# *RELAXATION IN INHOMOGENEOUSLY BROADENED EPR LINES*

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Relaxation processes in inhomogeneously broadened EPR lines are studied theoretically and experimentally. The theory is developed for the case of strong inhomogeneous broadening and takes account of cross-relaxation processes within the line. Estimates are given of the form of the relaxation curves, both for the usual pulse saturation method and for the case of quenching of the cross-relaxation in the line. Results are given of an experimental investigation of the EPR lines of $Nd^{3+}$ in $Ca_5(PO_4)_3F$. The temperature dependence of the relaxation rate in conditions of quenched cross relaxation is studied. A technique is developed for constructing the probability density function w(x), where x is the frequency detuning, for cross-relaxation transitions. This function is determined for the EPR line of $Nd^{3+}$ in $Ca_5(PO_4)_3F$.

## 1. INTRODUCTION

A large number of papers have been devoted to the investigation of inhomogeneously broadened magnetic resonance lines. In particular, the stationary saturation of such lines[1-3], spectral diffusion and its effect on the dynamic polarization of the nuclei[4-6], and the spin-echo effect[7] have all been studied experimentally and theoretically. In a number of investigations[7,8], it was found that spectral diffusion plays an extremely important part in pulse saturation processes (including discrete saturation[8,9]) and paramagnetic relaxation.

The general form of the relaxation curve describing the recovery of level populations after saturation is determined by both spin-lattice and cross-relaxation processes. The dynamics of these processes and their effect on each other have been insufficiently studied, especially on the theoretical level.

In the present paper, relaxation processes in inhomogeneously broadened EPR lines are studied experimentally and theoretically. Experimental data are given for $Nd^{3+}$ ions in crystals of fluoroapatite $Ca_5(PO_4)_3F$; in particular, the phenomenon of quenching of the cross-relaxation within an inhomogeneously broadened line[10] is considered.

## 2. THEORY

An inhomogeneously broadened line is an aggregate of a large number of narrow spectral components ("spin packets"[1]) with a greater or lesser degree of overlap between them. As is well known, by saturating such lines it is possible to "burn out a hole" in them; the dynamics of the generation of the "hole" are determined essentially both by spin-lattice relaxation and by cross-relaxation between different spin packets. On the basis of the kinetic equations for the populations, we shall study the basic relationships governing these processes and shall give some estimates of the form of the burnt-out "hole" for the case of appreciable inhomogeneous broadening of the EPR lines.

### The Basic Equation

An inhomogeneously broadened line can be represented in the form of the system of levels shown in Fig. 1 ($\omega_0$ is the frequency of an electron transition and corresponds to the center of the line). The splitting $\hbar\omega_0$ is caused, e.g., by the internal crystal field, and the broadening $\Delta\omega$ can be due to very different causes[1]. In addition, it is assumed that dipolar interactions are present in the system, leading to homogeneous broadening $\Delta\omega' \ll \Delta\omega$ of the components and to cross-relaxation processes (between different spin packets) within the EPR line.

We shall assume that only the electron transitions of frequency $\omega_i$ shown in Fig. 1 are allowed in the system. In the case of inhomogeneous broadening due to interaction with the nearest magnetic nuclei, this assumption means that the probabilities of transitions with simultaneous reorientation of nuclear spins are small. (Exactly this case is realized in the inhomogeneously broadened lines of $Nd^{3+}$: $Ca_5(PO_4)_3F$ in the experiments described below.)

The linearized equation for the population differences $\Delta n_i$ of the i-th pair of levels has the form[11,12]

$$\frac{d\Delta n_i}{dt} = -\frac{1}{T_1}(\Delta n_i - \Delta n_i^0) + \sum_{j\neq i} w_{ij}'(N_i\Delta n_j - N_j\Delta n_i), \qquad (1)$$

where $w'_{ij}$ is the probability of cross-relaxation between the i-th and j-th pairs of levels, $T_1$ is the spin-lattice relaxation (SLR) time, which we shall assume to be the same for all the components, and $N_i$ is the total population of the i-th pair of levels.

We make the following simplifying assumptions.

1) The intensity of an inhomogeneous line is constant over its width $\Delta\omega$: $N_i \equiv N$. Computation of the

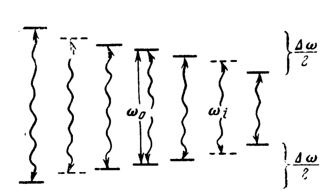


FIG. 1. Level scheme of an inhomogeneously broadened EPR line. Wavy lines denote spin-lattice transitions and straight lines denote transitions induced by the high-frequency field.

shape of the line in the first approximation reduces to superimposing "holes" on a function of this shape. For the limits of applicability of this assumption, see Remark 1 (at the end of this section).

2) $\hbar\omega_0 \ll kT$; $\Delta\omega \ll \omega_0$.

