Spin packets and spectral diffusion in a magnetically dilute system with a dipole interaction

V. A. Atsarkin, G. A. Vasneva, and V. V. Demidov

Institute of Radio Engineering and Electronics, Academy of Sciences of the USSR, Moscow
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A method, based on periodic pulsed saturation, was developed for an experimental investigation of the profile of spin packets and of spectral diffusion in inhomogeneous ESR lines. This method was applied at helium temperatures to study the spin system of Ce^{3+} impurity ions present in concentrations of 1.4×10^{18} and 1.1×10^{19} cm^{-3} in $CaWO_4$ crystals. It was found that the spin packet width governed by the magnetic dipole-dipole interactions of impurity ions is about 0.2 of the statistical dipole width, and that the profile of the packets in the wings is close to a simple exponential dependence. The results indicated that the Lorentzian dipole profile of an ESR line of a dilute paramagnet could not be regarded as homogeneous but consisting of spin packets coupled by relatively slow spectral diffusion.

1. INTRODUCTION

The concept of spin packets, first introduced by Portis[1] to describe inhomogeneously broadened ESR lines, is widely used in the theory and practice of magnetic resonance spectroscopy.[2–5] According to Portis,[1] a spin packet is the homogeneous part of an inhomogeneous line formed by a set of equivalent paramagnetic centers ("spins") which have the same Larmor frequency ω_i. The question of the width and profile of a spin packet is closely related to the problem of the short time (τ_2) during which an irreversible phase relaxation takes place and the system goes over to a state which can be described in terms of spin temperatures.

In spite of the fundamental importance of the concept of a spin packet, it still remains phenomenological and in some cases has not been provided with a serious theoretical basis. When the Bloch equations are applicable (for example, in the case of fast motion, etc.), the problem simplifies: the packet profile naturally becomes Lorentzian. However, the hypothesis of a Lorentzian packet is frequently applied also to a fundamentally different case when the broadening of a packet is due to the dipole-dipole interactions in a rigid lattice. This point of view has gained wide acceptance (see, for example, Refs. 2–5) and it is usually justified by reference to a statistical theory[6,7] predicting a Lorentzian ESR line profile for dilute dipole systems. In fact, the theory given in Refs. 6 and 7 gives only the spectrum of a spin of system, i.e., the distribution of local dipole fields, and it says nothing about the rate of establishment of an internal equilibrium in this spectrum. Therefore, there is no reason to assume a priori that such a line is homogeneous, i.e., that it can be identified with a spin packet. (We note that a Lorentzian profile is obtained also in the case of purely static dipole interactions of the $S_i^zS_j^z$ type.) Recent experiments on spin dynamics in $TiO_2{:}Cr^{3+}$ crystals also support the hypothesis of an inhomogeneous nature of the dipole broadening of lines of a dilute system.[8]

The experimental data on the profile of dipole spin packets are very scarce. In the usual method for the construction of the continuous saturation curves[2,3] the packet profile is not determined from the experimental results, but is postulated (it is usually assumed to be Lorentzian). Moreover, in similar steady–state methods it is fundamentally impossible to separate the true width of a packet from the effects of spectral diffusion. More valuable information can be obtained by the method of "hole burning" in an ESR line by a short saturating microwave field pulse (see, for example, Ref. 9). However, direct observations of the profile of a hole are usually insufficient to determine accurately its far wings, which play a decisive role in checking the hypothesis of the Lorentzian packet profile.

It should be noted that the results of Ref. 9 provide indirect evidence of an approximately Gaussian spin packet profile of $Ca_5(PO_4)_3F{:}Nd^{3+}$ crystals. The Gaussian profile of packets in ruby crystals was reported by Boskaino *et al.*[10,11] who used a special pulse method with recording of the second harmonic of a microwave field. However, as demonstrated by recent investigations by the same group, spectral diffusion was not allowed fully in the analysis of the experimental results. Moreover, the objects investigated by Boskaino *et al.*[10] where characterized by an important role played by hyperfine interactions of paramagnetic centers with the nuclei in the environment, which complicated interpretation of the data.

In this situation it seemed particularly important to carry out a direct experimental investigation of the profile of spin packets (particulary of their wings) in magnetically dilute systems with the dipole interaction. This was the main purpose of the present investigation.

2. METHOD

We shall consider a spin system characterized by an inhomogeneously broadened ESR line $G(\omega-\omega_0)$ with the central frequency at ω_0 and a half-width Δ_0. We shall assume that this line consists of homogeneous spin packets with the form factors $g(\omega-\omega_i)$ and a half-width δ. This system is assumed to be initially in equilibrium with the lattice at a

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temperature $T_0 = \beta_0^{-1}$ and it is subjected to a pulse of a resonance magnetic microwave field with the half-amplitude H_1 of frequency $\Omega = \omega_0 + \Delta$ and duration t_p. We shall assume that $\omega_i = \gamma_\perp H_1 \ll \delta$ (here $\gamma_\perp$ is the transverse component of the spectroscopic splitting of a vector). Then, the evolution of the spin system under the action of a microwave pulse can be described by the usual rate equations for the Zeeman temperatures $[\beta(\omega_i)]^{-1}$ of spin packets:

$$d\beta(\omega_i)/dt = -W(x_i)\beta(x_i), \tag{1}$$

where $x_i = \Omega - \omega_i$ and $W(x_i) = \pi\omega_1^2 g(x_i)$ (for simplicity, we shall assume that the spin is $S = 1/2$).

