FREE INDUCTION SIGNAL IN EXCHANGE PAIRS

R. V. SHUBINA

Kazan' Physico-technical Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor July 20, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 50, 936–942 (April, 1966)

Formulas are derived for the initial amplitude and shape of the free induction signal (FIS). Usual conditions for magnetic resonance are assumed, and the time-dependent wave equation solution for the interaction of two coupled spins in fields of arbitrary intensity is employed. The temperature dependence of the signal is taken into account. It is demonstrated that because of the relaxation terms, decay of the FIS is of an oscillatory nature. The signal amplitude contains oscillations with a frequency proportional to the interaction constant of the coupled-spin pair. It is shown that the shape of the FIS depends on the temperature T. Near T = 0 decay of the FIS becomes weaker. The results of the theory are considered for the case of Nd^{3+} pairs in lanthanum ethyl sulfate (LaES).

1. INTRODUCTION

In magnetic resonance one frequently has to consider the interaction of groups of two or more spins with the magnetic field. This interaction differs from the interaction of single spins with the magnetic field.

Recently there has been much emphasis on the study of exchange pairs, by which it has been possible to explain a number of phenomena in maser theory. The spin-lattice relaxation of exchange pairs at low temperatures explains a number of phenomena that contradict the Kronig–Van Vleck theory, e.g., the strong dependence of the spin-lattice relaxation time T_1 on the concentration of paramagnetic particles, the weak dependence of T_1 on magnetic field, and the anomalous dependence of T_1 on temperature.

Of considerable interest are exchange pairs with an exchange interaction comparable to the Zeeman energy. The study of the EPR spectra of such exchange pairs makes it possible to determine the exchange interaction with high accuracy. Such pairs can interact with the single spins relatively well.

In this paper we shall consider pairs of two spins $s = 1/2$. The interaction between the spins is comparable to the interaction of one spin with the magnetic field. The Schrödinger equation is solved for a spin system consisting of the pair of interacting spins and acted upon by a pulsed field. Formulas are obtained for the decay of the free induction signal (FIS). The source of the decay is the dipole-dipole interaction of the pairs with each other and with single spins.

The decay of the signal contains oscillations due to the aforementioned dipole-dipole interactions, and, in addition, "beats" appear, as a result of the pairing of spins. The decay owing to the interaction of the pairs among themselves (see Fig. 2) differs from the decay due to the interaction of the pairs with single spins (see Fig. 3), firstly in that the first decay is slower and secondly in that as the temperature $T \to 0$, it weakens. The curve in Fig. 3 changes insignificantly with temperature.

The calculation we have carried out in the case of the dipole pairs of Nd^{3+} in lanthanum ethyl sulfate (LaES) shows the possibility of experimentally observing an electron spin echo in this substance. Along with the steady-state methods of studying EPR, the pulse method allows one to study the exchange pairs in ruby, exchange pairs of Ni^{2+} in $ZnSiF_6 \cdot 6H_2O$, and in other substances.[1]

In Sec. 2 of this paper we give a general mathematical solution of the problem based on the evolution operator method. In contrast to the work of Lowe and Norberg,[2] in which the problem of finding the evolution operator was solved exactly for nuclei with spin $I = 1/2$, in our work we give an exact solution of the problem of two interacting spins, $s = 1/2$, with temperature dependence taken into account.

2. SOLUTION OF THE SCHRODINGER EQUATION

Two coupled spins $\hat{K}$ and $\hat{J}$ with coupling energy

$$a_\parallel \hat{K}_z \hat{J}_z + {}^1/_2 a_\perp (\hat{K}_+ \hat{J}_- + \hat{K}_- \hat{J}_+)$$

