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Formation mechanisms and properties of electron spin echoes in solids

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Abstract. In addition to the ordinary Hahn mechanism of electron spin echoes (ESEs), i.e. the non-linear amplitude-dependent excitation of spin precession, two new mechanisms, namely amplitude-dependent shift $\Delta\omega(M_z)$ of resonance frequency (pulling) and amplitude-dependent damping $\Gamma(M_z) = T_2^{-1}(M_z)$ (M_z is the z component of the magnetization), are proposed. The latter two mechanisms are due to the effect of instantaneous diffusion. A qualitative picture and a quantitative theory of ESEs in solids are elaborated, taking into account all three non-linear mechanisms. A new method based on the modulation effect of echo damping is presented to obtain the parameters T_1, T_2 and $\Delta\omega$. The modulation effect is due to the simultaneous action of the three non-linear mechanisms.

1. Introduction

The time decay of electron spin echoes (ESEs) in solids is due to the interaction of resonant spins with each other, with non-resonant spins and with the lattice degrees of freedom. Among these factors of the decay, the mechanism of instantaneous diffusion [1–3] plays an important role. The remarkable property of this mechanism is its dependence on the amplitude of the applied RF pulses $H_j(t)$ (here $j = 1, 2, 3$ is the number of the excitation pulses). This property can be understood as follows. The exciting pulses change the dipole moments of active ions and as a consequence affect the dipole–dipole interaction. As a result, the precession frequency $\Omega = \Omega(M_z)$ and damping parameter $\Gamma(M_z) = T_2^{-1}(M_z)$ of active spins depend on $H_j(t)$ and the pulse duration t_j. It will be shown below that the amplitude dependences of Ω and Γ are a source of the new non-linear mechanisms of ESE formation, namely amplitude-dependent dispersion and amplitude-dependent damping, which are different from the non-linear excitation mechanism of the ordinary Hahn echo [3]. The situation here is similar to that observed in NMR multiple echoes in solid ^{3}He [4], cyclotron echoes in plasmas [5], NMR echoes in antiferromagnetics [6], and polarization echoes in powders [7]. Occasionally the above mechanisms are referred to as the anharmonic oscillator or the Gould mechanisms, and the signals are called Gould-type echoes.

The purpose of this paper is to present a qualitative picture and a quantitative study of ESE formation in solids, taking into account all three non-linear mechanisms.

2. Qualitative picture of echo formation

Considering the theory of ESEs, let us begin with the Bloch equations which may be written in the reference frame rotating with RF field frequency ω_0 as follows:

$$\dot{M}_x = -\Gamma(M_z)M_x - \omega'(M_z)M_y \qquad \dot{M}_y = \omega'(M_z)M_x - \Gamma(M_z)M_y - \omega_j M_z$$
$$\dot{M}_z = \omega_j M_y - (M_z - M_{z0})/T_1 \qquad \omega'(M_z) = \Omega(M_z) - \omega_0 \qquad \omega_j = \gamma H_j. \tag{1}$$

Here M_{z0} is the equilibrium value of the magnetization M_z. Equations (1) contain all three non-linear mechanisms. Indeed, non-linear amplitude-dependent excitation is confined with the term $-\omega_j M_z$. Since M_z itself depends on $H(t)$ during the pulse, the exciting force is non-linear in $H(t)$. This is the source of the Hahn-type echo.

As was mentioned above, the parameters $\Gamma(M_z)$ and $\Omega(M_z)$ are not constants. They depend on the dipole–dipole interactions of paramagnetic centres and provide the basis of new non-linear mechanisms in echo formation. Instead of attempting to specify the functions $\Omega(M_z)$ and $\Gamma(M_z)$ explicitly and to proceed with solving the non-linear equations (1), it is worth beginning by considering a simple qualitative model of echo formation similar to that proposed by Gould [5].

Therefore, let us neglect the decay mechanisms (i.e. put $T_1 = T_2 = \infty$) and neglect inhomogeneous broadening during the excitation pulses, so that all spin packets (isochromats) are assumed to be excited by pulses resonantly: $\omega' = 0$. At the end of the first pulse of duration t_1, equations (1) yield

$$M_+(t_1) = M_x(t_1) + \mathrm{i}M_y(t_1) = -\mathrm{i}M_{z0}\sin(\omega_1 t_1) = -\mathrm{i}M_{z0}\sin\theta_1$$
$$M_z(t_1) = M_{z0}\cos\theta_1. \tag{2}$$

Under the resonance approximation adopted, the vectors $M_+(t_1)$ of all spin packets have identical values and directions in the phase plane (M_x, M_y). Let us assign this direction as the positive direction of the x axis of the rotating reference frame (figure 1(a)).

