

EFFECT OF SPIN DIPOLE-DIPOLE INTERACTION ON PHASE RELAXATION IN
MAGNETICALLY DILUTE SOLID BODIES

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A theory is developed of electron spin phase relaxation due to modulation of dipole-dipole interaction of paramagnetic centers by random variation of the longitudinal spin orientation. An exact asymptotic expression for the kinetics of the echo-signal decay is determined for arbitrary random variation of spin orientations when the echo observation times are relatively large. An upper bound of the phase relaxation rate is given for comparatively small echo observation times. A model is proposed which explains the experimental data on electron spin echo of free radicals in solid bodies.

INTRODUCTION

USUALLY in experiments on electron spin echo (ESE) in solids, not all the paramagnetic centers take part in the formation of the echo signal; the microwave pulses excite only a part of the spins (spins A). The remaining spins (spins B) make no direct contribution to the echo signal, but interaction with them accelerates the decay of the echo signal of spins A, since the spins B produce at the positions of spins A local magnetic fields that vary randomly in time as a result of the flip of the spins B due to the spin-lattice interactions (samples of type T₁) or flip-flop transitions of the electron spins (samples of type T₂)^[1].

It was established experimentally^[2-4] that when organic free radicals and ion radicals assume the role of spins B, they cause a decrease in the signal of the primary ESE. This decrease is frequently described by the relation

$$V(2\tau) = V_0 \exp(-2b\tau), \quad b \cong 10^{-13} C, \quad (1)$$

where C is the concentration of the spins B, and τ is the time interval between the pulses making up the echo signal. We note that the indicated paramagnetic particles are characterized by relatively long spin-lattice relaxation times ($T_1 \ll \tau$). The existing model theories^[1,5-8] do not explain the experimental data in (1). In the present paper, on the basis of a general analysis of the role of the spins B in the decay of the echo signals, we propose a model capable of adequately describing the ESE signals of free radicals in solids.

STATISTICAL THEORY

In the quasiclassical approximation, the contribution of the spins B to the shift of the resonant frequency of the k-th spin A is equal to^[1,5]

$$\Delta\omega_k(t) = \sum_p A_{kp} m_p(t), \quad (2)$$

where m_p is the z-projection of the p-th spin B and varies in random fashion as a result of the spin-lattice interaction or the flip-flop transitions. For the case of dipole-dipole interaction of spins with $S = 1/2$, which is considered here, we have

$$A_{kp} = \frac{\gamma_A \gamma_B \hbar}{r_{kp}^3} (1 - 3 \cos^2 \theta_{kp}), \quad (3)$$

where r_{kp} is the distance between the k-th and p-th spins, and θ_{kp} is the angle between r_{kp} and the z axis. We note that all the results can be readily generalized to include arbitrary multipole interactions $A_{kp} \sim r_{kp}^{-n}$ and for arbitrary spins S. Just as in^[1], we assume that the contributions made to (2) by the frequency shifts produced by different spins B are independent of each other. This assumption is certainly valid for samples of type T₁, while for samples of type T₂ it yields only a rough approximation to the real picture of the frequency fluctuations of spins A in a magnetically-diluted system.

In the case of the procedures customarily used in experiments for primary and stimulated ESE, the contribution of the spins B to the decay of the echo signal can be represented in the form

$$V(t) = V_0 \left\langle \left\langle \exp \left(i \int_0^t s(t) \Delta\omega_k(t) dt \right) \right\rangle \right\rangle_k, \quad (4)$$

where $s(t) = 1$ in the interval $(0, \tau)$ and $s(t) = -1$ in $(\tau, 2\tau)$ for the primary ESE; $s(t) = 1, 0,$ and -1 in the intervals $(0, \tau), (\tau, T + \tau),$ and $(T + \tau, T + 2\tau)$, respectively for stimulated ESE. Here $\langle \dots \rangle_t$ denotes averaging over all realizations of the random process $m_p(t)$, and $\langle \dots \rangle_k$ is averaging over the realizations of the spatial distribution of spins B around the spins A.