($a_{\|}$ and $a_{\perp}$ are the interaction constants) are situated in a constant field $\mathbf{H}_0$ directed along Oz (axis of quantization) and in a field $\mathbf{H}_1$ rotating about Oz with angular velocity ω. The time-independent part of the spin Hamiltonian is

$$\hat{\mathscr{H}}_0 = \omega_{0j}\hat{J}_z + \omega_{0k}\hat{K}_z + a_{\|}\hat{K}_z\hat{J}_z + {}^1/_2\, a_{\pm}(\hat{K}_+\hat{J}_- + \hat{K}_-J_+);$$
$$\omega_{0j} = \gamma_j H_0, \quad \omega_{0k} = \gamma_k H_0;$$

here γ_j and γ_k are the gyromagnetic ratios for the spins $\hat{J}$ and $\hat{K}$, respectively. The time-dependent part of the spin Hamiltonian

$$\hat{\mathscr{H}}_1(t) = {}^1/_2(\omega_{1j}\hat{J}_+ + \omega_{1k}\hat{K}_+)e^{-i\omega t} + {}^1/_2(\omega_{1j}\hat{J}_- + \omega_{1k}\hat{K}_-)e^{i\omega t}$$

($\omega_{1j} = \gamma_j H_1$, $\omega_{1k} = \gamma_k H_1$), which is associated with the field rotating in the xy plane, can be made independent of time by transforming to a coordinate system rotating about Oz with angular velocity ω:

$$\hat{\mathscr{H}}_1' = \exp[i\hbar^{-1}\hat{F}_z\omega t]\,\hat{\mathscr{H}}_1 \exp[-i\hbar^{-1}\hat{F}_z\omega t]$$
$$= \omega_{1j}\hat{J}_x + \omega_{1k}\hat{K}_x, \quad \hat{F}_z = \hat{K}_z + \hat{J}_z.$$

The solution of the wave equation $i\hbar^{-1}\partial\psi/\partial t = (\hat{\mathscr{H}}_0 + \hat{\mathscr{H}}_1)\psi$ is described by the function $\psi(t) = \hat{L}(t)\psi(0)$, where $\hat{L}(t)$ is the system evolution operator:

$$\hat{L}(t) = \exp[-i\hbar^{-1}\hat{F}_z\omega t]\exp[-i\hbar^{-1}(\hat{\mathscr{H}}_0 + \hat{\mathscr{H}}_1' - \omega\hat{F}_z)t]. \quad (1)$$

Let us consider the simplest system, that of two coupled spins K and J for which $k = {}^1/_2$ and $j = {}^1/_2$. Let $\hat{F}$ be the total angular momentum of the pair of spins J and K. If the interaction between the spins of the pair is comparable to the Zeeman part $\hat{\mathscr{H}}_0$, the energy levels must be considered in the representation of the coupled spins.[3] The energy level diagram for the pair is given in Fig. 1. We symbolize the energy of the levels (1, 1), (0, 0), (1, 0), and (1, −1) respectively by

$$E_1 = \hbar\lambda_1, \quad E_2 = \hbar\lambda_2, \quad E_3 = \hbar\lambda_3, \quad E_4 = \hbar\lambda_4,$$

where

$$\lambda_1 = {}^1/_2(\omega_{0j} + \omega_{0k} + {}^1/_2\omega_F{}^{\|}),$$
$$\lambda_2 = {}^1/_2[-(\omega_0{}^2 + \omega_F{}^{\perp 2})^{1/2} - {}^1/_2\omega_F{}^{\|}],$$
$$\lambda_3 = {}^1/_2[(\omega_0{}^2 + \omega_F{}^{\perp 2})^{1/2} - {}^1/_2\omega_F{}^{\|}],$$
$$\lambda_4 = {}^1/_2(-\omega_{0j} - \omega_{0k} + {}^1/_2\omega_F{}^{\|}),$$
$$\omega_0 = \omega_{0j} - \omega_{0k}, \quad \omega_F{}^{\|} = a_{\|}\hbar, \quad \omega_F{}^{\perp} = a_{\perp}\hbar.$$

We shall consider transitions between levels 1, 3, and 4. Then the evolution operator $\hat{L}(t)$ in the coupled-spin representation is found by diagonalizing a third-order matrix extracted from the fourth-order matrix of $(\hat{\mathscr{H}}_0 + \hat{\mathscr{H}}_0' - \omega\hat{F}_z)$ (see [3]):

$$\hat{L}(t) = \begin{vmatrix} L_{11} & 0 & L_{13} & L_{14} \\ 0 & L_{22} & 0 & 0 \\ L_{31} & 0 & L_{33} & L_{34} \\ L_{41} & 0 & L_{43} & L_{44} \end{vmatrix},$$