Equation (1) ignores the influence of the lattice. This is justified if the spin-lattice relaxation time obeys the inequalities $\tau_1 \gg t_p$, $1/W(x_i)$. At this stage we shall ignore spectral diffusion (cross-relaxation between packets) in the time interval t_p. Finally, Eq. (1) does not contain terms allowing for the temperature β_d^{-1} of the dipole-dipole reservoir.[12] This is partly justified by the fact that we are interested only in the area of a burnt hole, which—as shown in Ref. 4—is not very sensitive to β_d provided $\Delta_0 \gg \delta$. We shall assume that this condition is satisfied.

The solution of Eq. (1) is of the form

$$\beta(\omega_i) = \beta_0 \exp[-\pi\omega_1^2 g(x_i) t_p];$$

it describes the spectral distribution of the Zeeman temperatures over an inhomogeneous line as established at the end of the applied pulse. The area of the hole which is formed in this distribution, with allowance for the statistical weights of the packets $G(\omega_i - \omega_0)$, determines the reduction in the total longitudinal magnetization M_z compared with its equilibrium value M_{z0}:

$$m \equiv \frac{M_{z0} - M_z}{M_{z0}} = \int_{-\infty}^{\infty} G(\Delta - x)[1 - \exp(-\pi\omega_1^2 g(x) t_p)]dx. \tag{2}$$

Our aim was to use the experimentally determined "saturation curves," i.e., the dependences of m on the microwave pulse power $P \propto \omega_1^2$ and on its duration t_p, to find the packet profile $g(x)$. Since $g(x)$ occurs in Eq. (2) under the integral, the problem is generally multivalued, but—as shown below—it is solvable in one of the limiting cases.

We shall begin by considering weak saturation, corresponding to $Wt_p \ll 1$, where $W \equiv W(0) = \pi\omega_1^2 g(0)$. Taking $G(\Delta)$ outside the integral, we obtain from Eq. (2)

$$m \approx \pi\omega_1^2 G(\Delta) t_p. \tag{3}$$

This formula predicts a direct proportionality between m and the total microwave pulse energy $E_p = Pt_p$. It does not contain information on the packet profile or even on its existence, because it is obviously valid in the case of a homogeneous ESR line.

The situation is different in the case of strong saturation which corresponds to $Wt_p \gg 1$. In this case all the packets within the frequency interval $\Omega \pm \tilde{\delta}$, where $\tilde{\delta}$ is the half-width of the burnt hole, are saturated practically completely. If $\tilde{\delta} \gg \delta$, the half-width of a hole can be found approximately from the condition $W(\tilde{\delta})t_p = 1$, i.e.,

$$Wt_p = g(0)/g(\tilde{\delta}). \tag{4}$$

On the other hand, the area under the hole is then

$$m \approx 2\tilde{\delta} G(\Delta). \tag{4'}$$

The formulas (4) and (4') give the required single-valued relationship between the saturation curve $m(E_p)$ and the packet profile. It should be stressed that we are speaking here of the case when $\tilde{\delta} \gg \delta$, i.e., we are discussing only the profile of the fairly distant parts of the wings of the function $g(x)$.

We shall now give examples.

1. The packet's Lorentzian profile is described by

$$g(x) = \delta[\pi(\delta^2 + x^2)]^{-1}. \tag{5}$$

If $x \gg \delta$, we find that $g(0)/g(x) \approx x^2/\delta^2$, and then Eqs. (4) and (4') give

$$m = 2\delta G(\Delta)(Wt_p)^{1/2} \propto E_p^{1/2}. \tag{5'}$$

2. In the case of the Gaussian profile, we find that

$$g(x) = (1/\sqrt{2\pi}\sigma)\exp(-x^2/2\sigma^2), \quad \sigma = \delta/2(\ln 2)^{1/2}. \tag{6}$$

Proceeding as in case 1, we obtain

$$m = 2\sigma G(\Delta)(2\ln Wt_p)^{1/2} \propto (\ln E_p)^{1/2}. \tag{6'}$$

3. The simple exponential profile is

$$g(x) = (2\delta_e)^{-1}\exp(-|x|/\delta_e), \quad \delta_e = \delta/\ln 2, \tag{7}$$

$$m = 2\delta_e G(\Delta)\ln Wt_p \propto \ln E_p. \tag{7'}$$

It is clear from the above formulas that different spin packet profiles have very different asymptotes of the $m(E_p)$ curves. It should be noted that these asymptotes (5')–(7') are functions which are inverse with respect to $g(0)/g(x)$ if $x \gg \delta$. We can easily show that this rule is of general validity and follows directly from Eqs. (4) and (4').

The formulas (5')–(7') are approximate. The results of a more rigorous numerical calculation carried out using Eq. (2) directly in the cases described by Eqs. (5)–(7) are plotted in Fig. 1 (we assumed that the form factor of an inhomogeneous line varies little in the interval $\tilde{\delta}$ and can be taken outside the intergral). We can see that in the weak saturation

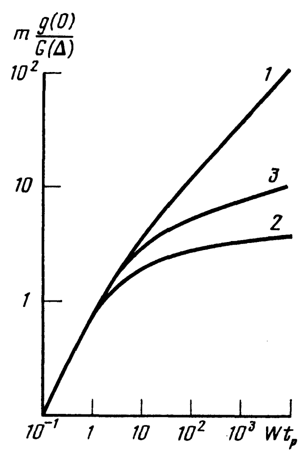

FIG. 1. Theoretical pulsed saturation curves for the Lorentzian (1), Gaussian (2), and exponential (3) profiles of a spin packet.

region all three curves coincide, but if $Wt_p \gtrsim 1$, then they diverge considerably and approach the asymptotes described by Eqs. (5')–(7'). This justifies the use of the present method in practical situations in order to determine the profile of the spin-packet wings.

