can be factorized,

$$f_{\tilde{D}'} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega\tilde{D}'} f(\omega)^N, \quad (17)$$

where

$$f(\omega) \equiv \frac{1}{\pi R^2} \int_0^{2\pi} d\varphi \int_0^R r dr \exp\left(-\frac{i\omega g_D(\varphi)}{r}\right). \quad (18)$$

In equation (11) we assumed for simplicity that all dislocations are of the same type.

As we shall see, in equations (17, 18), $\omega \sim R_c \ll R$ for $N \gg 1$, thus the argument of the exponential in equation (18) is small and $f(\omega)$ is close to unity. Then the exponential can be expanded and integrated, with a log accuracy, in the interval $|\omega| \lesssim r < R$. Given that $\langle g_D(\varphi) \rangle = 0$, the result has the form

$$f(\omega) \cong 1 - \frac{\omega^2 \langle g_D(\varphi)^2 \rangle}{R^2} \ln \frac{c_0 R}{|\omega| \sqrt{\langle g_D(\varphi)^2 \rangle}}, \quad (19)$$

where c_0 is a constant of order unity. Now with the use of equations (12, 14) one can write

$$\begin{aligned} f(\omega)^N &\cong 1 - \frac{\omega^2 \langle g_D(\varphi)^2 \rangle}{R_c^2} \ln \frac{c_0 R}{|\omega| \sqrt{\langle g_D(\varphi)^2 \rangle}} \\ &\cong \exp \left[-(\omega \tilde{D}'_c)^2 \ln \frac{c_0 \sqrt{N}}{|\omega| \tilde{D}'_c} \right]. \end{aligned} \quad (20)$$

At this point one may forget about the initial assumption on the circular form of the spatial region. The shape of the crystal only affects the value of the constant c_0 under the logarithm. Equation (20) confirms the assumption $\omega \sim 1/\tilde{D}'_c \sim R_c$ made above. Now we are prepared to write down the final result which is convenient to formulate in terms of the function f_α defined by equation (15)

$$f_\alpha \cong \frac{1}{\pi} \int_0^\Lambda du \cos(\alpha u) \exp\left(-u^2 \ln \frac{c_0 \sqrt{N}}{u}\right). \quad (21)$$

Here the cutoff Λ satisfies $1 \ll \Lambda \ll \sqrt{N}$; one cannot integrate up to ∞ since the form of the integrand is only valid for $u \ll \sqrt{N}$. Clearly, for large enough crystals with

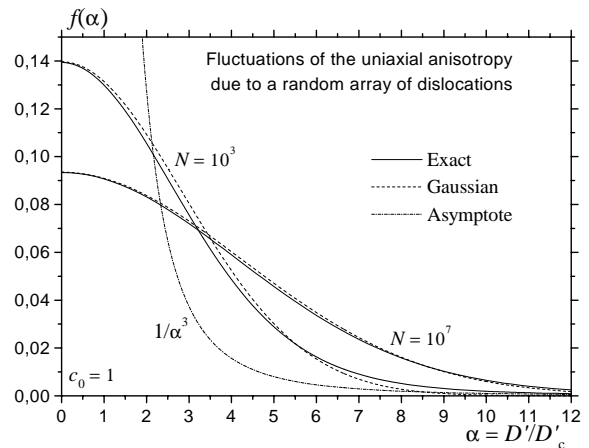


Fig. 2. Distribution of the uniaxial anisotropy due to a random array of edge dislocations.

$N \gg 1$ the result does not depend on Λ . We remind that for the edge dislocations along the Y -axis, the distribution of transverse anisotropies is an even function. The distribution is shown for $\tilde{D}' > 0$ in Figure 2.

Integrating equation (21) by parts three times, one can recover the asymptote of f_α at $|\alpha| \gg 1$ which is given by equation (16). This power-law asymptote is a consequence of the logarithmic singularity of the integrand in equation (21) at $u \rightarrow 0$ and it leads to the divergence of the second moment of f_α . On the other hand, for large N the distribution function may be well approximated by Gaussian for not too large α . Indeed, for large N the logarithm in equation (21) is weakly dependent on u and can be replaced by a constant. The best value of this constant corresponds to u for which the argument of the exponential equals one. This requires solving a transcendental equation that can be done in a perturbative way. With a good accuracy one can use

$$\ln \frac{c_0 \sqrt{N}}{u} \Rightarrow L = \ln \left[c_0 \sqrt{N \ln(c_0 \sqrt{N})} \right] \quad (22)$$

which results in the approximation

$$f_\alpha \cong \frac{1}{2\sqrt{\pi L}} \exp\left(-\frac{\alpha^2}{4L}\right) \quad (23)$$

which is also shown in Figure 2.