Unlike^[1,5-8], we first average the ESE signal over the random distribution of the spins in the lattice. This can be done for an arbitrary process $m(t)$. Indeed, we introduce the random quantity X:

$$X = X_p(t) = \int_0^t s(t) m_p(t) dt \quad (5)$$

and, taking into account the independence of the individual terms in (2), we rewrite (4) in the form

$$V(t) = V_0 \lim_{N \rightarrow \infty} \left\{ \frac{1}{v} \int d^3r \int \varphi_t(X) \exp(iXA(t)) dX \right\}^N, \quad \frac{N}{v} = C, \quad (6)$$

where N is the number of spins B, $\varphi_t(X)$ is the distribution density of the quantity X, v is the volume of the sample, and C is the concentration of the spins B.

From this, with the aid of Markov's method^[9], since $\varphi_t(X)$ is even, we obtain

$$V(t) = V_0 \exp \left[-\frac{8\pi^2}{9\sqrt{3}} \gamma_A \gamma_B \hbar C \int |X| \varphi_t(X) dX \right]. \quad (7)$$

The result admits of an interesting physical interpretation: the argument of the exponential in (7) has the meaning of the mean absolute value of the phase which the spin A acquires by the instant the echo signal is observed in the local magnetic field of one spin B located at an average distance $C^{-1/2}$ from the spin A.

Equation (7) enables us to establish certain general laws governing the influence of the spins B on the kinetics of the phase relaxation. We consider the case when the times t of observation of the echo signal are longer than the characteristic time τ_c of reorientation of the spins B. On the basis of the central limit theorem of probability theory, the distribution density of the sum (5) tends asymptotically, as $t/\tau_c \rightarrow \infty$, to the normal form

$$\varphi_t(X) dX = \frac{1}{\sqrt{2\pi \langle X^2 \rangle}} \exp \left(-\frac{X^2}{2 \langle X^2 \rangle} \right) dX. \quad (8)$$

From (7) and (8) we find that the kinetics of the decay of the ESE signals tends at $t \gg \tau_c$ to the asymptotic value

$$V(t) = V_0 \exp \left(-\frac{8\pi^2}{9\sqrt{3\pi}} \gamma_A \gamma_B \hbar C \sqrt{2 \langle X^2 \rangle} \right), \quad (9)$$

where

$$\begin{aligned} \langle X^2 \rangle &= \int_0^t \int_0^t dt_1 dt_2 s(t_1) s(t_2) \langle m(t_1) m(t_2) \rangle, \\ &= \int_0^t \int_0^t dt_1 dt_2 s(t_1) s(t_2) \langle m(0) m(t_1 - t_2) \rangle. \end{aligned} \quad (10)$$

It follows therefore that when $t > \tau$ we have $\langle X^2 \rangle \rightarrow \tau \tau_c$ for the primary and stimulated ESE, where the correlation time τ_c is given by

$$\tau_c = 4 \int_0^\infty \langle m(0) m(t) \rangle dt. \quad (11)$$

Thus, for an arbitrary process $m(t)$ at $t > \tau_c$ the contribution made by the spins B randomly distributed in the lattice to the decay of the ESE signals is given by

$$V(2\tau) = V(T + 2\tau) = V_0 \exp \left(-\frac{8\pi^2}{9\sqrt{3\pi}} \gamma_A \gamma_B \hbar C \sqrt{2\tau\tau_c} \right). \quad (12)$$