We note that according to Eq. (2) the quantity m depends only on the product $\omega_1^2 t_p$ proportional to the total energy E_p of a microwave pulse. This important feature is a direct consequence of the adopted model of noninteracting spin packets and can be used as an experimental criterion of its validity. If the spectral diffusion during the action of a pulse cannot be ignored, the right-hand side of Eq. (1) should be supplemented by the corresponding cross-relaxation term,[13] which results in an additional rise of m on increase in t_p. A more detailed analysis of this case will be made in Sec. 3.

We shall now deal with the problem of determination of the quantity m. This problem becomes serious when $m \ll 1$, i.e., when only a small proportion of the spins contributing to an inhomogeneous line is saturated. This is precisely the situation in the case of pulsed saturation of the far wings of an ESR line, which are practically inaccessible to direct observations. We shall solve this problem by the method of periodic pulsed saturation.

We shall assume that microwave pulses of frequency Ω acting on an ESR line are applied periodically and the period obeys $T \gg t_p$, as well as

$$\tau_D \ll T \ll \tau_1, \tag{8}$$

where τ_D is the characteristic time for the establishment of an internal equilibrium between all the packets due to spectral diffusion. The first of these inequalities means that at the moment of arrival of the next pulse the Zeeman temperature is the same throughout the inhomogeneous line and we shall denote this temperture by $1/\beta(0)$. The microwave pulse disturbs this internal equilibrium and creates a frequency distribution of the temperatures of spin packets $\beta(x) = \beta(0) f(x)$, where $f(x)$ describes the profile of the burnt hole. After a time τ_D the hole disperses and the same temperature $1/\beta'$ is again established throughout the line; the new temperature is related to $\beta(x)$ by the condition of conservation of the total magnetization of the spin system:

$$\beta' = \beta(0) \int_{-\infty}^{\infty} f(x) G(x)\, dx. \tag{9}$$

Next, in a time interval T the spin temperature varies under the action of spin-lattice relaxation, so that by the moment of arrival of the next pulse it amounts to

$$\beta(T) = \beta_0 + (\beta' - \beta_0)\exp(-T/\tau_1) \approx \beta_0 T/\tau_1 + \beta'(1 - T/\tau_1). \tag{10}$$

Substituting Eq. (9) into Eq. (10), using the cyclic steady-state condition $\beta(T) = \beta(0)$, and noting that $m = \int G(x)[1 - f(x)]dx$, we obtain

$$s \equiv \frac{\beta_0 - \beta(0)}{\beta(0)} = \frac{\tau_1}{T} m. \tag{11}$$

Equation (11) related directly the required quantity m to the effective saturation factor s, which is easily determined from the reduction in the ESR line amplitude, recorded by the usual methods in the intervals between the pulses. It can be seen from Eq. (11) that the value of s increases effectively by a factor $\tau_1/T \gg 1$ because of the "accumulation" of the saturation by periodic pulses.

We can show that the condition (8) is far too stringent. We can obtain the result of Eq. (11) simply if the hole spreads basically within a time T, and total internal equilibrium in the inhomogeneous line is established rapidly compared with τ_1. In any case the experimental criterion of the validity of Eq. (11) is the proportionality between s and τ_1/T which can be checked experimentally.

If the pulsed saturation of an ESR line is characterized by a detuning $\Delta \neq 0$, the establishment of a single Zeeman temperature β' may be prevented by cooling of the dipole-dipole reservoir. We avoided this difficulty by simultaneous periodic pulsed saturation of the opposite wings of a line characterized by the detuning $\pm\Delta$. It was known from Refs. 15 and 16 that in this case the value of $|\beta_d|$ does not increase.

3. EXPERIMENTS

Our experiments were carried out on $CaWO_4$ crystals containing Ce^{3+} paramagnetic impurity ions (effective spin 1/2, g tensor components: $g_\parallel = 2.915$ and $g_\perp = 1.423$— see Ref. 17). These crystals were attractive because they were practically free of magnetic nuclei (with the exception of the ^{183}W isotope present in a concentration of 14.4% and characterized by a very small magnetic moment), so that the hyperfine interactions played no significant role. Table I lists the properties of the investigated samples.

The concentration n of paramagnetic centers was determined from the area under the ESR line. The values of the dipole half-width given in Table I were calculated using a statistical theory of Ref. 7 allowing only for the z component of the g factor:

$$\delta_d = 2.53\hbar\gamma_\parallel^2 n,$$

where $\gamma_\parallel = g_\parallel \mu_B \hbar^{-1}$ and μ_B is the Bohr magneton.

Our experiments were carried out on an ESR spectrom-

TABLE I. Properties of investigated samples and summary of experimental results.

