Square root relaxation: two possible mechanisms

J. Villain[a]

Département de Recherche Fondamentale sur la Matière Condensée D.S.M., Commissariat à l'Énergie Atomique, 17 Avenue des Martyrs, 38054 Grenoble Cedex 9, France

Abstract. Magnetic relaxation in large spin molecular paramagnets is often found to behave as $\delta M(t) \sim \sqrt{t}$ at short times t. This behaviour was explained by Prokofiev & Stamp as arising from dipole interactions between molecular spins. However, as observed by Miyashita & Saito, the same behaviour can arise from a different mechanism which, in the present work, is related to hyperfine interactions. The Miyashita-Saito scheme is found to be possible at short times if the nuclear longitudinal spin relaxation is very slow. In the case of moderately slow nuclear spin relaxation, the electronic magnetization variation $\delta M(t)$ is initially proportional to t, then to $\sqrt{t}$ and finally to $\exp(-t/\tau)$. This behaviour may be mostly expected in dilute systems.

PACS. 05.30.-d Quantum statistical mechanics – 05.40.Fb Random walks and Levy flights – 75.50.Xx Molecular magnets

1 Introduction

Synthetic molecular nanomagnets [1] provide reproducible microscopic systems with a large magnetic moment which may have macroscopic properties. The most widely studied materials are, in the usual terminology, $Mn_{12}ac$ (with a relaxation time of 2 months for the magnetization at 2 K) and Fe_8, whose faster relaxation allows easier experiments.

Magnetic relaxation of these materials at low temperature is a challenging problem. The material is initially magnetized by a strong magnetic field H^- in the easy magnetization direction z. At $t = 0$, the external field is suddenly given the value H_{ext}, also in the z direction. One measures the magnetization $M_z(t) = M_z(0) + \delta M_z(t)$. At low enough temperature, the following behaviour is observed for short times in Fe_8 [2,3] and Mn_{12} [4,5]

$$\delta M_z(t) = \delta M_z(\infty) A\sqrt{t} \qquad (1)$$

where A is a positive constant. This square root behaviour is in contrast with usual relaxation which is exponential, and therefore linear for short times, $\delta M_z(t) = \delta M_z(\infty) A't$.

The square root behaviour (1) was predicted theoretically by Prokofiev and Stamp [6] for the demagnetization of a saturated sample. The molecule of interest can be modelled by a 'molecular' spin **S**, of electronic nature, whose modulus s is large ($s = 10$ for Mn_{12} and Fe_8).

[a] e-mail: jvillain@cea.fr

This spin is subject to an anisotropy hamiltonian which, in Mn_{12}, may be written as a first approximation as

$$\mathcal{H}_0 = -K S_z^2 \qquad (2)$$

where the constant K is positive.

Relaxation is slow because positive and negative values of S_z form two different potential wells separated by a barrier of height Ks^2. At temperatures and fields of interest ($k_B T \ll Ks^2$ and $g\mu_B s H_{ext} \ll Ks^2$ where μ_B is the Bohr magneton and g the Landé factor), thermal activation by phonon absorption is not possible and magnetic relaxation takes place by spin tunneling through the barrier under the effect of additional terms of the Hamiltonian which do not commute with S_z. Such a hamiltonian, adequate for Fe_8, is $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = -K S_z^2 + g\mu_B H_z S_z + B S_x^2$, where the magnetic field **H** has been introduced.

If **H** were constant, spin tunneling would be a periodic oscillation of S_z between $-s$ and s, which could be analyzed by diagonalization of the hamiltonian. In the relaxation mechanism, the environment plays an essential part. It will be mimicked for each molecular spin by a time-dependent magnetic field $H_z(t) = H_{ext} + \Delta H_z(t)$. The additional component $\Delta H_z(t)$ is produced partly by the dipole interaction with the other molecular spins, and partly by the 'hyperfine' interaction with the nuclear spins. The transverse components ΔH_x and ΔH_y, which slightly modulate the tunnel splitting $2\hbar\omega_T$, will be neglected. The z-component ΔH_z, though not larger, is very important. Indeed, spin tunneling is only possible between two eigenstates of equation (2) which have nearly the same

energy. This occurs if, and only if the local longitudinal field H_z is close to 0 or to particular values (or 'resonances') which depend on K. Attention will be focussed on one of these values which will be called H_1. Roughly speaking, the condition for tunneling is that H_z satisfies $g\mu_B s|H_z - H_1| < \hbar\omega_T$.

