CONTRIBUTION TO THE THEORY OF SPECTRAL DIFFUSION IN MAGNETICALLY DILUTED SOLIDS

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Spectral diffusion and the phase relaxation produced by it in a magnetically diluted system of spins in a solid due to a random modulation of the secular part of the dipole-dipole spin interaction by the process of spin-lattice relaxation are considered. Formulas are derived for the decay of the spin-echo in the two- and three-pulse versions; these formulas are in agreement with the experimental data on electron spin-echo. It is shown that spectral diffusion from the paramagnetic particles closest to the chosen spin (the region of a relatively strong interaction) may be described by a Lorentzian-Markoffian random process. The dipole-dipole interaction of spins separated by a distance greater than a certain critical value leads to homogeneous broadening of the ESR line and to an exponential decay of the spin-echo signals.

1. In magnetic resonance experiments, magnetically diluted systems with a strongly inhomogeneous broadening of the spectrum, which is usually due to spin-orbit and hyperfine interactions, are frequently encountered. Although in this case the magnetic dipole interactions of paramagnetic particles in practice do not influence the shape of the spectrum, important relaxation processes which in the literature have been given the name "spectral diffusion"[1,2] are associated with them in the systems under consideration. The so-called approximation of "non-equivalent spins,"[3] which corresponds to taking account in the dipole-dipole interaction of only the secular part which commutes with the Zeeman energy, is a valid approximation for an investigation of the systems of interest to us. The Hamiltonian of the system may be represented in the form

$$H = \hbar \sum_k \omega_k \hat{S}_z^k + \hbar \sum_{k<n} A_{kn} \hat{S}_z^k \hat{S}_z^n = H_0 + H_1, \qquad A_{kn} = \gamma^2 \hbar (1 - 3\cos^2\theta_{kn}) r_{kn}^{-3}. \tag{1}$$

H_1 essentially causes only a shift of the resonance frequencies of the spins. The quasisecular terms of the dipole-dipole interaction Hamiltonian, which are omitted in the first approximation in (1), may be taken into account by using perturbation theory and lead to processes involving cross relaxation, providing exchanges of energy between spins with different resonance frequencies. Since such an exchange is most effective for a small difference between the frequencies of the interacting spins, the process of energy transfer in the space of frequencies carries a clearly-expressed diffusion character.[1] Another relaxation process with the same name "spectral diffusion" was considered in[2]. Already in the approximation (1) H_1 may lead to a random modulation of the resonance frequencies of the spins if the finite lifetime of the spins in a given state due, for example, to spin-lattice relaxation is taken into account. Now there is reason to assert that this relaxation process at not too low temperatures turns out, as a rule, to be identifiable in the phase relaxation in magnetically diluted systems.

The first direct investigations of phase relaxation by the method of electron spin-echo (see, for example,[4]) led to interesting and unexpected results. A major one of these was the conclusion about the nature of the decay law for the stimulated echo (three-pulse method) of the form $\exp(-m\tau T)$, where τ is the interval between the first and second uhf pulses, and T is interval between the first and third pulses. In this connection the decay law for the spin-echo (two-pulse method) has the exponential form $\exp(-b\tau)$. In order to understand the results concerning the stimulated echo, Klauder and Anderson[2] invoked the existence of spectral diffusion in the same sense as discussed above; in this connection they were able to achieve excellent agreement with experiment. However, in the case of spin-echo, the relaxation process under consideration led to a decay law of the form $\exp(-m\tau^2)$. Therefore it was conjectured in[2] that the experimentally-observed exponential decay is due to the so-called "instantaneous diffusion" which is associated with relaxation processes at the moment of action of the uhf pulses.

Systematic investigations of the electron spin-echo in systems containing free radicals, undertaken recently,[5] led to the same qualitative conclusions with regard to the decay laws for the echo signals, but here it was shown that the mechanism of instantaneous spectral diffusion cannot explain the experimental results on spin-echo.[6] At the same time in article[7] and independently in article[8] one inadequacy of the theory of Klauder and Anderson was pointed out—this inadequacy consisting in the fact that their theory does not describe the "narrowing" phenomenon which is well-known in magnetic resonance.

In the present article the role of spectral diffusion in phase relaxation is considered within the framework of a somewhat different approach than the one used in[2]. A similar calculational scheme was recently discussed by Mims;[7] however, the differences between the model adopted in[7] and the model adopted in the present work led to essential differences in the results. This point will be discussed in more detail below.