Using 1) and 2), we can write $\Delta n_i^0 = \Delta n^0$, where $\Delta n_i^0$ is the equilibrium population difference.

3) The number of spin packets is so large that their distribution can be considered to be continuous.

With these assumptions, introducing the coordinate $x = \omega - \omega_0$ to define the position of a given spin packet in the spectrum, and putting $w = Nw'$ and $u(x) = \Delta n(x) - \Delta n^0$, we transform Eq. (1) to the form

$$\frac{\partial u(x,t)}{\partial t} = -\frac{1}{T_1}u(x,t) + \int_{\Delta\omega} w(x-x')\left[u(x',t) - u(x,t)\right]dx'. \quad (2)$$

We shall assume (see, e.g.,[12]) that the function $w(x)$ falls off over intervals $\Delta x_0$ such that in all cases $\Delta x_0 \ll \Delta\omega$. The integral in (2) can be extended to infinite limits. We put

$$1/T_\Sigma = \int_{-\infty}^{\infty} w(x)\,dx$$

($T_\Sigma$ is a certain parameter characterizing the cross-relaxation) and rewrite (2) in the final form:

$$\frac{\partial u(x,t)}{\partial t} = -\left(\frac{1}{T_1} + \frac{1}{T_\Sigma}\right)u(x,t) + \int_{-\infty}^{\infty} w(x-x')\,u(x',t)\,dx'. \quad (3)$$

Fourier-transforming this equation

$$\tilde{f}(y) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} e^{-iyx} f(x)\,dx,$$

we obtain

$$\frac{\partial \tilde{u}(y,t)}{\partial t} = -\left(\frac{1}{T_1} + \frac{1}{T_\Sigma} - \sqrt{2\pi}\,\tilde{w}(y)\right)\tilde{u}(y,t) \quad (4)$$

If the initial spectral distribution $u(x, 0)$ of the population differences is given (this has the form of a "hole" by the time the saturating pulse ends), then the solution of (4) will be

$$\tilde{u}(y,t) = \tilde{u}(y,0)\exp\left\{-t\left[\frac{1}{T_1} + \frac{1}{T_\Sigma} - \sqrt{2\pi}\,\tilde{w}(y)\right]\right\}, \quad (5)$$

and for the function $u(x, t)$ we obtain the expression

$$u(x,t) = \frac{1}{\sqrt{2\pi}}\exp\left\{-t\left[\frac{1}{T_1} + \frac{1}{T_\Sigma}\right]\right\}\cdot\int_{-\infty}^{\infty} e^{iyx}\tilde{u}(y,0)\exp\{\sqrt{2\pi}\,\tilde{w}(y)t\}\,dy. \quad (6)$$

The spectral shape of the spin packets (and, consequently, the form of the function $w(x)$, which is defined by the integral of their overlap) has been insufficiently studied. Usually we have the opportunity of calculating only the lower moments of these functions, and for the lineshape we take either a Gaussian curve with the calculated second moment or some other simple distribution. Experimental lineshapes usually have a narrower central part and enhanced wings compared with the corresponding Gaussian curve; there have, therefore, been repeated attempts to describe experimental lineshapes by other functions. Below we shall consider some of the methods of assigning $u(x, 0)$ and $w(x)$. Formula (6) provides a possibility of calculating the relaxation curve, if the form of the function $w(x)$ is known, and then a comparison with the experimental curve permits us to find the parameter $T_\Sigma$. In all real cases, the function $w(x)$, like its Fourier transform, will be bell-shaped, and the method of steepest descents often turns out to be applicable for estimating the asymptotic behavior of $u(x, t)$ as $t/T_\Sigma \to \infty$. Thus, if $d\tilde{w}(y)/dy\,|_{y=0} = 0$ and $d^2\tilde{w}(y)/dy^2\,|_{y=0} = k \neq 0$, then, for $t \gg T_\Sigma$,

$$u(x,t) \approx \frac{e^{-t/T_1}}{\sqrt{t/T_\Sigma}}\,\tilde{u}(0,0)\,|\sqrt{2\pi}\,T_\Sigma k|^{-1/2}. \quad (7)$$

Of special theoretical interest is the determination of $w(x)$ from the experimentally observable functions $u(x, t)$. That such a determination is possible follows from formula (5), which can be rewritten in the form

$$\tilde{w}(y) = \frac{1}{\sqrt{2\pi}}\left(\frac{1}{t}\ln\left[\tilde{u}(y,t)/\tilde{u}(y,0)\right] + \frac{1}{T_1} + \frac{1}{T_\Sigma}\right). \quad (8)$$

Fourier-transforming the experimental functions $u(x, t)$ numerically, we can obtain $\tilde{w}(y)$ and then $w(x)$. It is necessary to bear in mind that $\tilde{u}(y, t)$ contains a factor of the form $e^{-t/T_1}$, so that, effectively, the time $T_1$ does not occur in (8).