Prokofiev and Stamp [6] have shown that the dipole interaction with the other molecular spins leads to square root relaxation, formula (1). In their theory, this is related to the r^{-3} behaviour of dipole interactions. It was later suggested by Miyashita and Saito [7] that square root relaxation may follow from another, completely different mechanism which may be equivalently termed 'Wiener process', 'random walk', or 'diffusion'.

2 Basic assumptions

In the present note, interactions between molecular spins are ignored. The square root law (1) is shown to arise from hyperfine interactions only if nuclear spin relaxation is very slow. If it is not so slow, our results are different from those of Miyashita and Saito.

A simplified model will be used. The assumptions are the following:

1) Interactions between molecular spins are neglected, $\Delta H_z(t)$ is the hyperfine field.
2) The hyperfine field $\Delta H_z(t)$ is a sum of independent random components $H_i^z(t)$ which can take $(2I_i+1)$ different values with a definite probability per unit time of jumping from one value to the other. The index i labels the various nuclear spins.
3) The number of nuclear spins interacting with a given molecular spin $\mathbf{S}$ is large.
4) Each molecular spin has a probability λ per unit time to relax when the local field $H_z(t) = H_{ext} + \Delta H_z(t)$ acting on this spin is comprised between $H_1 - \epsilon$ and $H_1 + \epsilon$, where
$$\epsilon \simeq \hbar\omega_T/(g\mu_B s), \qquad (3)$$
otherwise there is no relaxation. The value of λ is expected to depend on the tunnel splitting, hyperfine field and nuclear spin dynamics.

An extreme case is when a molecular spin has completely relaxed at time t if, and only if, the local field $H_z(t) = H_{ext} + \Delta H_z(t)$ acting on this spin has been equal to H_1 at some time t' between 0 and t. This limiting case will be called 'very slow nuclear relaxation'.

Assumption (1) is not claimed to be a good approximation, but a simplification consistent with our purpose, to investigate $\sqrt{t}$ relaxation arising from hyperfine interactions only.

Assumption (2) implies that quantum coherence is lost after a short time. It is an oversimplification with respect to the real mechanism of nuclear relaxation. In Mn$_{12}$ below about 0.1 K, this mechanism seems to be complex, involving inhomogeneities of the crystal [8].

Assumption (3) is physically realistic since dipole interactions are long ranged.

Assumption (4) is appropriate when $H_1 \neq 0$, so a spin can tunnel from the lowest state of its initial well to an excited state of the other well, where it deexcites with phonon emission. In the case $H_1 = 0$, tunnelling takes place between the lowest states of each well and phonons have no effect. Then assumption (4) must be reformulated. This will be done in a separate section.

3 Analogy with a random walk

According to assumption (4) the magnetization at time t depends on the probability $p(h, t)$ that the hyperfine field $H^z(t')$ has taken the value H_1 for $0 < t' < t$ if the initial field was $H^z(0) = h$. The field H^z is the sum of contributions H_i^z of many nuclei. According to assumption (2), these nuclei flip by random, uncorrelated jumps. Thus, they are similar to the steps of a random walker. In the simplest case, the random walker has the same probability to go forward or backward. Then, the probability[1] $\rho(h, h', t)$ that a random walker is at $\Delta H_z = h'$ at time t if he started from h at time 0 satisfies the diffusion equation

$$\frac{\partial}{\partial t}\rho(h, h', t) = D(h')\frac{\partial^2}{\partial h'^2}\rho(h, h', t) \qquad (4)$$

where D is related to the relaxation time of nuclear spins. It will generally be assumed to be independent of h'. Then the solution of equation (4) is

$$\rho(h, h', t) = \frac{1}{2\sqrt{\pi Dt}}\exp\frac{-(h - h')^2}{4Dt}. \qquad (5)$$