№	n, cm^{-3}	$\Delta_0/2\pi$, MHz	$\delta_d/2\pi$, MHz	τ_1, sec	$\delta_e/2\pi$, MHz
1	$1.1 \cdot 10^{19}$	7.8	3.1	1.1	0.65
2	$1.4 \cdot 10^{18}$	2.6	0.4	2.8	0.13

eter operating in the 3-cm wavelength range using an external magnetic field H_0 oriented along the c axis of a crystal at $T_0 = 1.8$ K. The method of periodic pulsed saturation (described in Sec. 2) was employed and the value of m was found from Eq. (11). A strong sinusoidal modulation of the field H_0 at a frequency 50 Hz was used to scan the ESR line from one far wing to the other. The saturation curves were recorded in the $\Delta \neq 0$ case by selecting the modulation amplitude to be $\Delta/\gamma_{\parallel}$ and applying microwave pulses at the moments when the detuning reached its extremal value. In intervals $T = (2k+1) \times 10$ msec, where k is an integer, this ensured alternate pulsed saturation of both line wings with the detuning $\pm\Delta$. The duration of the pulses t_p did not exceed 1 msec, which guaranteed a negligible change in Δ during a pulse.

The specific values of T were selected from the conditions of validity of Eq. (11). Its validity was confirmed repeatedly by checking the proportionality between s and $1/T$ when $\tau_1 = \text{const}$ and the proportionality between s and τ_1 when $T = \text{const}$. The effective saturation factor s was measured by comparison of the amplitudes of the ESR absorption line under equilibrium conditions and in the intervals between the periodic microwave pulses. The field H_1 was calibrated in the absolute sense using the pulsed saturation curve recorded when $\Delta = 0$ and $Wt_p \ll 1$, and then applying Eq. (3). The results of this calibration were confirmed by direct calculation of the field in a cavity resonator when the microwave power $P_0 = 2.5$ W was known.

The directly observed profile of the central part of the ESR line was nearly Lorentzian. The more distant wings (up to $|\Delta| \leqslant 30\Delta_0$) were studied using the pulsed saturation curves obtained for $Wt_p \ll 1$ and applying Eq. (3). Their profiles were also nearly Lorentzian with a slight upward deviation on increase in $|\Delta|$. The Lorentzian profile $G(\omega - \omega_0)$ was in agreement with the inhomogeneous broadening mechanism due to elastic deformations created by point defects (which were the Ce^{3+} ions themselves and the compensating charges).[18] It should be noted that the electrostatic broadening of the ESR line by charged defects was not important, because in the $H_0 \| c$ configuration there was no linear electric-field effect.[19]

Figure 2 shows the pulsed saturation curves $m(P)$ for sample No. 1 obtained for $\Delta = \pm 7.2\Delta_0$ and different pulse duration t_p. We can see that in the case of weak saturation ($Wt_p \ll 1$) the law $m \propto P$, corresponding to Eq. (3), was obeyed always. An increase in the microwave power resulted in a deviation from this law and the curves became typical of saturation of an inhomogeneously broadened line. The best agreement with the experimental results was obtained by assuming a simple exponential profile of the spin packet described by Eq. (7) (continuous curves in Fig. 2). For comparison, we included in Fig. 2 the curve calculated for a Lorentzian packet with $\delta = \delta_d$; obviously, it differed radically from the experimental data.

It is clear from Fig. 2 that the saturation curves recorded for $t_p = 10\ \mu$sec and $100\ \mu$sec and completely identical profiles and were simply shifted parallel to one another by 10 dB along the abscissa (as illustrated by horizontal arrows identifying the point $Wt_p = 1$). Therefore, the value of m depended here on the total pulse energy $E_p = Pt_p$. Consequently, for pulse durations $t_p \leqslant 100\ \mu$sec the process of spectral diffusion was unimportant (see Sec. 2) and the parameter $\delta_e = 0.08\Delta_0$ (Table I) deduced from these curves did indeed represent the width of independent spin packets.

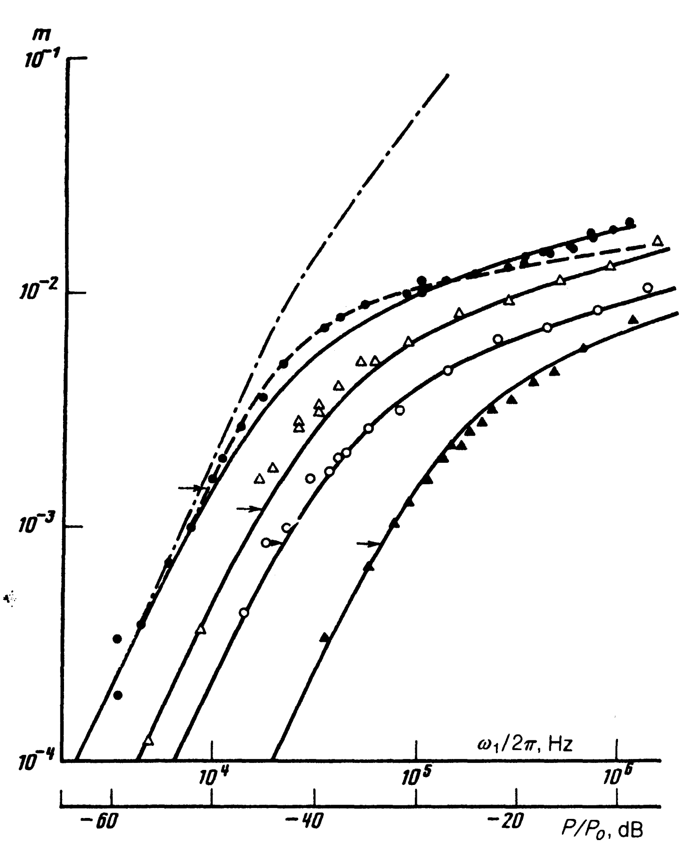

FIG. 2. Pulsed saturation curves for sample No. 1 obtained for $|\Delta| = 7.2\Delta_0$ using microwave pulses of different durations: $t_p = 0.01$ msec (▲) 0.1 msec (○), 0.3 msec (△), 1 msec (●). The continuous curves are calculated for the exponential profile of the spin packet. The dash-dot curve is calculated for the Lorentzian profile of a packet with $\delta = \delta_d$. The dashed curve is calculated allowing for spectral diffusion in accordance with Eq. (13). The arrows correspond to the points where $Wt_p = 1$.