### Solution of the Equation in Specific Cases

1. Let

$$w(x-x') = \frac{\alpha}{2T_\Sigma}\exp\{-\alpha|x-x'|\},$$
$$u(x,0) = -\Delta n^0\exp\{-\alpha\nu|x|\}. \quad (9)$$

The quantity $\alpha$ is essentially determined by the second moment $M_2 \approx 2/\alpha^2$ of the line formed by the mutual overlap of two spin packets; in those cases in which the shape of the "hole" at the moment the saturating pulse ends is determined only by spin-lattice and cross-relaxation processes, the quantity $\nu \approx (1 + T_1/T_\Sigma)^{-1/2}$ (see below), and in real cases $\nu \ll 1$. With the initial conditions (9), formula (6) gives the following result:

$$u(x,t) - \frac{\Delta n^0}{\pi}\int_{-\infty}^{\infty} e^{iyx}\frac{\alpha\nu}{\alpha^2\nu^2 + y^2}\exp\left\{-t\left[\frac{1}{T_1} + \frac{y^2}{\alpha^2 + y^2}\frac{1}{T_\Sigma}\right]\right\}dy. \quad (10)$$

Since $0 \le y^2/(y^2 + \alpha^2) \le 1$, we can make for $t \ll T_\Sigma$ the transformation

$$\exp\left\{-\frac{y^2}{y^2+\alpha^2}\frac{t}{T_\Sigma}\right\} \approx 1 - \frac{y^2}{y^2+\alpha^2}\frac{t}{T_\Sigma},$$

after which we obtain

$$u(x,t) \approx -\Delta n^0\left(1 - \frac{t}{T_1}\right)\left(1 - \frac{\nu e^{-\alpha x} - \nu^2 e^{-\alpha\nu x}}{1-\nu^2}\frac{t}{T_\Sigma}\right). \quad (11a)$$

Formula (7) gives the asymptotic form

$$u(x,t) \approx -\frac{\Delta n^0}{\sqrt{\pi t/T_\Sigma}}\exp\left\{-\frac{t}{T_1}\right\}. \quad (11b)$$

It is clear from the latter formula, in particular, that the relaxation curve has an essentially non-exponential character even for $t \gg T_1$.

If $\nu \ll 1$ (e.g., $T_1 \gg T_\Sigma$), the integral (10) permits an estimate of a completely different kind. We note that, in this case, $\tilde{u}(y, t)$ falls off with $y$ considerably faster than $\alpha^2/(\alpha^2 + y^2)$. The essential contribution to the integral is made by $y \le \alpha\nu$; then, however, $y \ll \alpha$ and $\exp\{-[y^2/(\alpha^2 + y^2)]t/T_\Sigma\} \approx \{-[y^2/\alpha^2]t/T_\Sigma\}$. The error in this estimate decreases exponentially with increase of the ratio $t/T_\Sigma$. After calculations we obtain the expression

$$u(x,t) = -\frac{\Delta n^0}{2}\exp\left\{-t\left[\frac{1}{T_1} - \frac{\nu^2}{T_\Sigma}\right]\right\}\cdot$$

$$\times\left[\exp\{-\alpha\nu|x|\}\,\mathrm{Erfc}\left(\frac{2\nu t/T_\Sigma-\alpha|x|}{2\sqrt{t/T_\Sigma}}\right)\right.$$
$$\left.+\exp\{\alpha\nu|x|\}\,\mathrm{Erfc}\left(\frac{2\nu t/T_\Sigma+\alpha|x|}{2\sqrt{t/T_\Sigma}}\right)\right]. \qquad (12)$$

For $t = 0$, this function becomes equal to $u(x, 0)$, in complete accordance with (9); as $t \to \infty$, the asymptotic form is equivalent to (11b). In spite of the apparent complexity of expression (12), it provides good opportunities for a comparison with an experimental curve of the part of the relaxation process when $T_\Sigma < t \lesssim T_1$, since the error function Erf(s) is tabulated in detail.

2. We shall examine the case of Gaussian curves

$$w(x)=\frac{\alpha}{\sqrt{\pi}}\frac{1}{T_\Sigma}\exp\{-\alpha^2x^2\}, \qquad (13)$$
$$u(x, 0) = -\Delta n^0\exp\{-\nu^2\alpha^2x^2\} = -\Delta n^0\exp\{-\beta^2x^2\}.$$