Formulae (4) and (5) are not valid for long times. Indeed the field distribution $g(\Delta H_z)$ has a finite width ΔH (Fig. 1), so that the random walker cannot reach fields higher than ΔH. This can be accounted for by a force $f(h')$. The diffusion equation is thus replaced by the Fokker-Planck equation

$$\frac{\partial}{\partial t}\rho(h, h', t) =$$
$$\frac{\partial}{\partial h'}\left\{ D\left(h'\right)\left[\frac{\partial}{\partial h'}\rho(h, h', t) - f(h')\rho(h, h', t)\right]\right\} \quad (6)$$

which describes an Ornstein-Uhlenbeck process [7]. The force is easy to calculate by writing the equilibrium condition $\rho(h, h', \infty) = g(h')$. It follows

$$f(h) = \frac{d}{dh}\ln g(h). \qquad (7)$$

If $g(h)$ is a gaussian, $g(h) = (2\pi)^{-1/2}\Delta H^{-1}\exp[-h^2/(2\Delta H^2)]$ then $f(h) = -h/\Delta H^2$.

For short times, formulae (4) and (5) are still correct in the presence of the force $f(h)$. Indeed, the displacement of the random walker is the sum of a random part, of the order of $\sqrt{Dt}$, and a drift part $Df(h)t \simeq -Dht/\Delta H^2$. The former dominates the latter for short times.

---

[1] To simplify the language, the word 'probability' will often be used instead of 'density of probability'. The actual meaning is clear from the formulae.
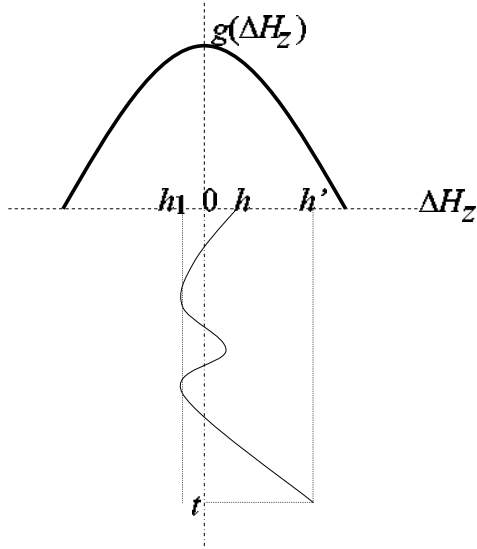
Fig. 1. The thick curve shows the hyperfine field distribution $g(\Delta H_z)$. The thin curve shows a possible evolution with time t of the hyperfine field ΔH_z on a particular molecular spin **S**.

4 Very slow nuclear spin relaxation

The resonance condition $|H_z(t) - H_1| < \epsilon$ is satisfied during a time of the order of ϵ^2/D. The flipping probability of a molecular spin during this time is $\lambda\epsilon^2/D$. If this quantity is of order unity or larger, the nuclear relaxation will be said to be 'very slow'. In that case, the proportion $n(t)$ of relaxed spins at time t is

$$n(t) = \delta M_z(t)/\delta M_z(\infty) =$$
$$\int_{-\infty}^{\infty} dh g(h) \int_{-\infty}^{\infty} dh' p_1(h_1, h, h', t) \quad (8)$$

where $p(h_1; h, h', t)$ is the probability that the random walker, who started from h at time 0, is at h' at time t and has reached $h_1 = H_1 - H_{ext}$ at some time t' between 0 and t. It is related to $\rho(h, h', t)$ by

$$\begin{cases} p_1(h_1; h, h', t) = \rho(h, h', t) \text{ if } (h - h_1)(h' - h_1) < 0 \text{ (a)} \\ p_1(h_1; h, h', t) = \rho(2h_1 - h, h', t) \text{ if } (h - h_1)(h' - h_1) > 0. \text{ (b)} \end{cases}$$
$$(9)$$

Relation (9a) is obvious and (9b) can easily be derived, or found in textbooks [9].

The integrand in equation (8) is very small unless $h - h_1$ and $h' - h_1$ are of the order of $\sqrt{Dt}$ or smaller. In that domain the integrand is of the order of $1/\sqrt{Dt}$. It follows that $\delta M(t) \sim \sqrt{Dt}$ in agreement with equation (1). The detailed calculation, based on equations (8, 9) and (5), yields

$$A = 8g(h_1)\sqrt{D/\pi} \int_0^{\infty} dx \int_0^{\infty} dy \exp\left[-(x+y)^2\right]. \quad (10)$$

There is no relaxation if $|h_1| > \Delta H$ (if resonances other than at H_1 are excluded). The maximum value of A (ob-

tained for $h_1 = 0$) is of the order of $1/\sqrt{\tau_H}$ where

$$\tau_H = \Delta H^2/D \quad (11)$$

is the longitudinal nuclear spin relaxation time. The notation T_1 has been avoided because it usually designates the spin-lattice relaxation time, related to spin-phonon interactions, which is extremely long at low temperature. The notation T_2 has also been avoided because it usually designates the transverse nuclear spin relaxation time.