In the other limiting situation ($t < \tau_c$), the kinetics of the decay of the echo signals depends essentially on the character of the random variation of the spin orientation, and can provide in general form only an estimate of the upper bound of the rate of decay of the ESE signals, an estimate expressed in terms of the correlation function $F(t) = \langle m(0) m(t) \rangle$. To this end, we use the estimate^[10]:

$$\int |X| \varphi_t(X) dX \leq (\langle X^2 \rangle)^{1/2}, \quad (13)$$

where $\langle X^2 \rangle$, in accord with (10), is determined fully by the correlation function F . For $F = \frac{1}{4} \exp(-t/\tau_c)$ we obtain from (10) at $\tau < \tau_c$

$$\langle X^2(2\tau) \rangle \cong \frac{1}{3} \frac{\tau^2}{\tau_c}, \quad \langle X^2(T + 2\tau) \rangle \cong \frac{1}{2} \tau^2 \left(1 - \exp \left(-\frac{T}{\tau_c} \right) \right). \quad (14)$$

It follows from (7), (13), and (14) that for an arbitrary

random process that describes the temporal behavior of the z -projection of a spin B and is characterized by a correlation function $F \sim \exp(-t/\tau_c)$ we have at $\tau < \tau_c$

$$V(2\tau) \geq V_0 \exp \left(-\frac{8\pi^2}{27} \gamma_A \gamma_B \hbar C \tau \sqrt{\frac{\tau}{\tau_c}} \right), \quad (15)$$

$$V(T + 2\tau) \geq V_0 \exp \left(-\frac{8\pi^2}{9\sqrt{6}} \gamma_A \gamma_B \hbar C \tau \left(1 - \exp \left(-\frac{T}{\tau_c} \right) \right)^{1/2} \right).$$

It follows from (15) that for any process $m(t)$ [Eq. (2)] with a correlation function $\sim \exp(-t/\tau_c)$, the decay of the primary-echo signal can be represented at $\tau < \tau_c$ in the form

$$V(2\tau) = V_0 \exp \left\{ -a\tau \left(\frac{\tau}{\tau_c} \right)^\beta \right\}, \quad (16)$$

where a is a constant and $\beta \geq 1/2$.

The foregoing analysis shows that among the random processes $m(t)$ (2) with a correlation function in the form $\langle m(0) m(t) \rangle = \frac{1}{4} \exp(-t/\tau_c)$ it is impossible to find a model that leads at $\tau < \tau_c$ to a primary echo signal decay in accordance with (1). The experimentally observed^[2-4] phase-relaxation kinetics in the form (1) could be due, in principle, to two factors. On the one hand, it may be connected with the need for introducing into consideration random processes $m(t)$ with more complicated correlation functions. For example, for $F = \frac{1}{4} \exp(-t^n/\tau_c^n)$ at $\tau < \tau_c$ we get

$$\langle X^2(2\tau) \rangle = \frac{2\tau^{n+2}}{(n+1)(n+2)\tau_c^n} (2^{n+1} - 1) + O \left(\tau^2 \frac{\tau^{n+1}}{\tau_c^{n+1}} \right)$$

and estimates similar to (13)–(16) yield a relation of the type of (16) with $\beta \geq (n/2)$, $n > 0$. On the other hand, a kinetics of type (1) can be expected also for processes $m_p(t)$ with a correlation function $F_p \sim \exp(-t/\tau_c)$ if an additional assumption is made that a distribution with respect to the correlation times τ_c exists for the spins B. The distribution of the spins B with respect to the reorientation rates can be connected with singularities in the mechanism of the spin-lattice relaxation^[11], or with a scatter in the rates of the flip-flop transitions of the spins B, which is characteristic of magnetically-diluted solids^[8,9]. We consider below (in connection with a discussion of samples of type T_2) a model in which there is a distribution of the reorientation rates for the spins B.

COMPARISON OF THE THEORIES

If it is assumed that X (5) has a normal distribution (8) at all t and that $\langle m(0) m(t) \rangle$ is an exponential function $\sim \exp(-t/\tau_c)$, then (9) and (10) account fully for the results of^[7].