For this case we easily obtain

$$u(x,t)=-\frac{\Delta n^0}{2\sqrt{\pi}\beta}\exp\left[-t\left(\frac{1}{T_1}+\frac{1}{T_\Sigma}\right)\right]\int_{-\infty} e^{iyx}\exp\left\{-\frac{y^2}{4\beta^2}\right\}$$
$$\times\exp\left\{\frac{t}{T_\Sigma}e^{-y^2/4\alpha^2}\right\}dy; \qquad (14)$$

$$u(x,t)\approx-\Delta n^0\left(1-\frac{t}{T_1}\right)\left(1-\frac{t}{T_\Sigma}\right)\left[\exp\{-\beta^2x^2\}\right.$$
$$\left.+\frac{t}{T_\Sigma}\frac{\alpha}{\sqrt{\alpha^2+\beta^2}}\exp\left\{-\frac{\alpha^2\beta^2x^2}{\alpha^2+\beta^2}\right\}\right],\quad t\ll T_\Sigma; \qquad (15a)$$

$$u(x,t)\approx-\frac{\Delta n^0}{\beta}\exp\{-t/T_1\}\exp\left\{-\left[\frac{1}{\beta^2}+\frac{1}{\alpha^2}\frac{t}{T_\Sigma}\right]^{-1}x^2\right\}$$
$$\times\left(\frac{1}{\beta^2}+\frac{1}{\alpha^2}\frac{t}{T_\Sigma}\right)^{-1/2},\quad \beta\ll\alpha. \qquad (15b)$$

The last formula describes the relaxation process especially clearly. Since $\nu \sim [1 + T_1/T_\Sigma]^{-1/2}$, it is clear, in particular, that we should expect a stronger temperature dependence of the relaxation curve than in the case of pure spin-lattice relaxation.

3. Let

$$w(x)=\frac{\alpha}{\pi T_\Sigma(1+\alpha^2x^2)},\quad u(x,0)=-\Delta n^0\frac{1}{1+\beta^2x^2}; \qquad (16)$$

Then

$$u(x,t)=-\frac{\Delta n^0}{2\beta}\exp\left\{-t\left(\frac{1}{T_1}+\frac{1}{T_\Sigma}\right)\right\}\int_{-\infty}^{\infty}e^{iyx}e^{-|y|/\beta}\cdot\exp\left\{\frac{t}{T_\Sigma}e^{-|y|/\alpha}\right\}dy. \qquad (17)$$

In this case, the method of steepest descents is inapplicable. However, by replacing the variable in the integral, we can obtain the following results (using the properties of the confluent hypergeometric function):

$$u(0,t)=-\Delta n^0\Phi\left(1,1+\frac{\alpha}{\beta};-\frac{t}{T_\Sigma}\right)e^{-t/T_1}; \qquad (18)$$

$$u(0,t)\approx-\Delta n^0\left(1-\frac{t}{T_1}\right)\left(1-\frac{\beta}{\beta+\alpha}\frac{t}{T_\Sigma}\right),\quad t\ll T_\Sigma; \qquad (19a)$$

$$u(0,t)\approx-\Delta n^0\frac{\alpha}{\beta}e^{-t/T_1}\frac{T_\Sigma}{t}\left[1+\frac{\alpha-\beta}{\beta}\frac{T_\Sigma}{t}\right],\quad \frac{t}{T_\Sigma}\to\infty. \qquad (19b)$$

4. We shall consider the case of quenching of the cross-relaxation within the line[10]. If the whole inhomogeneously broadened EPR line is subjected to saturation, the corresponding initial distribution must be taken in the form

$$u(x, 0) = -\Delta n^0,\quad \tilde{u}(y, 0) = -\sqrt{2\pi}\Delta n^0\delta(y) \qquad (20)$$

($\delta(y)$ is the Dirac-delta-function); from (6) we obtain

$$u(x, t) = -\Delta n^0e^{-t/T_1}, \qquad (21)$$

regardless of the form of the function $w(x)$. The fact that, in this case, experiment actually gives a relaxation curve with a good exponential shape indicates, in particular, that the existing true dependence of $T_1$ on $x$ can be either neglected or, in any case, only taken into account parametrically (the change of $T_1(x)$ over the width $\Delta\omega$ of the inhomogeneous line is found to be negligible).

### Estimate of the Shape of the "Burned-out Hole"

Our problem now will be to justify the initial conditions, used in the previous paragraphs, for the relaxation process. We shall consider a kinetic equation, analogous to (3) but during the period of action of the saturating pulse:

$$\frac{\partial u(x,t)}{\partial t}=-\frac{1}{T_1}u(x,t)+\int w(x-x')\,[u(x',t)-u(x,t)]\,dx'$$
$$-2p(x)\,[u(x,t)+\Delta n^0], \qquad (22)$$

where $p(x)$ is the probability density for induced transitions. In cases where it can be assumed that $u(x, t)$ decreases with $x$ appreciably more slowly than $p(x)$ (more correctly, when the overall steepness of the decay is determined by the function $p(x)$), the last term in (22) can be rewritten in the form $-2p(x)[u(0,t) + \Delta n^0]$. If we are considering a monochromatic saturating pulse, this replacement is always admissible, inasmuch as the spreading apart of $u(x, t)$ as a result of cross-relaxation gives this function a certain finite slope even at very small $t$. Taking this into account, we Fourier-transform Eq. (22):

$$\frac{\partial\tilde{u}(y,t)}{\partial t}=-\left[\frac{1}{T_1}+\frac{1}{T_\Sigma}-\sqrt{2\pi}\tilde{w}(y)\right]\tilde{u}(y,t)-2\tilde{p}(y)\,[u(0,t)+\Delta n^0]. \qquad (23)$$