When the pulse duration was $t_p > 100\ \mu$sec, the saturation curves began to "rise," indicating effective "broadening" of spin packets because of spectral diffusion. We shall discusss this aspect later.

The dependences $m(P)$ similar to those shown in Fig. 2 were obtained also for other values of the detuning in the range $0 \leqslant |\Delta| \leqslant 18\Delta_0$. Some of these are shown in Fig. 3. In all cases with the exception of $\Delta = 0$ the pulse duration $t_p = 100\ \mu$sec corresponded to a negligible contribution of spectral diffusion. In the $\Delta = 0$ case this condition was satisfied only when the pulse durations were short $t_p \leqslant 30\ \mu$sec (see curves 1 and 2 in Fig. 3). When the center of the line was saturated, calculations carried out using Eq. (2) had to be carried out rigorously without taking $G(\Delta)$ outside the integral.

At the maximum values of the microwave power the experimental values of m (Fig. 3) had a tendency to deviate

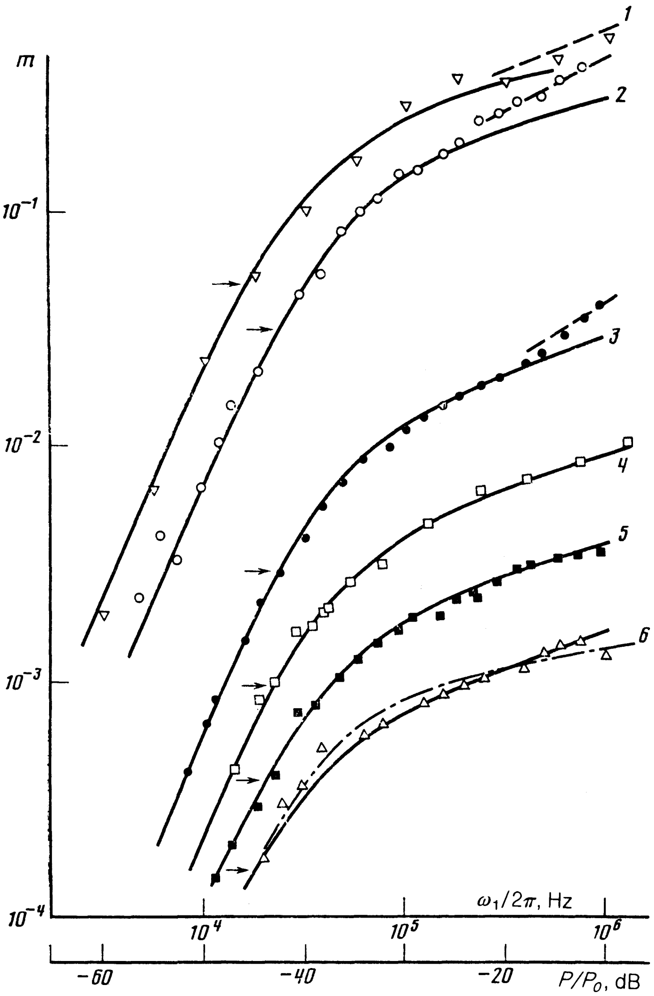

FIG. 3. Pulsed saturation curves of sample No. 1 obtained for different values of the detuning $|\Delta| = 0$ (curves 1 and 2), $3.6\Delta_0$ (curve 3), $7.2\Delta_0$ (curve 4), $12\Delta_0$ (curve 5), $18\Delta_0$ (curve 6). The points are the experimental results. The continuous curves are calculated for the exponential profile of a spin packet and the dash-dot curve represents the Gaussian profile. In the case of curves 1 and 3–6 the pulse duration was $t_p = 0.1$ msec and for curve 2 it was $t_p = 0.03$ msec. The dashed lines give the additional contribution calculated from Eq. (12). The arrows correspond to the points where $Wt_p = 1$.

upward from the calculated curves (this was more noticeable at low values of Δ). This was due to departure from the condition $\omega_1 \ll \delta$, essential for the validity of Eq. (1). We shall now estimate the additional contribution to m under these conditions.

We shall assume that the microwave pulse is turned on and off nonadiabatically, and that t_p exceeds the transverse relaxation time τ_2. Then, the magnetization M_{zi} of the ith packet as a result of the action of a pulse decreased to $M_{zi} \cos^2\theta$, where $\theta = \arctan[\omega_1/(\omega_i - \Omega)]$. Integrating this result over an inhomogeneous line, we can readily obtain the total relative reduction in the magnetization m'. In particular, for the Lorentzian profile of $G(\omega - \omega_0)$, we have

$$m' = \begin{cases} (\omega_1^2+\omega_1\Delta_0)/\Delta^2, & |\Delta| \gg \Delta_0 \\ \omega_1/(\omega_1+\Delta_0), & \Delta = 0 \end{cases}. \qquad (12)$$

Strictly speaking, the formulas in Eq. (12) are valid only if $\omega_1 \gg \delta$. However, in qualitative estimates of the influence of this mechanism in the case when $\omega_1 \sim \delta$ we can simply add m' to the values of m calculated earlier. The results are shown by dashed curves in Fig. 3. We can see that the agreement with the experimental results improves considerably at high values of P.