The asymptotic relation (12) obtained above for the decay of the echo signals at $\tau > \tau_c$ deviates from the corresponding results of the model theories^[1,5,6] in which an exponential kinetics of the type (1) was obtained for the echo-signal decay. The decrement b obtained in^[1,5,6] is respectively equal to $\Delta\omega_{1/2}$ and $0.22 \Delta\omega_{1/2}$ if $\Delta\omega^2 \tau_c^2 > 1$ and $\Delta\omega^2 \tau_c$ if $\Delta\omega^2 \tau_c^2 < 1$. Here

$$\Delta\omega_{1/2} = 3.8 \gamma_A \gamma_B \hbar C, \quad \Delta\omega^2 = \frac{1}{2} \pi^{-1} \Delta\omega_{1/2} \gamma_A \gamma_B \hbar r_{\min}^{-3}$$

r_{\min} is the closest-approach distance between spins A and B. This discrepancy is due to the fact that in^[1,5,6] they use a method of averaging over the

realizations of the spatial disposition of the spins B, in which it is assumed in fact that their disposition in the lattice is more or less regular and not random. The results of^[1,5,6] at $\tau > \tau_c$ are therefore applicable only to magnetically-concentrated solids, i.e., when, according to^[12], the degree of occupation of the lattice sites by the paramagnetic centers exceeds 0.01.

For short times $\tau < \tau_c$, the following kinetics was obtained in^[1,5] for the echo-signal decay:

$$V(2\tau) = V_0 \exp(-\kappa \Delta\omega_{1/2} \tau^2 / \tau_c), \quad \kappa \approx 1.$$

Relation (7) allows us to offer the following interpretation of this result: In^[1,5] they consider a model in which the orientation of the spins B changes jumpwise between positions, with an average transition frequency τ_c^{-1} . The realizations of the random process $m(t)$, at which n spin flips take place, yield for the primary ESE the following contribution to $\langle |X| \rangle$:

$$K_n \frac{\tau^{n+1}}{\tau_c^n} \exp\left(-\frac{2\tau}{\tau_c}\right). \quad (17)$$

The mean value of $|X|$ is equal to

$$\int |X| \varphi_n(X) dX = \sum_{n=0}^{\infty} K_n \frac{\tau^{n+1}}{\tau_c^n} \exp\left(-\frac{2\tau}{\tau_c}\right), \quad (18)$$

with $K_0 = 0$, $K_1 = 1$, and $K_2 = 1/3$. It follows therefore that the kinetics obtained in^[1,5] for the decay of the primary ESE signal at $\tau < \tau_c$ corresponds to allowance made only for such realizations of the process $m(t)$ at which not more than one flip of each spin B takes place ($n = 0$ or 1).

TYPE T₂ SAMPLES

The ESE signal decay due to random modulation of dipole-dipole interaction of the spins by spin diffusion, was considered in^[1], where it was assumed that in magnetically-dilute solids the flip-flop transitions can be characterized by a single spin-reorientation frequency. In magnetically-diluted systems, however, there exists a set of rates W of spin flip-flops. This set is connected with the presence of different realizations of the spatial disposition of the spins. The distribution density of W is given by^[11,13]

$$\Omega(W) dW = \frac{B}{2\sqrt{\pi}W^3} \exp\left(-\frac{B^2}{4W}\right) dW. \quad (19)$$

This distribution has a maximum at $W_{\max} = B^2/6$. For paramagnetic particles with relatively long times of the spin-lattice relaxation, when $\Delta\omega_{1/2} T_1 \gg 1$, the value of B is

$$B = 1.9 \cdot 10^{-12} C_k \frac{\sqrt{\Delta\omega_k}}{\Delta\omega_k} \ln\left(\frac{\Delta\omega_k}{2\Delta\omega_{1/2}}\right), \quad (20)$$

where C_k is the concentration of the spins B belonging to the k -th component of the EPR spectrum, $\Delta\omega_k$ is the width of this component, and $\Delta\omega_{1/2} = 3.8\gamma_B^2 \hbar C$.