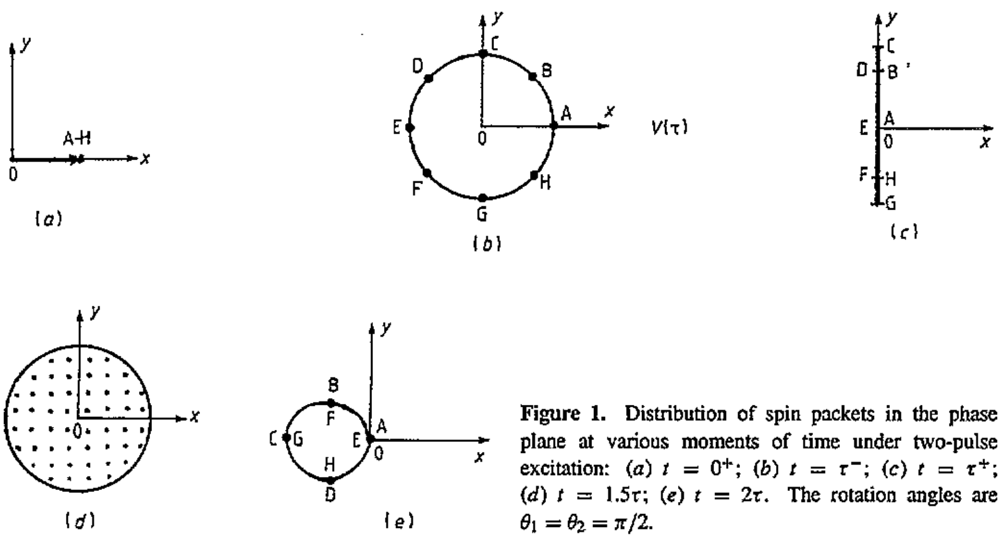

Figure 1. Distribution of spin packets in the phase plane at various moments of time under two-pulse excitation: (a) $t = 0^+$; (b) $t = \tau^-$; (c) $t = \tau^+$; (d) $t = 1.5\tau$; (e) $t = 2\tau$. The rotation angles are $\theta_1 = \theta_2 = \pi/2$.

Because of inhomogeneous line broadening, over the time interval $t \gg 2\pi(\langle\Delta\omega^2\rangle)^{1/2}$, where $(\langle\Delta\omega^2\rangle)^{1/2} = (T_2^*)^{-1}$ is the width of the line characterized by the distribution function $g_1(\omega)$, the spin packets $M_+(\omega, t_1)$ would be more or less evenly distributed over the circumference with radius $|M_+(t_1)| = M_{z0}\sin\theta_1$ positioned at the origin, according to the law

$$M_+(t) = M_+(t_1)\exp(\mathrm{i}\omega t) \qquad \omega = \Omega_0 - \omega_0. \tag{3}$$

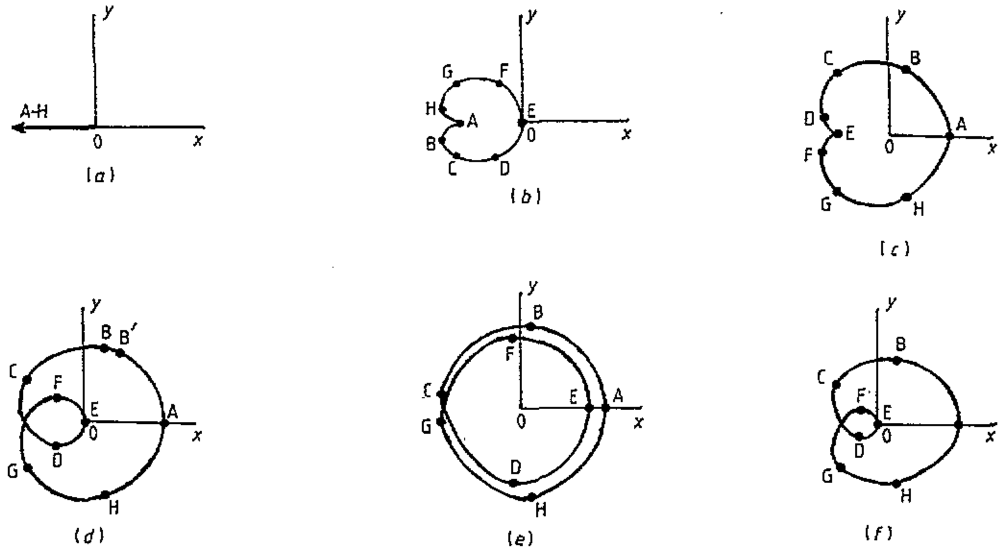

Figure 2. Distribution of spin packets in the phase plane at the time of formation of two-pulse echo ($t = 2\tau$) for various rotation angles θ_1 and θ_2: (*a*) $\theta_1 = \pi/2, \theta_2 = \pi$; (*b*) $\theta_1 = \theta_2 = 2\pi/3$; (*c*) $\theta_1 = \pi/4, \theta_2 = \pi/2$; (*d*) $\theta_1 = \theta_2 = \pi/4$; (*e*) $\theta_1 = \pi/4, \theta_2 = 0.1$; (*f*) $\theta_1 = \theta_2 = 0.01$.