2. In the adiabatic approximation one can write the echo signal in the form[2]

$$V(t) \sim \left\langle \left\langle \exp i \int_0^t s(t)\, \omega_k(t)\, dt \right\rangle_t \right\rangle_k, \tag{2}$$

where $s(t) = 1$ for the free induction signal; $s(t) = 1$ in the interval $(0, \tau)$ and $s(t) = -1$ in the interval $(\tau, 2\tau)$ for the spin-echo signal; $s(t) = 1$ in the interval $(0, \tau)$, $s(t) = 0$ in the interval (τ, T) and $s(t) = -1$ in the interval $(T, T + \tau)$ for the stimulated echo signal. The averaging in (2) is carried out over the time (t) and over the ensemble of spins (k) excited by the uhf pulse; ω_k is the resonance frequency of the k-th spin in the rotating coordinate system.

3. Calculation of $V(t)$ according to (2) for specific systems requires a knowledge of the nature of the corresponding random process $\omega(t)$. For samples containing a sufficiently high concentration of spins, the conjecture that the ensemble average is normal[9] or a Gaussian-Markoffian process is apprently valid. It is easy to show that for a normal process with a correlation function

$$\langle [\omega(t) - \bar{\omega}][\omega(t') - \bar{\omega}] \rangle = \overline{\Delta\omega^2} g(t - t'),$$

$$V(t) \sim \exp\left[-i\bar{\omega} \int_0^t s(t)\, dt \right]$$

$$\times \exp\left[-\frac{\overline{\Delta\omega^2}}{2} \int_0^t \int_0^t s(t') s(t'') g(t' - t'')\, dt'\, dt'' \right]. \tag{3}$$

One can find the corresponding solution for the case of a Gaussian-Markoffian process in articles[2,10]. We note that in the limiting case of rapid spectral diffusion when $\overline{\Delta\omega^2 T_1^2} < 1$ formula (3) gives $V(2\tau) \sim \exp(-\overline{\Delta\omega^2} T_1 \tau)$ for the spin-echo signal, and for the free induction signal it gives $V(t) \sim \exp(-\overline{\Delta\omega^2} T_1 t)$. This corresponds to the well-known situation of the narrowing of a resonance line due to spectral diffusion.[9]

For magnetically diluted systems the nature of the random process $\omega(t)$ remains obscure. Klauder and Anderson showed[2] that under specific assumptions $\omega(t)$ is a Lorentzian-Markoffian random process; in this connection the conditional probability is determined by the expression

$$P(\omega, t | \omega_0) = \frac{1}{\pi} \frac{\Delta\omega_{1/2} [1 - \exp(-t/T_1)]}{[\omega - \omega_0 \exp(-t/T_1)]^2 + \Delta\omega^2_{1/2} [1 - \exp(-t/T_1)]^2} \tag{4}$$

where $\Delta\omega_{1/2}$ is the line width due to the dipole-dipole interaction.[2]

A calculation of $V(t)$ with Eq. (4) taken into consideration gives the following results: as $T_1 \to \infty$ the free induction signal is given by

$$V(t) \sim \exp(-\Delta\omega_{1/2} T_1^{-1} t^2),$$

and the spin-echo signal is given by

$$V(T + \tau) \sim \exp(-\Delta\omega_{1/2} T_1^{-1} \tau T);$$

correspondingly, as $T \to 0$, one finds

$$V(t) \sim \exp(-\Delta\omega_{1/2} t),$$
$$V(2\tau) \sim V(\tau + T) \sim \exp(-\Delta\omega_{1/2} 2\tau). \tag{5}$$

As $T_1 \to 0$ the rate of spectral diffusion becomes so large that a narrowing effect must appear in analogy to the way this is realized for a normal process. Such an effect is actually observed in spin-echo experiments in systems containing two kinds of paramagnetic particles.[7,8] However, the theory of Klauder and Anderson does not predict this effect, apparently because the Lorentz-Markoff process (4) does not give a complete description of the spectral diffusion process in a magnetically diluted system.