To find the decay kinetics of the ESE signal with allowance for the distribution with the rates of the flip-flop transitions (19), we can use the results of the calculation in^[5], where the quantity (4) was time-averaged for a Poisson law of the random variations of $m_p(t)$. Using Eq. (11) from^[5] and averaging over the realizations of the random disposition of the spins B in the lattice (cf. (5), (7)), we find that the primary echo signal decay is described by the relation

$$V(2\tau) = V_0 \exp\left[-2\pi C \int dr (1 - v(r, W))\right], \quad (21)$$

where

$$v(r, W) = \exp(-2W\tau) \left[1 + \frac{W}{R} \operatorname{sh}(2R\tau) + \frac{2W^2}{R^2} \operatorname{sh}^2(R\tau)\right],$$

$$R^2 = W^2 - 1/4A^2(r)$$

and $A(r)$ is given by (3). Relation (21) can be directly generalized to include systems with spin-flip frequency distributions W . Using analogous reasoning for each subensemble of the spins B with given value of W , we obtain

$$V(2\tau) = V_0 \exp\left[-2\pi C \int \Omega(W) dW \int dr (1 - v(r, W))\right] \quad (22)$$

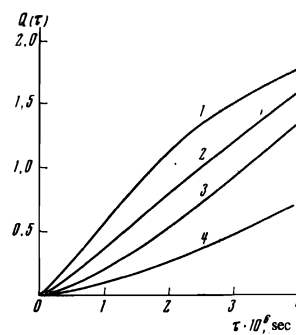
$$= V_0 \exp[-4\pi C \cdot 10^{-19} Q(\tau)].$$

We performed numerical calculations of the decay of the primary ESE signal, according to (21) and (22), for different positions of the maximum of the distribution density $\Omega(W)$. The calculated values of $Q(\tau)$ for several values of W_{\max} are shown in the figure. At $W_{\max} < 10^3 \text{ sec}^{-1}$, the condition $W\tau < 1$ is satisfied for most spins, and in accord with the foregoing discussion the decay of the primary echo signal is described by a relation of type (16). When the maximum of $\Omega(W)$ shifts towards larger values of W , the number of spins for which $W\tau \sim 1$ and $W\tau \gg 1$ increases, and these spins should give rise to echo-signal decays like $\exp(-\alpha_1\tau)$ and $\exp(-\alpha_2\sqrt{\tau})$ (12), respectively. As seen from the figure, at $10^4 \leq W_{\max} \leq 10^5 \text{ sec}^{-1}$ we can approximate $Q(\tau)$ satisfactorily by the linear relation $Q(\tau) \cong 4 \times 10^5$. With further increase of W_{\max} we have $Q(\tau) \rightarrow \sqrt{\tau}$. From this we find that the primary echo signal decay is described by the relation

$$V(2\tau) \cong V_0 \exp(-5 \cdot 10^{-13} C\tau) \quad (23)$$

if the maximum of the W distribution falls in the interval $10^4 - 10^5 \text{ sec}^{-1}$. Under conditions typical of experiments on ESE of free radicals in solids, i.e., at $5 \times 10^{18} < C < 5 \times 10^{19} \text{ cm}^{-3}$ and $\Delta\omega_k \approx 4 \times 10^8 \text{ sec}^{-1}$, an estimate of W_{\max} with the aid of (20) yields $10^4 \leq W_{\max} \leq 10^5 \text{ sec}^{-1}$. In this case one should expect the relation (23), which is close to the kinetics (1) observed in experiment for the ESE signal decay.

Thus, our analysis shows that random modulation of the dipole-dipole interaction by the spin-diffusion process in the system of spins B can play an important



Dependence of $Q(\tau)$ on τ calculated from^[19] and^[20]; $1 - W_{\max} = 1.07 \times 10^5$; $2 - 1.5 \times 10^4$; $3 - 3.25 \times 10^3$; $4 - 6 \times 10^2 \text{ sec}^{-1}$.

role in the phase relaxation of free radicals in magnetically dilute solids.

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