However, we cannot exclude the possibility that the experimental $m(P)$ plots obtained in the range $Wt_p \gg 1$ become somewhat less steep on increase in $|\Delta|$ and steeper on reduction in $|\Delta|$, than predicted by the calculated curves (Fig. 3). This may imply some change in the profiles of the spin packets, depending on their position within the inhomogeneous line profile. In particular, at the maximum value $|\Delta| = 18\Delta_0$ it is difficult to make the choice between the simple exponential function and the Gaussian profile (dash-dot curve in Fig. 3).

However, on the whole, the simple exponential profile of a packet described by Eq. (7) agrees satisfactorily with the experimental results and in the case of sample No. 1 we find that throughout the investigated range of the detuning Δ the parameter δ_e is practically the same and it amounts approximately to $0.2\delta_d$ (Table I).

A family of saturation curves obtained for a sample with a lower concentration of paramagnetic centers (sample No. 2) is shown in Fig. 4 for $|\Delta| = 3.6\Delta_0$. The results in this case are in reasonable agreement with the hypothesis of the

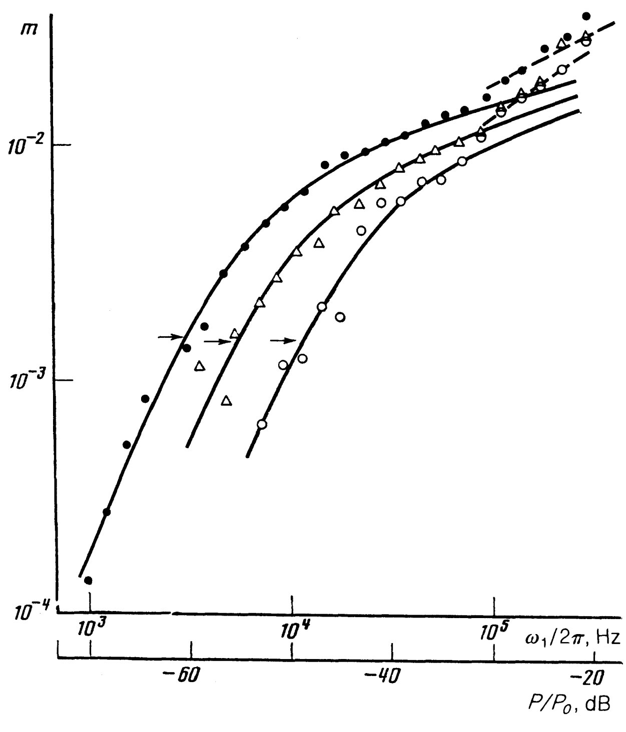

FIG. 4. Pulsed saturation curves for sample No. 2 obtained for $|\Delta| = 3.6\Delta_0$ using pulses of different durations; $t_p = 0.1$ msec (○), 0.3 msec (Δ), 1 msec (●). The continuous curves are calculated for the exponential profile of a packet and the dashed curves give the additional contribution calculated from Eq. (12). The arrows correspond to the points where $Wt_p = 1$.

exponential profile of spin packets, the width of which is now five times less than the width of packets in sample No. 1 (Table I). It should be noted that the rise of the saturation curves due to the contribution of m' now occurs at lower values of ω_1, in agreement wth the decrease of δ_e.

It should be pointed out that this method of determination of $g(x)$ is not very sensitive to the profile of the central part of a packet and it gives information only on its wings (see Sec. 2). An analysis shows that the "peak" at the center of the exponential function (7) can be replaced by any smooth curve without significant disagreement with the experimental results and the law $\exp(-|x|/\delta_e)$ has to be used only when $|x| \gtrsim 2\delta_e$. However, in any case the half-width of a packet deduced from the $m(P)$ curves is close to that given in Table I.

We shall now analyze the spectral diffusion processes. As pointed out above, they should be manifested by a change in the nature of the dependence $m(t_p)$. Curves of this kind recorded for sample No. 1 with $|\Delta| = 3.6\Delta_0$ and various fixed values of W are plotted in Fig. 5. The results are given as a function of the product Wt_p, which is proportional to the total energy E_p of a pulse. We can see that, beginning from a certain duration t_p (which increases on increase in the microwave power), the experimental points deviate from the curve calculated ignoring spectral diffusion. We shall explain his effect on the assumption that spectral diffusion during a microwave pulse is described by[13]

$$\frac{\partial\beta(x,t)}{\partial t} = D\,\frac{\partial^2\beta(x,t)}{\partial x^2} - W(x)\beta(x,t), \qquad (13)$$