Here Ω_0 is the precession frequency of an isochromat.

Figure 1(*b*) displays the status of the system prior to the second pulse $t = \tau^-$ arriving at time τ after the first pulse. Point A belongs to the isochromats whose vectors $M_+(t)$ have been rotated by the angle $(\omega\tau)_A = 0 \pm 2\pi n$ over this time interval; point B depicts spin packets with rotation angles $(\omega\tau)_B = \pi/4 \pm 2\pi n$, etc.

The expressions

$$\begin{aligned} &M_+(t_2) = -\mathrm{i}M_{z0}[a_0' \exp(-\mathrm{i}\omega\tau) + a_1' + a_2' \exp(\mathrm{i}\omega\tau)] \\ &a_0' = -\sin\theta_1 \sin^2(\theta_2/2) \qquad a_1' = \cos\theta_1 \sin\theta_2 \\ &a_2' = \sin\theta_1 \cos^2(\theta_2/2) \\ &M_z(t_2) = M_{z0}[\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\omega\tau)] \end{aligned} \tag{4}$$

describe the state of spin packets at the end of the second pulse (H_2, t_2). As an example, figure 1(*c*) illustrates the state of transverse components of isochromats for $\theta_1 = \theta_2 = \pi/2$.

After the second pulse, dephasing of the dipoles takes place again and, for instance after a time interval $t = 1.5\tau$ following the first pulse, the isochromats are more or less evenly spread either within a circle of corresponding radius (if $\theta_1 = \theta_2$), or a ring (when $\theta_1 \neq \theta_2$). In the case of pure Hahn echoes ($\theta_1 = \pi/2; \theta_2 = \pi$) the isochromats become evenly spread over the circumference of radius $M_{z0} \sin\theta_1 = M_{z0}$. The position of the transverse components of the isochromats can be described in this situation as

$$M_+(t > \tau + t_2) = M_+(t_2) \exp[\mathrm{i}\omega'(t - \tau)] \tag{5}$$

where ω' denotes the difference frequency after the second pulse.

Thus, most time spin packets are spread over the phase plane, and naturally there is no response signal. However, one can see that, at times $t = 2\tau, 3\tau, \ldots$, the isochromats become regrouped according to the diagram given in figure 1(*e*) for $t = 2\tau$ ($\theta_1 = \theta_2 = \pi/2$) and according to figure 2 for other values of the angles θ_1 and θ_2.

It is obvious from figures 1(*e*), 2(*a*) and 2(*b*), and less obvious from figures 2(*c*)–2(*f*), that the sum over all isochromats is

$$\sum_A^H M_+(t=2\tau) = \int_{-\infty}^{\infty} M_+(t,\omega) g_1(\omega)\,\mathrm{d}\omega < 0 \qquad (6)$$

i.e. the transverse magnetization is not equal to zero. This non-zero signal is provided by the mechanism of non-linear excitation [5], attaining its maximum at $\theta_1 = \pi/2$, $\theta_2 = \pi$ (the Hahn echo). At these angles the last two terms in the square brackets in the expression for $M_+(t_2)$ in equations (4) (which, as will be shown below, are responsible for echoes of the Gould type) are equal to zero, whereas the first term (the Hahn echo) has the maximum value.

Let us now consider the role of the other two mechanisms in the formation of echoes. The dipole–dipole interaction of active paramagnetic ions provides a contribution to the shift ω' and broadening of the absorption line (i.e. in the first moment $\mathcal{M}_1$ and second moment $\mathcal{M}_2$ of the line). It is found in the low-temperature approximation [8] that $\mathcal{M}_1 \sim \eta$, $\mathcal{M}_2 = \mathcal{M}_2(0)(1-\eta^2)^{1/2}$. Here $\eta = M_z/M_0$, $M_0 = \gamma\hbar n_0 S$, γ is the magnetomechanical ratio, $\hbar$ is the Planck constant, n_0 is the concentration of the active ions, S is the spin quantum number and $\mathcal{M}_2(0)$ is the high-temperature ($\eta = 0$) value of the second moment.

Thus, we can write

$$\omega' = \omega - \omega_\mathrm{d}\eta \qquad \omega = \Omega_0 - \omega_0 \qquad (7)$$

$$\Gamma = \Gamma_0 + \Gamma_\mathrm{d}(1-\eta^2)^{1/2} \qquad \Gamma_\mathrm{d} \simeq [\mathcal{M}_2(0)]^{1/2}. \qquad (8)$$

The parameters ω_d and Γ_d are functions of the local fields [8]. In the present study, ω_d, Γ_d and Γ_0 are considered as phenomenological parameters to be obtained from experiments on spin echoes.