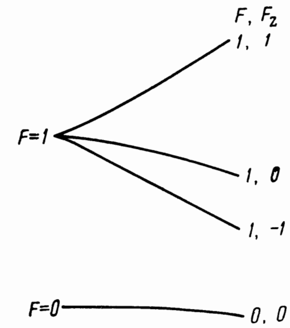

FIG. 1. Energy level diagram for a pair (energy vertical, magnetic field horizontal).

where

$$L_{11} = bca_i|\alpha_i|^2, \quad L_{22} = 1, \quad L_{33} = ca_i|\beta_i|^2,$$
$$L_{44} = b^{-1}ca_i|\gamma_i|^2, \quad L_{13} = bca_i\alpha_i\beta_i^*,$$
$$L_{14} = bca_i\alpha_i\gamma_i^*, \quad L_{31} = ca_i\alpha_i^*\beta_i,$$
$$L_{34} = ca_i\beta_i\gamma_i^*, \quad L_{41} = b^{-1}ca_i\alpha_i^*\gamma_i, \quad L_{43} = b^{-1}ca_i\beta_i^*\gamma_i$$

(the symbol for summation over i is omitted; i = 1, 2, 3);

$$b = e^{-i\omega t/\hbar}, \quad c = e^{-i\lambda_3 t}, \quad a_i = e^{-i\sigma_i t},$$
$$\sigma_{1,3} = {}^1/_2(\delta \pm (\delta^2 + \tilde{\omega}_1{}^2)^{1/2}), \quad \sigma_4 = \delta = \omega_{13} - \omega, \quad \omega = {}^1/_2\omega_{14};$$
$$\alpha_i = \left[1 + \frac{\delta - \sigma_i}{{}^1/_8\tilde{\omega}_1{}^2(1 - \cos\eta)} + \frac{1 + \cos\eta}{1 - \cos\eta}\right]^{-1/2},$$
$$\beta_i = -\alpha_i\frac{\delta - \sigma_i}{{}^1/_4\sqrt{2}\,\tilde{\omega}_1(1 - \cos\eta)^{1/2}}, \quad \gamma_i = \alpha_i\left(\frac{1 + \cos\eta}{1 - \cos\eta}\right)^{1/2},$$
$$\cos\eta = \omega_0(\omega_0{}^2 + \omega_F{}^{\perp 2})^{-1/2}, \quad \tilde{\omega}_1 = 2\gamma H_1.$$

3. INITIAL AMPLITUDE OF THE FREE INDUCTION SIGNAL

Let a pulse of an alternating magnetic field of frequency $\omega = {}^1/_2\omega_{14}$ act on a system consisting of c^2N pairs of coupled spins from time $t = 0$ to $t = t_0$ (c is the concentration of single spins, N the number of lattice sites). The duration of the pulse t_0 must satisfy the condition $t_0 \ll \tau$, where τ is the spin-spin relaxation time. Let us assume that the spin-lattice interactions are negligible. We take: 1) spins $\hat{J}$ and $\hat{K}$ identical ($\gamma_k = \gamma_j = \gamma$), 2) $\tilde{\omega}_1^2 \gg \delta^2$.

In the time interval $(0, t_0)$ the change of state of the system is described by the evolution operator $\hat{L}(t)$ according to Eq. (1). The average value of the physical quantity Q characterizing the non-equilibrium of the system is calculated from the well-known formula

$$\langle\hat{Q}(t)\rangle = \mathrm{Sp}\{\hat{\rho}_0\hat{L}^{-1}(t)\,\hat{Q}\hat{L}(t)\} \quad (2)$$

where $\hat{\rho}_0$ is the equilibrium density matrix.