5 Moderately slow nuclear spin relaxation

The nuclear spin relaxation will be called moderately slow when the relaxation of a molecular, electronic spin requires that $(H_1 - H_z)$ vanishes several times, but is already almost complete (at resonance, i.e. $h_1 = 0$) at $t = \tau_H$.

A qualitative description will be given in the case $h_1 = H_1 - H_{ext} = 0$. As seen from (5), the random walker explores in the time t a field interval $\delta h(t) \simeq \sqrt{Dt}$. The proportion of field values which have been explored at time t is thus

$$p(t) \simeq \delta h(t)/\Delta H. \quad (12)$$

This quantity $p(t)$ is also the proportion of molecular spins which have a chance to relax during the time t. For such a spin, tunneling is allowed during a time

$$t_{eff} \simeq \epsilon t/\delta h(t) \simeq \epsilon\sqrt{t/D}. \quad (13)$$

For a spin whose local field lies in the explored region $\delta h(t)$, the relative magnetization change, for short times, is λt_{eff}, and this evaluation is correct if $\lambda t_{eff} < 1$. The total relative magnetization change is for such times

$$\delta M_z(t)/\delta M_z(\infty) = p(t)\lambda t_{eff}$$

or, according to equations (12) and (13),

$$\delta M_z(t)/\delta M_z(\infty) \simeq \lambda\epsilon t/\Delta H. \quad (14)$$

This formula is different from that written by Miyashita and Saito, who assume $h = h_1$ at $t = 0$, so that $p(t)$ is replaced by 1 in equation (14), and the quantity they calculate is actually λt_{eff}, which is proportional to $\sqrt{t}$ as seen from equation (13), Therefore, they predict $\delta M_z(t) \sim \sqrt{t}$.

An expression of the maximum relaxation rate λ can be extracted from the equations of Miyashita and Saito. Indeed they find (this is their formula 3.9) $\lambda t_{eff} \simeq \alpha\hbar^2\omega_T^2\sqrt{t/D}$ where α is a constant quantity. Identifying this expression of λt_{eff} with that which can be derived from equations (13) and (3), one obtains

$$\lambda = \omega_T \tau_X \quad (15)$$

where $\tau_X = \alpha\hbar g\mu_B s$ is a constant time. Thus, Miyashita and Saito find that λ is independent of D and ΔH. This surprising result is based on the assumption of a fairly *fast* nuclear spin relaxation, and on the statement that "the

velocity of the field is proportional to $\sqrt{D}$". This point will not be discussed here.

When t becomes so large that $\lambda t_{eff} > 1$, the depolarization for an 'explored' field value is almost total and the average relative demagnetisation is $\delta M_z(t)/\delta M_z(\infty) = p(t) \simeq \sqrt{Dt}/\Delta H = \sqrt{t\tau_H}$ as in the case of very slow nuclear relaxation. This result holds if $|h_1|$ is appreciably smaller than ΔH. When $|h_1|$ approaches ΔH, the rate of change of the magnetisation can easily be shown to decrease to 0.

6 Long times

For times $t \gg \tau_H$, the random walker has lost the memory of its initial position h. Thus, to quote Miyashita and Saito, "the number of crossings" [of $H_z(t)$ with H_1 per unit time] "is ... constant in time, which causes a constant rate relaxation, i.e., the exponential relaxation". Two remarks should be added. First, the electronic spin relaxation time τ obviously depends on $h_1 = H_1 - H_{ext}$. Miyashita and Saito made detailed numerical studies, but only in the case of an external field tuned at resonance, $h_1 = 0$. When $h_1 \neq 0$ becomes larger than the width ΔH, τ obviously goes to ∞. The second remark is that, in the case of very slow or moderately slow nuclear spin resonance, which is addressed in the present note, the electronic spin relaxation is already very strong at $t = \tau_H$, i.e. $\delta M(\tau_H)/\delta M(\infty)$ is of order unity. This implies that the exponentially relaxing part is small.