4. The resonance frequency of a certain spin in the quasiclassical-stochastic-model approximation[2] for the Hamiltonian (1) is given by

$$\omega_k(t) = \bar{\omega}_k + {}^1/_2 \sum_n A_{kn} \sigma_n(t), \tag{6}$$

where σ_n denotes the eigenvalue of the operator $2\hat{S}_z^n$. Spin-lattice relaxation causes random changes of σ which lead to the time dependence of $\omega(t)$. For a magnetically diluted system the $\sigma_n(t)$ are, to a good approximation, independent random quantities. Therefore, in order to determine $V(t)$ given by expression (2) it is sufficient to know the law governing the random variation of $\sigma(t)$ since, from expressions (2) and (6) we have

$$V(t) \sim \left\langle \prod_n \left\langle \exp\left[\frac{i}{2} A_{kn} \int_0^t s(t) \sigma(t)\, dt \right] \right\rangle_t \right\rangle_k. \tag{7}$$

For a spin $S = {}^1/_2$ it is reasonable to assume that $\sigma(t)$ only takes the values ± 1, where the probability of a change in the sign of $\sigma(t)$ in the interval $(t, t + dt)$ is proportional to dt/T_1, i.e., $\sigma(t)$ is represented by a Poisson random process. For a Poisson process the probability that $N(t) = m$ transitions between the two possible values of σ occur during a time t is given by

$$P(N(t) = m) = \frac{1}{m!} \left(\frac{t}{T_1} \right)^m \exp\left(-\frac{t}{T_1} \right). \tag{8}$$

A random quantity $\sigma(t)$ may be represented in the form $\sigma(t) = \sigma(0)(-1)^{N(t)}$. The probability (8) for the number $N(t)$ of transitions during the time t completely specifies the random process $\sigma(t)$ and enables us to find the time average of the quantity

$$v(t) = \left\langle \exp\left(\frac{i}{2} A_{kn} \sigma(0) \int_0^t s(t) (-1)^{N(t)}\, dt \right) \right\rangle.$$

If $\sigma(0)$ takes both values with equal probability (the high-temperature approximation), then introducing the notation $|A_{kn}| = 2\Delta$ we have

$$v(t) = \left\langle \cos\left(\Delta \int_0^t s(t) (-1)^{N(t)}\, dt \right) \right\rangle.$$

Expanding in a series, we obtain

$$v(t) = \sum (-1)^k \Delta^{2k} \int_0^t dt_{2k} \int_0^{t_{2k}} dt_{2k-1} \ldots \int_0^{t_2} dt_1 s(t_{2k}) \ldots s(t_1) \langle (-1)^{\xi} \rangle, \tag{9}$$

where $\xi = \Sigma N(t_i)$. One can show that averaging the quantity $\langle (-1)^{\xi} \rangle$ with respect to the distribution (8) leads to the expression

$$\langle (-1)^{\xi} \rangle = \exp[-2T_1^{-1}(t_{2k} - t_{2k-1} + \ldots + t_2 - t_1)].$$

Further calculations require a specification of the variable $s(t)$, i.e., a concrete definition of the signal under consideration (compare with the definition of $s(t)$ in formula (2)).

It is convenient to carry out the integration in (9) by changing to the Laplace transform v(p). One can easily evaluate the multiple integrals which are encountered during the calculations (see[11]). Omitting the simple but cumbersome transformations, we present the final results. For the free induction signal

$$v(t) = (T_1^{-1}R^{-1}\,\mathrm{sh}\,Rt + \mathrm{ch}\,Rt)\exp(-tT_1^{-1}), \quad (10)$$

where $R^2 = T_1^{-2} - \Delta^2$. It is easy to verify that the Fourier transform (10) gives the well-known formula for the spectrum when collapse of the hyperfine structure of the spectrum occurs due to exchange.[3]

For the stimulated echo signal

$$v(T+\tau) = R^{-2}[\exp(-2\tau T_1^{-1})(T_1^{-2}\,\mathrm{sh}\,R\tau + R^2\,\mathrm{ch}^2 R\tau + RT_1^{-1}\,\mathrm{sh}\,2R\tau) + \exp(-2TT_1^{-1})\Delta^2\,\mathrm{sh}^2 R\tau]. \quad (11)$$

An expression for the decay of the spin-echo signal is obtained from (11) for the limiting transition $T \to \tau$.