In Eq. (2) all quantities are chosen in the coupled-spin representation. For the average value of the transverse components of the magnetic moment of the spin system at time $t = t_0$, we have the following expression:

$$\langle \mu_x(t_0)\mathbf{x} + \mu_y(t_0)\mathbf{y}\rangle = \mu(0)(\mathbf{x}\sin\omega t_0 - \mathbf{y}\cos\omega t_0)\sin\frac{\tilde{\omega}_1 t_0}{2}\cos\frac{\delta t_0}{2},$$

$$\mu(0) = \gamma\hbar c^2 N(R_4 - R_1); \tag{3}$$

R_α is a diagonal element of the equilibrium density matrix of the pair $\hat{\rho}_0$, $\alpha = 1, 2, 3, 4$:

$$R_\alpha = \exp(-E_\alpha/kT)\left\{\mathrm{Sp}\left[\sum_\alpha \exp(-E_\alpha/kT)\right]\right\}^{-1}.$$

The initial amplitude reaches a maximum if the duration of the pulse t_0 satisfies the condition $\tilde{\omega}_1 t_0/2 = \pi/2$. If spin-spin interactions are neglected after the pulse generator is turned off, we have the following expression for the average value of the transverse components (it is assumed that the condition $\tilde{\omega}_1 t_0/2 = \pi/2$ is fulfilled):

$$\langle \mu_x(t)\mathbf{x} + \mu_y(t)\mathbf{y}\rangle = \mu(0)(\mathbf{x}\sin\omega t - \mathbf{y}\cos\omega t)\cos\delta t'. \tag{4}$$

The time t varies from $t = 0$ to $t \to \infty$; $t' = t - t_0$. It is seen from Eq. (4) that in the absence of interactions in the xy plane, one will observe a precession of the transverse components of the magnetic moment with constant amplitude, i.e., there is no decay of the signal.

4. DECAY OF THE FREE INDUCTION SIGNAL

In the further behavior of the system, let us allow a dipole-dipole interaction between pairs of coupled spins $\hat{\mathcal{H}}_1^{jk}$ and an interaction between the pair and a single spin $\hat{\mathcal{H}}_2^{jl}$:

$$\hat{\mathcal{H}}_1^{jk} = A^{jk}\hat{F}_z^j\hat{F}_z^k + B^{jk}(\hat{F}_+^j\hat{F}_-^k + \hat{F}_-^j\hat{F}_+^k),\quad \hat{\mathcal{H}}_2^{jl} = \bar{A}^{jl}\hat{F}_z^j\hat{S}_z^l,$$

where

$$A^{jk} = (g_\parallel\beta)^2 r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}),$$

$$B^{jk} = (g_\perp\beta)^2 r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}),$$

$$\bar{A}^{jl} = g_\parallel\bar{g}_\parallel\beta^2\bar{r}_{jl}^{-3}(1 - 3\cos^2\bar{\theta}_{jl}).$$

Here θ_{jk} is the angle between $\mathbf{H}_0$ and the radius vector $\mathbf{r}_{jk}$ joining the pairs j and k; $\bar{\theta}_{jl}$ is the angle between $\mathbf{H}_0$ and the radius vector $\mathbf{r}_{jl}$ joining the pair j with a single spin l; g and $\bar{g}$ are the g factors of the pair and the single spin, respectively.

We shall apply the following formula for the calculation of the mean value:

$$\langle\hat{Q}(t)\rangle = \mathrm{Sp}\{\hat{\rho}_0\hat{L}^{-1}(t_0)\hat{L}^{-1}(t')\hat{Q}\hat{L}(t')\hat{L}(t_0)\},$$

where

$$\hat{L}(t') = \exp\left[-\frac{i}{\hbar}\sum_j \hat{\mathcal{H}}_0^j t'\right]\exp\left[-\frac{i}{\hbar}\sum_{j,k,l}(\hat{\mathcal{H}}_1^{jk} + \hat{\mathcal{H}}_2^{jl})t'\right]$$

$(\hat{\mathcal{H}}_0^j = \hat{\mathcal{H}}_0)$, and $\hat{L}(t_0)$ is given by Eq. (1)

In expanding $\hat{L}^{-1}(t')\hat{Q}\hat{L}(t')$ in series form we shall take into account 1) the first four terms of the expansion and 2) two-particle interactions. Two-particle interactions between spins are important, for example, when the concentration of paramagnetic ions in the crystalline lattice is small.