With the initial conditions $u(x, 0) = 0$, the solution of this equation has the form (essentially this is again an integral equation)

$$\tilde{u}(y,t)=-2\tilde{p}(y)\exp\left\{-t\left[\frac{1}{T_1}+\frac{1}{T_\Sigma}-\sqrt{2\pi}\tilde{w}(y)\right]\right\}$$
$$\times\int_0^t dt[u(0,t)+\Delta n^0]\exp\left\{t\left[\frac{1}{T_1}+\frac{1}{T_\Sigma}-\sqrt{2\pi}\tilde{w}(y)\right]\right\}. \qquad (24)$$

The following equation is obtained for $u(0, t)$:

$$u(0,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}dy\left[-2\tilde{p}(y)\exp\left\{-t\left[\frac{1}{T_1}+\frac{1}{T_\Sigma}-\sqrt{2\pi}\tilde{w}(y)\right]\right\}\right.$$
$$\left.\times\int_0^t dt\exp\left\{t\left[\frac{1}{T_1}+\frac{1}{T_\Sigma}-\sqrt{2\pi}\tilde{w}(y)\right]\right\}[u(0,t)+\Delta n^0]\right]. \qquad (25)$$

We shall calculate the stationary form of the curve $u(x, t \to \infty)$. For this we put $\Delta n(0, t \to \infty) = b\Delta n^0$, then $u(0, t \to \infty) = -\Delta n^0(1 - b)$. Here $b = 1/(1 + S_{eff})$, and $S_{eff}$ is the effective saturation factor. For $p(x)$, we take the $\delta$-shaped function $p(x) = ph\, e^{-h^2x^2}/\sqrt{\pi}$ (if $h \to \infty$, $p(x) \to \delta(x)$) and let $w(x) = (\alpha/2T_\Sigma)^{-\alpha|x|}$. We find $\tilde{u}(y, t \to \infty)$:

$$\tilde{u}(y,t\to\infty)=-\frac{2pb\Delta n^0}{\sqrt{2\pi}}\exp\left\{-\frac{y^2}{4h^2}\right\}\frac{\alpha^2+y^2}{\nu^2\alpha^2+y^2}T_1\nu^2,$$

where $\nu^2 = (1 + T_1/T_\Sigma)^{-1}$. For the function $u(x, t)_{stat}$, we obtain the following estimate:

$$u(x, t)_{stat} \propto -\Delta n^0e^{-\nu\alpha|x|}. \qquad (26)$$

It is clear from this last formula that $u(x, t)_{stat}$ falls off at distances of the order $\alpha^{-1}\sqrt{1 + T_1/T_\Sigma}$, and this quantity can be used to characterize the half-width of the "hole" burned out as the result of the action of a long saturating pulse. The estimates given are, of course, valid only for the case when the shape of the "hole" is determined only by spin-lattice relaxation and cross-relaxation processes.

Remark 1. In Eq. (1) we put $\Delta n_i' = \Delta n_i/N$. Then Eq. (3) will take the form

$$\frac{\partial u'(x,t)}{\partial t} = -\frac{1}{T_1}u'(x,t) + \int_{-\infty}^{\infty} N(x')w'(x-x')[u'(x',t)-u'(x,t)]dx'. \quad (27)$$

Hence it can be seen that in those cases when $N(x)$ changes negligibly over intervals $\Delta x_0$ ($\Delta x_0$ characterizes, as above, the half-width of the function $w(x)$), the computation of the lineshape reduces to superposing the function $N(x)$ describing this shape on the function of the spectral "hole"

$$u(x,t) = N(x)u'(x,t), \quad (28)$$

Here all the formulae given above for $u'(x, t)$ are valid[1)].

Remark 2. It is also possible within the framework of the proposed theory to make estimates of the "hole" shape for other than the stationary case, provided that a physically reasonable function for $u(0, t)$ can be assigned a priori (e.g., in the form $u(0, t) = -\Delta n^0(1 - b)(1 - e^{-rt})$ or with allowance for cross-relaxation processes). However, the expressions obtained in this way are very cumbersome and for such estimates it is better to use numerical methods, based on formula (24).