where

$$W(x) = \pi\omega_1^2(2\delta_e)^{-1}\exp(-|x|/\delta_e)$$

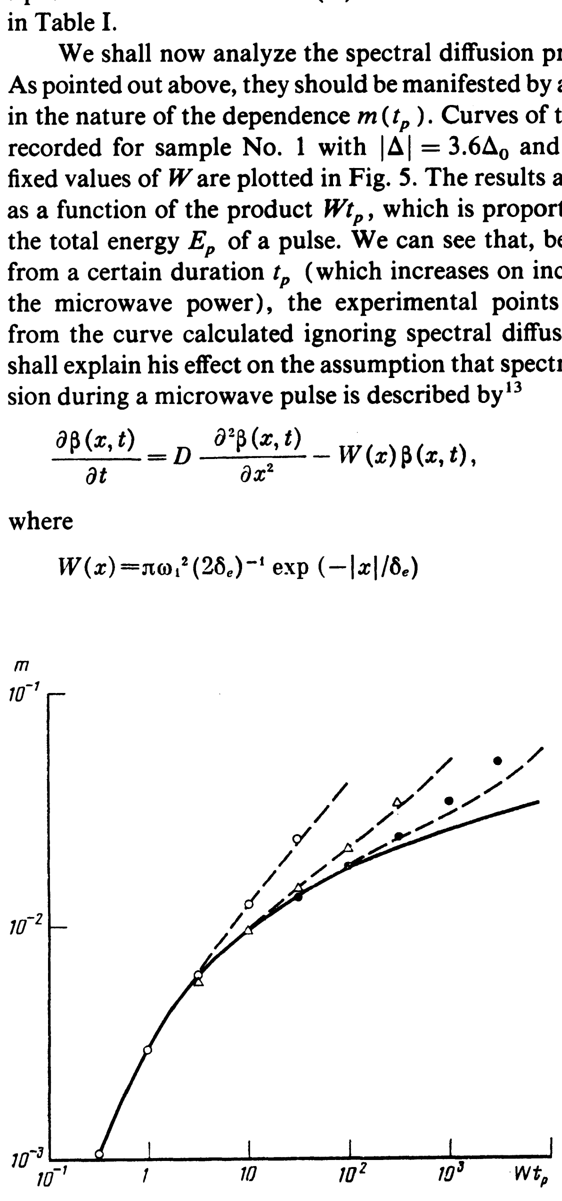

FIG. 5. Dependence of the reduction in the magnetization m of sample No. 1 on the factor Wt_p when $|\Delta| = 3.6\Delta_0$ and $W = 3\times10^4$ sec^{-1} (○), 3×10^5 sec^{-1} (△), 3×10^6 sec^{-1} (●). The dashed curves represent the solution of the spectral diffusion equation (13) for the same values of W on the assumption that $D = 5\times10^{17}$ sec^{-3}. The continuous curve is calculated ignoring spectral diffusion.

and D is the spectral diffusion coefficient assumed to be constant in the interval $\tilde{\delta} \ll |\Delta|$. A comparison of a numerical solution of Eq. (13) with the experimental results (see Fig. 5 and the dashed curve in Fig. 2) demonstrates that the agreement is reasonable and it allows us to determine D. This gives $D/\delta_e^2 = 3\times10^4$ sec^{-1} for $|\Delta| \leqslant 7\Delta_0$ and in the more distant wings of the line it decreases proportionally to $G(\Delta)$.

We also investigated spectral diffusion in sample No. 1 by a different method: we used the curve representing recovery of the ESR signal $A(t)$ until it reached its equilibrium value A_0 after saturation of the line center by a short microwave pulse in the case when $Wt_p < 1$. Two relaxation processes could be readily distinguished: a fast one (spectral diffusion) and a slow one (characterized by a time τ_1). As expected, the ratio of their amplitudes was equal to Δ_0/δ. The initial part of the relaxation curve is shown in Fig. 6. This figure gives also the dependence

$$A_0 - A(t) = [A_0 - A(0)]\exp(Dt/\delta_e^2)[1 - \mathrm{erf}((Dt)^{1/2}/\delta_e)), \qquad (14)$$

representing diffuse spreading of a hole with an initial profile of $\exp(-|x|/\delta_e)$ and with the parameter $D/\delta_e^2 = 4.5\times10^4$ sec^{-1}. This value is only slightly higher than that found above for $|\Delta| = 3.6\Delta_0$ (Fig. 5).

4. DISCUSSION AND CONCLUSIONS

The main result of the present investigation is the establishment that spin packets due to the dipole interaction in a magnetically dilute solid do not have extended Lorentzian wings. It follows that the Lorentzian dipole profile predicted by the statistical theory of Refs. 6 and 7 cannot be regarded as homogeneous but consisting of many spin packets.

The physical meaning of this interpretation becomes clearer in the case when the "standard" inhomogeneous broadening mechanisms (due to defects, hyperfine fields, etc.) are absent, so that $\Delta_0 = \delta_d$. The the position of the ith spin packet ω_i in the profile of an ESR line is governed solely by the local dipole fields, i.e., by the spatial configuration of the immediate environment of a given paramagnetic center. In particular, the spins which have several nearest neighbors at a distance $r_{ij} \approx \bar{r} = n^{-1/3}$ form packets with $\omega_i \approx \omega_0$ located near the center of the ESR line. The profiles of these packets should clearly be close to the profile characteristic of spatially regular systems, i.e., it should be close to the Gaussian curve.

On the other hand, a paramagnetic center with a specific nearest neighbor at a distance $r_{ij} \ll \bar{r}$ should be regarded together with this neighbor as a cluster representing a dipole-coupled pair with the interaction energy obeying $\varepsilon_{ij} \sim \mu_B^2 r_{ij}^{-3} \gg \hbar\delta_d$. The spectrum of such a pair is known as the Pake doublet[20] and represents two lines shifted symmetrically in both directions from the frequency ω_0 by an interval of the order of $\varepsilon_{ij}/\hbar$. A set of such doublets is responsible for the extended Lorentzian wings of a statistical dipole profile $G(\omega_i - \omega)$. The profile of such spin packets should again be close to the Gaussian curve, because it is governed by the interaction between the cluster and its neighbors located at distances of the order of $\bar{r}$ from the cluster pair.