Using the conditions enumerated above, we obtained the following expression for the average value of the x component of the magnetic moment of the spin system:

$$\langle\mu_x(t)\rangle = \mu(0)[f_1(t')\sin\omega t + f_2(t')\cos\omega t] + \mu(0)\bar{f}(t')\sin\omega t; \tag{5}$$

here

$$f_1(t') = Q_{2n}(t')\cos\delta t' + Q_{2n+1}(t')\sin\delta t',$$

$$f_2(t') = -\delta\tilde{\omega}_1^{-1}(R_4 - R_1)[P_{2n}(t')\cos\delta t' + P_{2n+1}(t')\sin\delta t'],$$

$$\bar{f}(t') = \bar{Q}_{2n}(t')\cos\delta t',$$

$$Q_{2n}(t') = 1 - \frac{(t')^2}{2!}\frac{1}{2}(\langle\nu_2\rangle_{1,0} + \langle\nu_2\rangle_{0,-1}) + \frac{(t')^4}{4!}\frac{1}{2}(\langle\nu_4\rangle_{1,0} + \langle\nu_4\rangle_{0,-1}) - \ldots$$

$$= 1 - \frac{(t')^2}{2!}\left\{(2B^{jk})^2(R_1 + R_3 + R_4) + [(A^{jk})^2 - A^{jk}(2B^{jk})]\frac{R_1 + 2R_3 + R_4}{2}\right\}$$

$$+ \frac{(t')^4}{4!}\left\{(2B^{jk})^4(R_1 + R_3 + R_4) + [(A^{jk})^4 + 6(A^{jk})^2(2B^{jk})^2 - 2(A^{jk})^3(2B^{jk}) - 2A^{jk}(2B^{jk})^3]\frac{R_1 + 2R_3 + R_4}{2}\right\} + \ldots,$$

$$Q_{2n+1}(t') = -\frac{(t')^3}{3!}\frac{1}{2}(\langle\nu_3\rangle_{0,-1} - \langle\nu_3\rangle_{1,0}) + \ldots$$

$$\ldots = -\frac{(t')^3}{3!}\left[3(A^{jk})^2(2B^{jk})\frac{R_1 + 2R_3 + R_4}{4}\right] + \ldots,$$

$$P_{2n}(t') = -\frac{(t')^2}{2!}2A^{jk}(2B^{jk}) + \frac{(t')^4}{4!}[A^{jk}(2B^{jk})^3 + (A^{jk})^3(2B^{jk})] - \ldots,$$

$$P_{2n+1}(t') = \frac{t'}{1!}(2B^{jk}) - \frac{(t')^3}{3!}[(2B^{jk})^3 + 3(A^{jk})^2(2B^{jk})] + \ldots$$

$$\bar{Q}_{2n}(t') = 1 - \frac{(t')^2}{2!}\langle\nu_2\rangle_{1/2,-1/2} + \frac{(t')^4}{4!}\langle\nu_4\rangle_{1/2,-1/2}$$

$$= 1 - \frac{(t')^2}{2!}\left(\frac{\bar{A}^{jl}}{2}\right)^2 + \frac{(t')^4}{4!}\left(\frac{\bar{A}^{jl}}{2}\right)^4 - \ldots$$

(the signs of summation over j ($\neq$k) and j ($\neq l$) are omitted), $\langle \nu_n \rangle_{1,0}$, $\langle \nu_n \rangle_{0,-1}$, $\langle \nu_n \rangle_{1/2,-1/2}$ are the reduced moments of the n-th order for the corresponding transitions.

The average value of the y component of the magnetic moment of the spin system $\langle \mu_y(t) \rangle$ is obtained from (5) with the following replacement:

$$\sin \omega t \cos \delta t' \leftrightarrow -\cos \omega t \cos \delta t',$$
$$\sin \omega t \sin \delta t' \leftrightarrow \cos \omega t \sin \delta t'.$$

As is seen from the above, only spin-spin interactions were taken into account in calculating the FIS decay. However, for sufficiently strong exchange, modulation of the anisotropic exchange interaction by lattice vibrations can produce a significant spin-phonon interaction for the spins of a pair.

We shall estimate the spin-lattice relaxation time T_1 for pairs of Cr^{3+} in ruby.[4] For this we make use of the three-reservoir model of Bloembergen and Wang[5] and Morocha's result.[6] We assume that the contribution of high-frequency phonons is small. Then for a magnetic field corresponding to the frequency $\nu = 10^{10}$ Hz and for a Cr^{3+} concentration c = 0.1%, Morocha's Eq. (38) gives $T_1 \sim 10^{-3}$ sec at T = 2° K and $T_1 \sim 10^{-6}$ sec at T = 300° K.