## 3. EXPERIMENT

An investigation of the electron paramagnetic resonance of $Nd^{3+}$ in monocrystals of fluoroapatite (FAP) $Ca_5(PO_4)_3F$ was carried out at a frequency $\omega_0/2\pi = 9430$ MHz. The EPR spectrum of $Nd^{3+}$ in $Ca_5(PO_4)_3F$[8] consists of three lines, corresponding to three magnetically-inequivalent complexes. The strong anisotropy of the spectrum ($g_{\parallel} = 6.02 \pm 0.02$, $g_{\perp} = 0.18 \pm 0.02$) leads to significant inhomogeneous line-broadening close to the perpendicular orientations ($\theta = 80°$). The $Nd^{3+}$ EPR lines in FAP are thus a very suitable object for the study of relaxation processes in inhomogeneously broadened lines, and correspond well to the mathematical model treated in the theoretical part.

The paramagnetic relaxation was studied on a superheterodyne spectroscope in the temperature region 1.7–14°K, both by the usual method of pulse saturation[11] (of the center of the line) and in conditions of quenching of the cross-relaxation (on saturation of the whole inhomogeneous line). Thus latter was attained by a rapid magnetic sweep of the line during the saturation[10].

It was found that the relaxation curves obtained by the usual pulse saturation method are not described by a single-exponential law for all durations $\tau_S$ of the saturating pulse (right up to $\tau_S > T_1$); the shape of these curves depends on $\tau_S$ (see Fig. 2, lower curve).

[1)]The quantity $T_\Sigma$ depends parametrically on x: $T_\Sigma(x) = T_\Sigma N(0)/N(x)$.

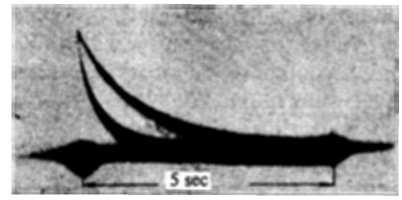


FIG. 2. Quenching of the cross-relaxation in the inhomogeneously broadened EPR line of $Nd^{3+}$ in $Ca_5(PO_4)_3F$. The lower relaxation curve was obtained by the usual pulse saturation method and the upper curve in conditions of quenching of the cross-relaxation. The concentration of $Nd^{3+}$ was 0.15 at.%, and T = 4.2°K.

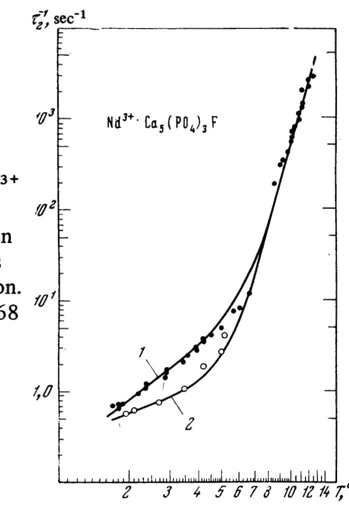


FIG. 3. Temperature dependence of the relaxation rate of $Nd^{3+}$ in $Ca_5(PO_4)_3F$. Curve 1 was obtained by the usual pulse saturation method, and curve 2 in conditions of quenching of the cross-relaxation. The concentration of $Nd^{3+}$ was 0.68 at.%.

In most cases it was found that the relaxation function can be represented with satisfactory precision in the form of a sum of two exponentials (for the technique for treating the relaxation curves, see[11]). The characteristic times $\tau_1$ and $\tau_2$ of the rapid and slow exponentials respectively display dependence on temperature. For a sample with concentration 0.68 at.% $Nd^{3+}$, the temperature dependence of $\tau_2$ follows the law $\tau_2^{-1} = 0.21\ T^2 + 5.2 \times 10^{-7}\ T^9$ (Figs. 3, curve 1). Analogous dependences have been obtained for samples with other $Nd^{3+}$ concentrations[8].

We must note that the dependence $\tau_2^{-1} \sim T^2$ found in the region of temperature from 1.7° to ~4° is apparently not related to the phonon-heating effect[13]. Evidence for this is provided by the fact that the measured relaxation times are not affected by direct contact of the sample with liquid helium, and also by the relatively small concentrations of $Nd^{3+}$ in the sample and the actual form of the concentration dependence[8].

The anomalous temperature dependence of the characteristic relaxation times can be explained on the basis of the theory given above; it is related to the essentially non-exponential character of the relaxation and to the fact that the initial form of the "hole" is largely determined by the relation between the times $T_1$ and $T_\Sigma$ (see e.g., the formulae (15) et seq.). Approximating the relaxation curve by exponentials leads to distortion of the temperature dependence and to appreciable errors in the determination of the time $T_1$ by the usual pulse saturation method.

For the correct determination of the spin-lattice relaxation times and an elucidation of the true character of the temperature dependence, we carried out experiments in conditions of quenching of the cross-relaxation within the inhomogeneous line.