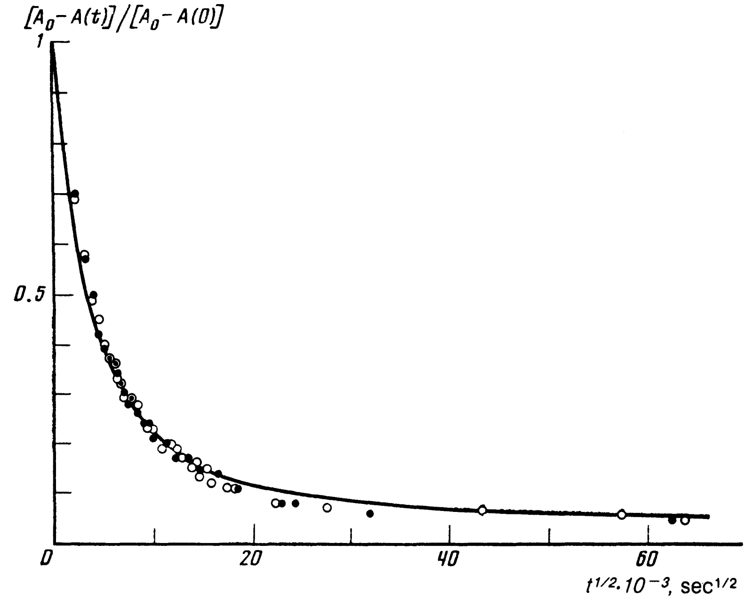

FIG. 6. Relaxation of the ESR absorption signal $A(t)$ to its equilibrium value A_0 obtained for sample No. 1 after the application of a pulse of $t_p = 15\,\mu$sec duration (●) and of $20\,\mu$sec duration (○) in the case when $\Delta = 0$. The continuous curve is calculated using Eq. (14).

Naturally, this very qualitative picture cannot account for intermediate cases when $\varepsilon_{ij} \gtrsim \hbar\delta_d$ and it is pointless to discuss such fine features as the difference between the Gaussian of Eq. (6) and the simple exponential curve of Eq. (7). Nevertheless, even such a coarse model allows for the chief feature of magnetically dilute systems: the spins with different local environments are physically inequivalent. In particular, this means that each given spin cannot experience, in reasonable time, the action of all possible local fields described by a statistical distribution $G(\omega_i - \omega_0)$, as is sometimes assumed.[17]

A more detailed analysis would require consistent configurational averaging as well as an allowance for the standard inhomogeneous broadening mechanism. Moreover, the mechanism of elementary processes resulting in the formation of spin packets of specific width is still not clear. However, we are justified even now in concluding that there is a qualitative agreement between the physical picture provided above and the experimental results. For example, the profile of packets in sample No. 1, where the dipole broadening is comparable with Δ_0, is practically identical at the center of the ESR line and in its far wings. The half-width of the packets is then about $0.2\delta_d$, i.e., it is comparable with the dipole interaction at a distance $\bar{r}$. When the concentration is reduced by a factor of eight (sample No. 2), the value of δ_e decreases by a factor of five. This slight deviation from direct proportionality can be explained by the hyperfine interaction of the Ce^{3+} ions with the ^{183}W nuclei, which increases m somewhat because of the discrete saturation effect.[21] Finally, the unusual exponential profile of the wings of the function $g(x)$ may be compared with a similar dependence of the cross-relaxation rate, observed frequently in experiments and clearly due to fundamental physical reasons.

It should also be pointed out that the value of δ_e found by us is comparable with the rate of decay of an electron spin echo, which for many substances is of the order of $0.1\delta_d$ (Ref. 23). However, it is difficult to compare directly our results with the spin echo data, because the ESR saturation experiments are carried out on a different time scale and a different configurational averaging procedure is needed in their interpretation. Nevertheless, the nature of a spin packet is undoubtedly related to the mechanism of phase relaxaion and it should be explained within the framework of a unified model.

Another important result is that energy transfer between spin packets is a relatively slow process. Even in the case of sample No. 1, in which the homogeneous broadening is relatively weak, the minimum spectral diffusion time in the interval δ_e amounts to according to our data-about 30 μsec, which is almost two orders of magnitude longer than the irreversible phase relaxation time.[17] Such a difference between times of formation of packets and the interaction time is a necessary condition for the validity of the spin packet model.

The results on spectral diffusion obtained in the present study cannot yet be interpreted finally. The agreement between the experimental results and the solution of the diffusion equation (13), demonstrated in Fig. 5, cannot be regarded as very significant. The very weak dependence of D on Δ agrees poorly with the current ideas on spectral diffusion.[4,13,24] Moreover, when an allowance is made for our estimate of D, it is difficult to account for the establishment of the same temperature throughout the ESR line, including its far wings in a time interval $\tau_D \ll \tau_1$. We cannot exclude the possibility that spectral migration of energy includes a contribution also from multispin cross-relaxation processes. For example, we can imagine simultaneous reversal of both spins in a dipole cluster in one direction accompanied by the transfer of an energy $2\hbar\omega_0$ simultaneously to two "isolated" centers. Such processes conserve the total Zeeman energy and can transfer excitation directly over large frequency intervals and for long time intervals they may be more effective than the usual spectral diffusion. This aspect also needs a more thorough theoretical analysis.

The results obtained nevertheless show that the establishment of a final internal equilibrium in the system of dipole-dipole interactions is a relatively slow process in magnetically dilute systems and it requires a time $\tau_D \gg \tau_2$. This conclusion is reached in Ref. 8 as a result of observations of the dipole temperature; it is confirmed in the present study by direct experiments on spin packets.

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