Let us consider the cases of fast $(T_1^{-1} > \Delta)$ and slow $(T_1^{-1} < \Delta)$ spectral diffusion. For $T_1^{-1} > \Delta$, the situation corresponding to narrowing, the free induction signal will be given by

$$v(t) \sim \exp\left(-\frac{\Delta^2}{2}T_1 t\right), \quad (12)$$

and the spin-echo signal is given by

$$v(T+\tau) \sim v(2\tau) \sim \exp\left(-\frac{\Delta^2}{2}T_1\cdot 2\tau\right). \quad (13)$$

For $T_1^{-1} < \Delta$ we have the following result for the echo signal:

$$v(T+\tau) \sim \exp(-2\tau T_1^{-1})\left\{1 + \frac{T_1^{-1}}{\Delta}\sin 2\Delta\tau - {}^1\!/_2[\exp(-2(T-\tau)T_1^{-1}) - 1](\cos 2\Delta\tau - 1)\right\}. \quad (14)$$

As is well-known,[12] in the case of the stimulated echo spin-lattice relaxation causes an exponential decay of the signal, $\exp\{-(T-\tau)T_1^{-1}\}$, where $T-\tau$ is the time interval between the second and third pulses. Therefore, in order to observe the effects of spectral diffusion it is necessary that the relation $(T-\tau)T_1^{-1} < 1$ be satisfied. Then one can represent expression (14) in the form $(T_1^{-1} < \Delta)$

$$v(T+\tau) \sim \exp\left[-2\tau T_1^{-1} + \frac{T_1^{-1}}{\Delta}\sin 2\Delta + (T-\tau)T_1^{-1}(\cos 2\Delta\tau - 1)\right]. \quad (15)$$

5. The decay of the spin-echo signal in a magnetically diluted system is determined by formula (7). As already noted, the averaging in this expression is carried out with respect to the time and with respect to all realizations (k) of the spins over the cells. The time averaging of the quantities $v_k(\tau + T)$ which appear after the product sign in (7) was carried out above. The statistical averaging of the quantities in (7) remains to be carried out. Let there be N spins and B cells per unit volume. Then the total number of different realizations of the distribution is equal to C_B^N. Let us introduce the quantities w_k^α, which characterize the occupation of the k-th cell in the α-realization: $w_k^\alpha = 0$ or 1. By definition one can write the average of (7) over all realizations in the form

$$w(T+\tau) = \frac{1}{C_B^N}\sum_\alpha \prod_k^B v_k^{w_k^\alpha}. \quad (16)$$

In each realization $w_k = 1$ for N cells and $w_k = 0$ for B − N cells. The average probability that a cell is occupied in any realization is given by $\bar{w} = N/B$.

In order to carry out averaging of the type (16) in a statistical theory the line broadening was assumed to be an approximation of the following kind:

$$\frac{1}{C_B^N}\sum_\alpha \prod_{k=1}^B v_k^{w_k^\alpha} \sim \left[\frac{1}{B}\sum_{k=1}^B v_k\right]^N. \quad (17)$$

For a solid the inadequacy of this approximation is due to the fact that $B^N - C_B^N$ realizations are taken into account in which the multiple occupation of the cells is encountered.

Another possible approximation for (16) is given by

$$\frac{1}{C_B^N}\sum_\alpha \prod_{k=1}^B v_k^{w_k^\alpha} \sim \prod_{k=1}^B v_k^{\bar{w}} \sim \exp\left(\bar{w}\sum_{k=1}^B \ln v_k\right). \quad (18)$$

The summation in the argument of the exponential function is carried out over all lattice sites. It should be noted that a method of averaging which is equivalent to (18) has been applied in order to calculate the moments of the resonance lines in a magnetically diluted system.[3] It is obvious that Eq. (18) becomes exact in the case N = B. On the other hand, Eq. (17) becomes exact for N = 1. In connection with the statistical line width of a magnetically diluted system, averaging according to (17) gives a result which is in agreement with the result which is obtained by averaging according to (18) for $N/B < 0.01$. Therefore the validity of one or the other method of averaging depends on the value of the ratio N/B. We note that for a given value of N the value of the ratio N/B may be different for different systems. As an example one can cite the case of a system containing free radicals in which the situation involving a close distribution of radicals is not realized by virtue of their high reaction capabilities. In this case one can expect that N/B is sufficiently large for relatively low spin concentrations ($B \ll N_0$, where N_0 denotes Avogadro's number). Ionic crystals containing large hydrated spheres can represent another example of relatively large values of N/B.

In the case under consideration, however, the situation simplifies somewhat since one can easily verify that for small values of τ and T both methods, (17) and (18), of averaging lead to the same result. In fact, in this case the asymptotic expansions (13) and (14) have the form $v \sim 1 - \alpha$, $\alpha \ll 1$, and substitution into Eqs. (17) and (18) gives the same result, $V \sim \exp(-\bar{w}\bar{\alpha})$.