7 The case $H_1 = 0$

In most of the experiments done so far, $H_1 = 0$, i.e. tunnelling takes place between the lowest state of each well. This case is peculiar. 1) The main feature is that (if phonons are completely ignored) the system of electronic and nuclear spins ignore the temperature T of the crystal, and relax to an equilibrium state which generally corresponds to another temperature T_{eff}. Indeed, only a part of the Zeeman energy of the molecular spins can be transferred to nuclear degrees of freedom. Only for $H_{ext} = 0$, when the Zeeman energy vanishes, $T_{eff} = T$; 2) if nuclear spin relaxation is not very slow, the above treatment is still acceptable for short times, because spin reversal and relaxation are nearly the same thing; 3) let the case of very slow nuclear spin relaxation be discussed. Then, when the hyperfine field ΔH_z crosses the value $-H_{ext}$, S_z follows the field adiabatically and changes sign. Thus, if $S_z(0) = s$ then $S_z(t) = s$ if $(h - h_1)$ and $(h' - h_1)$ have the same sign, while $S_z(t) = -s$ if they have a different sign. Thus, the spin never loses the memory of its initial state, which is quite unusual in a relaxation processs. For short times, formula (1) can then be derived from an argument similar, but not identical to the above one, and A turns out to be given by equation (10) again. For long times, the hyperfine field distribution is probably affected by relaxation and depends on time.

8 Validity of the very slow nuclear relaxation scheme

For a spin able to tunnel between two localized states $|-\rangle$ and $|+\rangle$, the wave function $x(t)|+\rangle + y(t)|-\rangle$ satisfies

$$\dot{x}(t) = \frac{1}{i\hbar}x(t)E^{(+)}(t) - i\omega_T y(t);$$

$$\dot{y}(t) = -i\omega_T x(t) + \frac{1}{i\hbar}y(t)E^{(-)}(t) \quad (16)$$

where the unperturbed energies $E^{(\pm)}(t)$ satisfy $E^{(-)}(t) - E^{(+)}(t) = 2g\mu_B[H_z(t) - H_1]s$.

Equation simplifies if one introduces the notations $u(t) = (1/\hbar)\int_{t_0}^t dt' E^{(+)}(t')$, $w(t) = \frac{1}{\hbar}\int_{t_0}^t dt' E^{(-)}(t')$, $x(t) = \exp[-iu(t)]X(t)$, and $y(t) = \exp[-iw(t)]Y(t)$. Moreover, the initial condition $X(0) = 1$ will be assumed, and the time will be assumed so short that $X(t)$ may be approximated by $X(0) = 1$. Then equation (16) yields $\dot{Y}(t) = -i\omega_T \exp[-iU(t)]$ where

$$U(t) = (2g\mu_B s/\hbar)\int_{t_0}^t dt'[H_z(t') - H_1]. \qquad (17)$$

Let the initial value of the local field be tuned so as to allow tunnelling. If the tunnelling window remains open until a time of the order of the tunnel period $1/\omega_T$, nuclear relaxation is very slow in the sense defined above. The condition for very slow relaxation is thus $U(1/\omega_T) < 1$. According to equation (17), $U(t)$ can be roughly evaluated as the product of $(2g\mu_B s/\hbar)$ by $\sqrt{Dt} = \Delta H\sqrt{t/\tau_H}$ and a factor t because of the integration. The condition for very slow relaxation reads

$$\frac{2g\mu_B s\Delta H}{\hbar\omega_T\sqrt{\omega_T\tau_H}} < 1. \qquad (18)$$

The hyperfine width ΔH is never smaller than 0.001 Tesla. Thus, equation (18) requires large values of τ_H and ω_T. For instance, a nuclear relaxation time $\tau_H = 1$ s implies $\omega_T \geq 10^6$ s^{-1}.

An additional condition is $\omega_T\tau_H > 1$, but condition (18) is probably stronger.