Thus, at least at helium temperatures and below, we may neglect spin-lattice relaxation due to the indicated spin-phonon interaction mechanism, since the spin-spin relaxation time T_2 for Cr^{3+} pairs in ruby is much shorter.

5. TEMPERATURE DEPENDENCE OF THE FIS

Equation (5) permits us to judge the temperature dependence of the FIS. The functions $f_1(t')$ and $\bar{f}_1(t')$ vary insignificantly with temperature. The quantity $f_2(t')$ on the other hand changes markedly with temperature. As $T \to \infty$ it vanishes, but near T = 0 its contribution, generally speaking, is important. However, the shape of the FIS does not change noticeably, because of the condition we have introduced ($\tilde{\omega}_1^2 \gg \delta^2$). The curve drawn in Fig. 2 as a fine line represents the contribution of $f_2(t')$ to the FIS at T = 2° K.

As was mentioned above, the spin-lattice interactions are considered to be negligibly small. If they were strong, the sample would have to be investigated at low temperatures, and, as is clear from the preceding discussion, the shape of the FIS would then depend on temperature.

6. FIS IN LaES-Nd^{3+}

Consider the pairs of interacting Nd^{3+} ions in LaES containing from 1 to 10% Nd.[7] For two

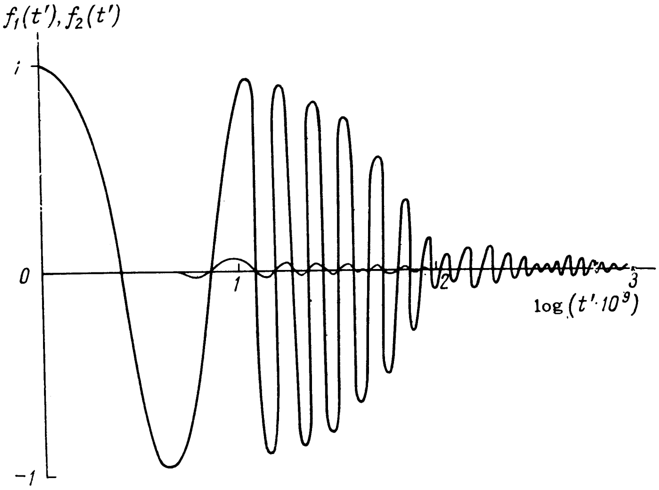

FIG. 2. FIS decay curve of Nd^{3+} pairs in LaES, due to interaction between the pairs; T = 2°K. Curve $f_2(t')$ is indicated by the fine line.

nearest-neighbor identical Nd^{3+} ions forming a dipole pair, the Hamiltonian and energy levels are such (see [7], Appendix) that our theory is applicable to this material. We shall assume that the concentration of Nd^{3+} ions is c = 10%, the dc field $H_0 \approx 1800$ G, the ac field $H_1 \approx 170$ G, with $\omega = \frac{1}{2}\omega_{14} = 9.5 \times 10^9$ Hz. The initial amplitude of the FIS is a maximum when $\tilde{\omega}_1 t_0 = \pi/2$, where the pulse duration $t_0 \approx 10^{-9}$ sec.

To determine the shape of the FIS it is necessary to know the lattice sums appearing in Eq. (5). These have been evaluated with account taken of over 99% of all the neighbors of a pair (see [8]). The direction of the field $\mathbf{H}_0$ is taken along the symmetry axis of the internal crystalline electric field, and T = 2° K. The lattice sums have the following values:

$$2B^{jk} = -2.72 \cdot 10^{-20} \text{ erg}, \quad (2B^{jk})^2 = 3.21 \cdot 10^{-38} \text{ erg}^2,$$
$$(A^{jk})^2 = 1.28 \cdot 10^{-36} \text{ erg}^2, \quad A^{jk}(2B^{jk}) = -2.03 \cdot 10^{-37} \text{ erg}^2,$$
$$(2B^{jk})^3 = -9.13 \cdot 10^{-57} \text{ erg}^3, (A^{jk})^2(2B^{jk}) = -5.16 \cdot 10^{-55} \text{ erg}^3,$$
$$(2B^{jk})^4 = 2.23 \cdot 10^{-74} \text{ erg}^4, \quad (A^{jk})^4 = 3.63 \cdot 10^{-71} \text{ erg}^4,$$
$$(A^{jk})^3(2B^{jk}) = -1.19 \cdot 10^{-71} \text{ erg}^4,$$
$$(A^{jk})^2(2B^{jk})^2 = 9.18 \cdot 10^{-73} \text{ erg}^4,$$
$$A^{jk}(2B^{jk})^3 = -0.33 \cdot 10^{-72} \text{ erg}^4,$$
$$(\bar{A}^{jl})^2 = 2.6 \cdot 10^{-35} \text{ erg}^2, \quad (\bar{A}^{jl})^4 = 2.08 \cdot 10^{-69} \text{ erg}^4$$

(signs of summation over j($\neq$k) and j($\neq l$) are omitted).

The shape of the FIS at T = 2° K is shown in Figs. 2 and 3.

The curve in Fig. 2 describes the FIS decay due to the dipole-dipole interaction of the pairs with each other $\mathcal{H}_1^{jk}$. This interaction leads to an oscillatory character of the decay. Superposed on the

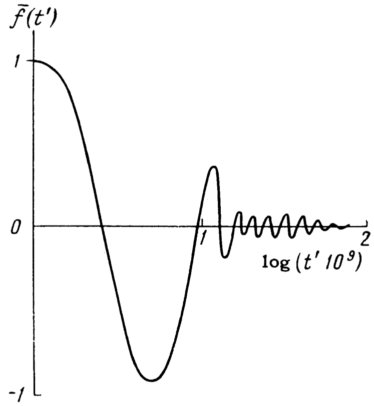

FIG. 3. FIS decay curve of Nd^{3+} pairs in LaES, due to interaction between the pairs and single spins; T = 2°K.

decay associated with the pair-pair relaxation mechanism, one sees beats, the frequency of which is determined by the interaction of the two spins in a pair and equals 5×10^8 Hz. The decay time $\tau_{pp} \approx 8 \times 10^{-7}$ sec.

The decay curve in Fig. 3 is determined by the dipole-dipole interaction of the pairs with single spins $\hat{\mathscr{H}}_2^{jl}$ and also has an oscillatory character. The decay contains beats of frequency 5×10^8 Hz. The decay time for this relaxation mechanism is $\tau_{ps} \approx 9 \times 10^{-8}$ sec.

Let us compare the curves in Figs. 2 and 3. The pair–single ion relaxation mechanism (Fig. 3) provides faster decay. In Eq. (5) the terms in $f_1(t')$, which contain the odd moments, give a contribution to the decay represented by the curve $f_1(t')$ in Fig. 2.

The author thanks U. Kh. Kopvillem for guidance in this work.

[1] L. Rimai, H. Statz, M. J. Weber, G. A. de Mars, and G. F. Koster, Phys. Rev. Letters **4**, 125 (1960); J. Owen, J. Appl. Phys. **32**, 213S (1961); S. A. Al'tshuler and R. M. Valishev, JETP **48**, 464 (1965), Soviet Phys. JETP **21**, 309 (1965).

[2] I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

[3] W. Franzen and M. Alam, Phys. Rev. **133**, A460 (1964).

[4] H. Statz, L. Rimai, M. J. Weber, G. A. de Mars, and G. F. Koster, J. Appl. Phys. **32**, 218S (1961).

[5] N. Bloembergen and S. Wang, Phys. Rev. **93**, 72 (1954).

[6] A. K. Morocha, FTT **4**, 2297 (1962), Soviet Phys. Solid State **4**, 1683 (1963).

[7] J. M. Baker, Phys. Rev. **136**, A1341 (1964).

[8] U. Kh. Kopvillem, Dissertation, Kazan State Univ., 1958; I. Svare and G. Seidel, Phys. Rev. **134**, A172 (1964); N. G. Koloskova and U. Kh. Kopvillem, Izv. vuzov, Fizika, **3**, 223 (1960).

Translated by L. M. Matarrese
118