6. In the case of a magnetically diluted system under consideration, upon performing the averaging according to (18) one can represent the spin-echo signal in the form

$$w(T+\tau) \sim \exp\left[\bar{w}\sum_k^{B_1}\ln v_k + \bar{w}\sum_k^{B_2}\ln v_k\right], \quad (19)$$

where B_1 is the number of cells for which the condition $\Delta_k T_1 \le 1$ is satisfied, and $B_1 + B_2 = B$. Since $\Delta \sim r^{-3}$, then the summation over the B_1 cells reduces to a summation over all of the lattice sites inside a sphere of radius R_0, which is defined by the relation

$$^1\!/_2\gamma^2\hbar R_0^{-3}T_1 = 1. \quad (20)$$

In order to estimate the sums in (19) let us assume that for all sites B_1 inside the sphere R_0 the expansion (15) is valid for $v_k(t)$, and expansion (13) is valid for all sites outside the sphere R_0. Then (19) takes the form

$$v(T+\tau) \sim \exp\Big[-2\tau\overline{w}B_1T_1^{-1} + \overline{w}T_1^{-1}\sum_k^{B_1}\frac{\sin 2\Delta_k\tau}{\Delta_k} + \overline{w}(T-\tau)T_1^{-1}\sum_k^{B_1}(\cos 2\Delta_k\tau - 1) - \overline{w}T_1\sum_k^{B_2}\Delta_k^2\tau\Big]. \quad (21)$$

Replacing the lattice sums in (21) by integrals, with (20) taken into account we obtain

$$V(T+\tau) \sim \exp\left[-m\tau T - 2b\tau\right],$$
$$m = \frac{8\pi^2}{9\sqrt{3}}\gamma^2\hbar N T_1^{-1}, \quad b = \frac{4\pi}{15}\gamma^2\hbar N. \quad (22)$$

The first term in (22) represents the contribution from spins which are localized inside the sphere R_0 (the first three terms in (21)). A comparison with the theory of Klauder and Anderson shows that the spectral diffusion due to this group of spins apparently can be satisfactorily described by the model of a Lorentzian-Markoffian random process. The second term inside the argument of the exponential function in (22) is related to the spins located outside the sphere R_0 (the last term in (21)). It should be emphasized that the parameter b does not depend on T_1.

In the two-pulse version the law governing the decay of the spin-echo has the form

$$V(2\tau) \sim \exp(-2b\tau - m\tau^2),$$

and for the usual concentrations $N \sim 10^{19}$ particles/cm^3 and $T_1 \geq 10^{-5}$ the decay law is exponential, i.e., $\exp(-2b\tau)$. The obtained expressions give a good description of the experimental data on electron spin-echo in a system containing free radicals.[6] In the case of small values of T_1, this model leads to a narrowing phenomenon, which is also observed experimentally.

In the article by Mims[7] cited above, the time variation of $\sigma(t)$ was approximated by a Gaussian-Markoffian random process. The latter approximation did not enable the author to show that, for a system of spins possessing a dipole interaction, a weak spin-interaction region exists which leads to an exponential decay law. This is the major difference between the results of the present article and the results of article[7]. It should be noted that from a physical point of view the model of a Gaussian-Markoffian process (a process involving small steps) is hardly valid for the case $S = 1/2$ and apparently would be applicable only for $S \gg 1/2$.

[1] A. M. Portis, Phys. Rev. 104, 584 (1956).
[2] J. R. Klauder and P. W. Anderson, Phys. Rev. 125, 913 (1962).
[3] A. Abragam, The Principles of Nuclear Magnetism, Oxford, 1961 (Russ. Transl., IIL, M. 1963).
[4] W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. 123, 2059 (1961).
[5] A. M. Raĭtsimring, Yu. D. Tsvetkov, G. M. Zhidomirov, V. E. Khmelinskiĭ, and A. G. Semenov, Dokl. Akad. Nauk SSSR 172, 895 (1967).
[6] G. M. Zhidomirov, K. M. Salikhov, A. M. Raĭtsimring, and Yu. D. Tsvetkov, ZhSKh 10, 18 (1969).
[7] W. B. Mims, Phys. Rev. 168, 370 (1968).
[8] A. M. Raĭtsimring, K. M. Salikhov, G. M. Zhidomirov, and Yu. D. Tsvetkov, Dokl. Akad. Nauk SSSR 182, 389 (1968).
[9] P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. 25, 269 (1953).
[10] B. Herzog and E. L. Hahn, Phys. Rev. 103, 148 (1956).
[11] Mark Kac, Probability and Related Topics in Physical Sciences, Wiley, 1959.
[12] N. M. Pomerantsev, Usp. Fiz. Nauk 65, 99 (1958).

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