Usual nuclear spin-lattice relaxation is expected to be extremely slow at low temperature. However, measurements by Morello et al. [8] in Mn_{12}ac reveal that τ_H does not increase beyond about 0.01 second. The zero field tunnel splitting of the ground doublet does not seem to satisfy the requirement $\omega_T\tau_H > 1$ (Barbara, private communication). Thus, nuclear spin relaxation is not very slow and therefore the hyperfine field is not expected to give rise to $\sqrt{t}$ relaxation in zero external field in Mn_{12}ac, but rather to exponential relaxation.

It is of interest to recall that square root relaxation has been observed in Fe_8 on times of the order of a minute. The nuclear spin lattice relaxation times T_1 which have been reported (for instance when observing negative spin temperatures [10]) are of the same order of magnitude, but it is not clear whether so long nuclear longitudinal relaxation times can be reached in molecular nanomagnets.

9 Real systems: effect of dipole interactions

In real systems, dipole interactions between molecular spins are present and contribute to the local field by an amount which will be called 'dipole field'. This contribution adds to the hyperfine field addressed above. Total magnetic relaxation requires that the dipole field, as well as the hyperfine field, explores the whole allowed region. In Fe_8, the dipole field created by electronic spins is about 10 times as large as the hyperfine field, and therefore 90% of the relaxation cannot be explained by the Miyashita-Saito mechanism described above, but only by the Prokofiev-Stamp mechanism.

10 Conclusion

In the present work it is shown that the $\sqrt{t}$ behaviour can in principle arise from hyperfine interactions alone. This can happen for any value of the external field and for any initial state provided it is not the equilibrium state. However, very slow nuclear spin relaxation is necessary. In the case of moderately slow nuclear spin relaxation, the decay is found to be linear at short times, in contrast with the statements of Miyashita and Saito. This discrepancy occurs because Miyashita and Saito assumed the initial condition $h = h_1$ which is not fulfilled by nuclear spins. After some time the decay crosses over to the $\sqrt{t}$ behaviour and finally becomes exponential at long times. The constant A of formula (1), and the relaxation rate $1/\tau$ which describes the long time behaviour, go to 0 when the tuning parameter $(H_{ext} - H_1)$ becomes large with respect to the hyperfine width ΔH.

When $H_1 = 0$ and $H_{ext} \simeq 0$, spin relaxation has remarkable features when the spin-lattice relaxation time is very long. The spin temperature can then be quite different from the lattice temperature.

The present work contains several shortcomings. The possibility of simultaneous reversal of the electronic spin and a few nuclear spins has been disregarded. Such processes have been treated by Prokofiev and Stamp [11] in the case of superparamagnetic grains. They might be less crucial for molecular nanomagnets since each molecular spin interacts in a significant way with a restricted number of nuclear spins. On the other hand, the possible dependence of D and λ with respect to the local field has also been ignored (as in the work of Miyashita and Saito). Such a dependence would modify the value (10) of the coefficient A.

The present theory may be relevant, for instance, in two cases. i) $Mn_{12}ac$ if a transverse field is applied in order to increase ω_T and to fulfill the condition (18) of very slow nuclear spin relaxation; ii) diluted samples of Fe_8, where the dipole interaction between molecular spins is smaller than the hyperfine field.

References

1. R. Sessoli, D. Gatteschi, Angew. Chem. **115**, 278 (2003)
2. T. Ohm, C. Sangregorio, C. Paulsen, Eur. J. Phys. B **6**, 195 (1998)
3. W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, C. Paulsen, Phys. Rev. Lett. **82**, 3903 (1999)
4. L. Bokacheva, A.D. Kent, M.A. Walters, Phys. Rev. Lett. **85**, 4803 (2000)
5. L. Thomas, A. Caneschi, B. Barbara, (1999) Phys. Rev. Lett. **83**, 2398
6. N.V. Prokofiev, P. Stamp, Phys. Rev. Lett. **80**, 5794 (1998) J. Low. T. Phys. **113**, 1147 (1998)
7. S. Miyashita, K. Saito, J. Phys. Soc. Jpn **70**, 3238 (2001)
8. A. Morello, O.N. Bakharev, H.B. Brom, R. Sessoli, de Jongh LJ (2004) Phys. Rev. Lett. **93**, 197202
9. W. Feller, *An introduction to probability theory and its applications* (Wiley, New York, 1970)
10. M. Goldman, in *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Clarendon Press, Oxford, 1970)
11. N.V. Prokofiev, P.C.E. Stamp, J. Low Temp. phys. **104**, 143 (1996)