As the number N of dislocations in the crystal increases, the function f_α of equation (21) becomes closer and closer to the Gaussian, whereas the power-law asymptote given by equation (16) becomes shifted to the region of very large α where it is hardly visible. This effect is due to the accumulation of small contributions from dislocations situated at large distances from the observation point (of order of the linear dimension of the crystal). Such small contributions from distant dislocations, which lead to the Gaussian distribution f_α , win over contributions from close dislocations responsible for equation (16). Gaussian approximation for the function $f_{\tilde{D}'}$, with the help

of equation (15) can be written in the form

$$f_{\tilde{D}'} \cong \frac{1}{2\tilde{D}'_c\sqrt{\pi}} \exp\left(-\frac{\tilde{D}'^2}{(2\tilde{D}'_c)^2}\right), \quad (24)$$

where

$$\tilde{D}'_c \equiv \tilde{D}'_c\sqrt{L} = \sqrt{\pi\langle g_D(\varphi)^2 \rangle}\tilde{c}, \quad \tilde{c} \equiv cL. \quad (25)$$

The standard deviation of \tilde{D}' according to equation (24) is $\sigma_{\tilde{D}'} = \sqrt{2}\tilde{D}'_c$. One can see that the accumulation of contributions from distant dislocations leads to the effective logarithmic renormalization of the concentration of dislocations c with L defined by equation (22). For edge dislocations running along the z -axis, the quantity $\sqrt{\langle g_D(\varphi)^2 \rangle}$ is given by

$$\sqrt{\langle g_D(\varphi)^2 \rangle} = \frac{g_0}{2\sqrt{2\pi}} \frac{1-2\sigma}{1-\sigma}, \quad (26)$$

where σ is the Poisson elastic coefficient. For $g_0 = 1$ and $\sigma = 0.25$ one has $\sqrt{\langle g_D(\varphi)^2 \rangle} \approx 0.075$. For edge dislocations running perpendicular to the z -axis one obtains

$$\sqrt{\langle g_D(\varphi)^2 \rangle} = \frac{1}{8\pi(1-\sigma)} [8\sigma^2(g_0 - g'_0)^2 - 4\sigma(g_0 - g'_0)(3g_0 - g'_0) + 5g_0^2 - 2g_0g'_0 + (g'_0)^2]^{1/2} \quad (27)$$

which for $g_0 = g'_0$ simplifies to $\sqrt{\langle g_D(\varphi)^2 \rangle} = g_0/[4\pi(1-\sigma)]$. For $g_0 = 1$ and $\sigma = 0.25$ one has $\sqrt{\langle g_D(\varphi)^2 \rangle} \approx 0.106$.

The experimentally studied Mn_{12} crystals are rather large, about $0.5 \times 0.5 \text{ mm}^2$, which corresponds to the cross-section of about 10^{11} lattice cells. Even for the concentration of dislocations as small as $c = 10^{-4}$ per cell, the number of dislocation in the crystal is about $N \approx 10^7$. For $c_0 = 1$ this gives $L = 9.1$, *i.e.*, the effective concentration of dislocations increases by an order of magnitude, $\tilde{c} = 0.91 \times 10^{-3}$. The corresponding value of \tilde{D}'_c that follows from equations (25, 27) for the edge dislocations running perpendicular to the z axis is $\tilde{D}'_c = 0.567 \times 10^{-2}$. For $c = 10^{-3}$ one obtains $L = 10.3$, thus $\tilde{D}'_c = 1.91 \times 10^{-2}$. The renormalization of the concentration of dislocations and the Gaussian distribution of transverse anisotropies for large crystals are clearly seen in Figure 2: The distribution broadens in the α -scale due to the increase L with N , equation (22).

The dislocation mechanism proposed in this paper can qualitatively explain the experimentally observed tunneling [15] and EPR [5,6] linewidths in Mn_{12} Ac. For the realistic concentrations of dislocations $c = 10^{-3}$ the standard deviation $\sigma_{\tilde{D}'} = \sqrt{2}\tilde{D}'_c \approx 0.027$ is in accord with the fit $\sigma_D = 0.02D$ of reference [6].