In Fig. 2 are shown oscillographs of the relaxation processes in a sample with a concentration of 0.15 at.% $Nd^{3+}$ at 4.2°K. (The two curves were obtained consecutively on the screen of a long-persistence oscilloscope and, for clear representation, were photographed on one frame.) The lower curve corresponds to the usual pulse saturation method and can be approximated by a sum of two exponentials with characteristic times $\tau_1 = 83$ msec and $\tau_2 = 420$ msec. The upper curve was obtained in conditions of quenching of the cross relaxation and is a good exponential with time $T_1 = 710$ msec. Thus, the usual pulse saturation method gives a time constant that differs by a factor greater than 1.5 from the spin-lattice relaxation time ($T_1 = 1.7\tau_2$).

The study of spin-lattice relaxation for a sample with concentration 0.68 at.% $Nd^{3+}$ in conditions of quenching of the cross relaxation leads, in the region from 1.7° to ~4°K, to a temperature dependence $T_1^{-1} = 0.29T$, which is characteristic for the direct process, in contrast to the anomalous temperature dependence $\tau_2^{-1} \sim T^2$ obtained by the usual pulse saturation method. We note that the conditions for obtaining the effect of quenching of the cross relaxation within the line deteriorate with increase of the relaxation rate: these conditions require that the sweep of the line during the action of the saturating pulse be rapid compared with the rate of the relaxation processes. Therefore, the true temperature dependence in the region $T > 4$°K is still not completely clear.

We have also studied the dynamics of the "hole" burnt out in an inhomogeneously broadened line. The experiment was set up as follows.

The magnitude of the constant magnetic field corresponding to the centre of the EPR line was determined and a saturating UHF pulse of duration $\tau_S$ was applied. An angular magnetic sweep of the line (cf.[10]) was switched on by the trailing edge of the pulse, and the change in time of the EPR lineshape was recorded on the screen of an oscilloscope. In Fig. 4 is shown the oscillogram of the recovery of the line for a sample with concentration 0.68 at.% $Nd^{3+}$ at 4.2°K. The parallel shift of the curves is due to a reduction in the constant component of the signal by means of an input capacitance in the oscilloscope. (The horizontal straight line corresponds to the absence of scanning in the period before the saturating pulse was switching on). The duration of the saturating pulse was 7 msec and the time interval between neighboring curves was 10 msec.

## 4. DISCUSSION OF THE RESULTS

Analysis of the formulae (6) and (7) shows that taking account simultaneously of spin-lattice and cross-relaxation results in the relaxation curves having an essentially non-exponential character. Processes of population recovery in conditions of quenching of the cross relaxation within the line are an exception. In those cases when a large number of spin packets take part in the cross-relaxation process, the redistribution of energy within the inhomogeneously broadened line can be characterized by the parameter $T_\Sigma$. This

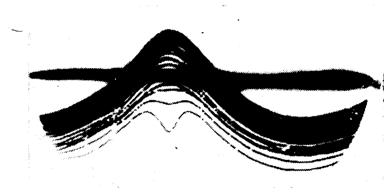

FIG. 4. Oscillograms of the recovery process in the inhomogeneously broadened EPR line of $Nd^{3+}$ in $Ca_5(PO_4)_3F$. The concentration of $Nd^{3+}$ was 0.68 at.%, and T = 4.2°K.

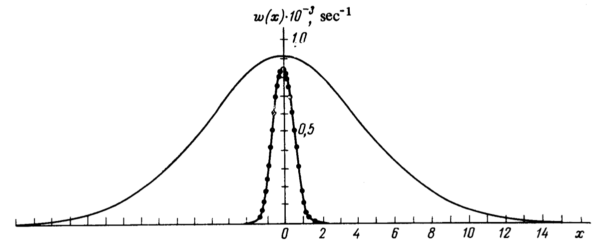


FIG. 5. Graph of the function w(x) for a sample with concentration 0.68 at.% $Nd^{3+}$. For comparison the form of the inhomogeneous EPR line is given, on the same scale along the x-axis and in arbitrary units along the ordinate axis.

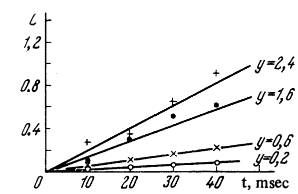


FIG. 6. Experimental plots of $L = \ln[\tilde{u}(y, 0)/\tilde{u}(y, t)]$ against t for different y for a sample with concentration 0.68 at.% $Nd^{3+}$. The scatter in the points for $y \geqslant 1.6$ is associated with the imprecise determination of the wings of the inhomogeneous line and of the form of the "hole" from Fig. 4.

parameter is determined by comparing the experimental relaxation curves with the functions (11), (12), (15) and (19) (the time $T_1$ occurring in these formulae is determined experimentally in conditions of quenching of the cross relaxation).