Now we consider another model of distribution of dislocations in the crystal: Dislocations of opposite signs bound into pairs at the distance d . Distributions of this kind are more likely than a completely random distribution since here the energy of elastic strains is lower. At the distances $r \gg d$ from equation (10) one obtains

$$D' = -D \frac{d}{r^2} A(\varphi), \quad A(\varphi) \equiv \frac{\partial}{\partial \varphi} [g_D(\varphi) \sin \varphi], \quad (28)$$

where φ is the angle between the vectors \mathbf{r} and \mathbf{d} . The calculations following after equation (11) should be now redone with D' given by equation (28) and the parameters N , c , and R_c designating the number, concentration, and the average distance between the *dislocation pairs*. For $d \ll R_c \ll R$ the characteristic values of ω and r are $\omega \sim R_c^2/l$ and $r \sim \sqrt{\omega l} \sim R_c$. The function $f(\omega)$ in equation (17) then reads

$$\begin{aligned} f(\omega) &\cong 1 - \frac{1}{\pi R^2} \int_0^{2\pi} d\varphi \int_0^\infty r dr \left[1 - \cos\left(\frac{\omega d}{r^2} A(\varphi)\right) \right] \\ &= 1 - \frac{\pi l |\omega|}{2R^2} \langle |A(\varphi)| \rangle. \end{aligned} \quad (29)$$

This results in

$$f(\omega)^N \cong 1 - \frac{\pi l |\omega|}{2R_c^2} \langle |A(\varphi)| \rangle \cong \exp\left(-\frac{\pi l |\omega|}{2R_c^2} \langle |A(\varphi)| \rangle\right). \quad (30)$$

Finally, equation (17) yields

$$f_{\tilde{D}'} \cong \frac{1}{\pi} \frac{\tilde{D}'_c}{(\tilde{D}')^2 + (\tilde{D}'_c)^2} \quad (31)$$

with

$$\tilde{D}'_c \equiv \frac{\pi l}{2R_c^2} \langle |A(\varphi)| \rangle = \frac{\pi^2 c l}{2} \langle |A(\varphi)| \rangle. \quad (32)$$

In contrast to the random-dislocation model which is characterized by Gaussian fluctuations of the uniaxial anisotropy D , here the distribution of D is Lorentzian and its reduced width \tilde{D}'_c is by a factor $l/R_c \ll 1$ smaller than that of equation (14). The asymptote $f_{\tilde{D}'} \cong (1/\pi)\tilde{D}'_c/(\tilde{D}')^2$ at $\tilde{D}' \gg \tilde{D}'_c$ is due to a single dislocation pair, as can be checked by an independent calculation similar to that for random dislocations (*cf.* Eq. (14)). For edge dislocations running perpendicular to the z -axis and $g_0 = g'_0$, one has $\langle |A(\varphi)| \rangle = 3^{3/2}g_0/[4\pi^2(1-\sigma)]$, which for $g_0 = 1$ and $\sigma = 0.25$ yields $\langle |A(\varphi)| \rangle \approx 0.175$. For the concentration of dislocations $c = 10^{-3}$ the average distance between dislocations is according to equation (12) $R_c \approx 17.8$, in lattice units. For the size of the dislocation pair $l = 5$ which satisfies the applicability condition $l \lesssim R_c$ of equation (31) one obtains the reduced width of the distribution of the anisotropy constant $\tilde{D}'_c \approx 4.3 \times 10^{-3}$ which is expectedly smaller than that for randomly distributed single dislocations.

If the distance between dislocations in a dislocation pair l is comparable with the average distance between dislocations R_c , the distribution of D will be neither Gaussian nor Lorentzian. It still can be obtained numerically by the method described above. A more realistic model should include distribution of the dislocation-pair length l . We do not attempt to consider these more complicated models here since too little is known about the dislocations and their interaction in Mn_{12} and other molecular magnets. More detailed experimental investigation of the tunneling resonance and EPR lineshapes, as well as X-ray

scattering investigations, are needed to elucidate the distribution of dislocations in these materials. Still, the first results reported on in this paper show that dislocations at reasonable concentrations can be made responsible for the experimentally observed linewidths in Mn₁₂.

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