The function w(x) characterizes more fully the processes within an inhomogeneous line; in addition, this function contains information about the shape of the spin packets and their overlap. The theory given above enables us to find the function w(x) at consecutive moments of time from the observed forms of the "holes," and to compare it with the results of microscopic calculation.

On the basis of the experimental data on the dynamics of the "burnt-out hole" (see Fig. 4), we have determined the function w(x) for a FAP sample with concentration 0.68 at.% $Nd^{3+}$ by means of a Fourier transformation performed numerically; the value $T_\Sigma = 2.5$ 1.0 msec was obtained. The error is associated with an imperfection in the experimental technique used to observe the dynamics of the "hole," which leads to distortions in the wings of the inhomogeneous bulk of the spectrum. We hope in the future to improve significantly the accuracy of the determination of $T_\Sigma$ and of the construction of w(x). This function has been determined from (8) for different moments of time. In Fig. 5 an average result is given.

The extent of the deviation from the averaged function depicted in the Figure of the $w(x)$ which we have constructed can be judged from Fig. 6, in which are shown values of the function $L = \ln[\widetilde{u}(y, 0)/\widetilde{u}(y, t)]$ calculated from the experimental data. According to (8), if the variable $y$ is fixed, this function must be linear in $t$. We see that, on the whole, the theory given above corresponds well with the experimental results, although the error, especially in the wings of the function $w(y)$, is fairly large. Since the value of $T_\Sigma$ is actually determined from the wings of $w(y)$, an exact determination of this parameter is difficult.

The quantity $T_\Sigma$ was also obtained by comparing the initial part of the relaxation curve for the same sample (on saturation by a pulse of duration $\tau_S > \tau_1$) with the functions (11a) and (19a). We note, incidentally, that the initial part of the relaxation curve is practically independent of the form of the function $w(x)$: the expansions (11a) and (19a) and those analogous to them, are equivalent. We have obtained $T_\Sigma = 3.8 \pm 0.5$ msec, which agrees well with the value given above for this parameter. (To make the above comparison possible, the limiting slope of the relaxation curve as $t \to 0$ was determined).

As has already been mentioned, the function $w(x)$ carries information on the shape of the spin packets. Since the distribution of the latter is assumed to be continuous, the time for establishing equilibrium within a spectral component can be established from the width of this function; however, analysis is required for such an estimate to be possible.

We see from Fig. 5 that the assumption of small variation in the intensity of the inhomogeneous line over spectral distances of the order of $\Delta x_0$ is satisfactory in the central part of the spectrum, and, therefore, the most accurate results of a comparison with the functions (11) and (12) and with the functions analogous to them can be obtained by studying the relaxation curves for the central spin packets. In all calculations, we should, of course, bear Remark 1 in mind.

In the preceding treatment the function $w(x)$ was assumed, essentially, to be averaged over the spatial distribution of the spins. It is clear that such a treatment is admissible in those cases when there is no correlation between the spatial and spectral distances. Analysis of relaxation processes with allowance for the spatial distribution of the paramagnetic impurities is also, evidently, of considerable theoretical interest.

## APPENDIX

### Determination of the Function $w(x)$ in the Case of an Arbitrarily Broad "Hole"

We shall examine in more detail the technique for calculating $w(x)$. If we take account of Remark 1, formula (8) is, strictly speaking, valid when the following two assumptions are satisfied with sufficient accuracy:

1) the function $N(x)$ varies insignificantly over spectral intervals $\Delta x_0$ in which the function $w(x - x')$ differs appreciably from zero;

2) one can neglect the variation of the function $N(x)$ over the width of the "hole."

The second condition is usually much stronger.

We denote by $a(y, t)$ and $b(y, t)$ the Fourier transforms of the functions $u'(x, t)$ and $u'(x, t)N(x)$ respectively. If we keep only the first assumption and Fourier-transform Eq. (27), we obtain

$$\frac{\partial a(y,t)}{\partial t} = -\frac{1}{T_1} a(y,t) - \frac{1}{T_\Sigma} b(y,t) + \sqrt{2\pi}\,\widetilde{w}(y)\, b(y,t).$$

From this equation we can find the function $\widetilde{w}(y)$, since $a(y, t)$ and $b(y, t)$ can be determined from the experimental data. We write:

$$\widetilde{w}(y) = \frac{1}{\sqrt{2\pi}}\left[a(y,t) - a(y,0) + \frac{1}{T_1}\int_0^t a(y,t')\,dt' + \frac{1}{T_\Sigma}\int_0^t b(y,t')\,dt'\right]\left(\int_0^t b(y,t')\,dt'\right)^{-1}. \qquad (29)$$

which is in a form convenient for numerical calculations. For $N(x) = \text{const.}$, formula (29) reduces to the results (8) obtained earlier.

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