The non-linear process of echo formation under conditions of amplitude-dependent decay and dispersion develops after the second pulse. Therefore, we may put $\eta(t_2) = M_z(t_2)/M_0$ in equations (7) and (8). Assume that the formation of the echo is controlled by the amplitude-dependent dispersion (7). As an example, let us consider the schematic diagram given in figure 2(*d*) ($\theta_1 = \theta_2 = \pi/4$). A in figure 2(*d*) is the point for which $M_z(t_2) = 0$ does not change its position; other points (for instance point B′) are delayed in phase by $\omega_\mathrm{d}\tau(M_z/M_0)$, if $\omega_\mathrm{d} > 0$. When $\omega_\mathrm{d}\tau \ll 1$, the contribution to the echo from the a_1'-term in equations (4) is linear in $\omega_\mathrm{d}\tau$. It is delayed in phase with respect to the Hahn echo by $\pi/2$ (directed along the y axis). When $\omega_\mathrm{d} < 0$, it is ahead of the Hahn echo by $\pi/2$. The contribution of the a_2'-term in $M_+(t_2)$ (equations (4)) is an even function of $\omega_\mathrm{d}\tau$ and coincides in direction with the Hahn echo.

In the case of amplitude-dependent decay (8) the latter exhibits the maximum value for isochromat A in figure 2(*d*) equal to $\Gamma_\mathrm{A} = \Gamma_0 + \Gamma_\mathrm{d}$, gradually decreasing to its minimum value $\Gamma_\mathrm{E} = \Gamma_0 + \Gamma_\mathrm{d}(1-\eta_0^2)^{1/2}$, $\eta_0 = M_{z0}/M_0$ at point E. Therefore, owing to the different relaxation rates of points A, B, C, …, the centre of the dipole moments of the system on the phase plane (i.e. the 'centre of mass' of the curve shown in figure 2(*d*)) is displaced and the additional contribution to $M_+(2\tau)$ occurs at the time when the echo appears (figure 2(*d*)). This contribution summed over eight isochromats A, B, C, …, H in the limits $\eta_0^2 \ll 1$ and $(\Gamma_\mathrm{d}\tau\eta_0^2)^2 \ll 1$ equals

$$M_+(2\tau) \sim -\mathrm{i}M_{z0}[(-0.937a_1' + 0.25a_2')\eta_0^2\Gamma_\mathrm{d}\tau + 8a_0']$$

where $a'_0 \simeq -0.1$, $a'_1 \simeq 0.5$ and $a'_2 \simeq 0.6$. Therefore, in this case the echo caused by non-linear decay is added to the Hahn echo.

In the general case the value and direction of the echoes depend on the amplitudes of pulses, on ω_d, on Γ_d and on the interval τ. Below we shall consider the impact of these parameters on the echo.

Generalizing the qualititative approach proposed to the case of three-pulse excitation is self-evident.

3. Quantitative consideration: two-pulse echoes

The character of operation of the above non-linear mechanisms in the echo formation process makes it possible to put forward some simplifying suggestions prior to solving the non-linear equations (1). Thus, during short pulses $t_j \ll \tau \simeq T_2$, one can neglect decay and the change in the frequency shift. This means that, during the first pulse, $\Gamma = 0$ and $\omega'(0) = \omega - \omega_d \eta_0$. Moreover, usually $T_2 \ll T_1$; therefore, in the case of a two-pulse echo, one may omit longitudinal relaxation. Under these conditions, equations (1) can be easily solved, and one finds that, at a time $t > \tau + t_2$ after the first pulse,

$$
\begin{aligned}
&M_+(t > \tau + t_2) = M_+(t_2) \exp\{[-\Gamma_2 + \mathrm{i}\omega'(t_2)](t-\tau)\} \\
&M_+(t_2) = M_{z0}\{a_0 \exp[-\mathrm{i}\omega'(t_1)\tau] + a_1 + a_2 \exp[\mathrm{i}\omega'(t_1)\tau]\} \\
&a_0 = \mathrm{i}(\omega_1\omega_2^2/\Omega_1\Omega_2^2) \sin\theta_1 \sin^2(\theta_2/2) \exp(-\Gamma_1\tau)\{1 - [\mathrm{i}\omega'(0)/\Omega_1]\tan(\theta_1/2)\} \\
&a_1 = -(\mathrm{i}\omega_2/\Omega_1^2\Omega_2)[\omega'^2(0) + \omega_1^2\cos\theta_1]\sin\theta_2\{1 + [\mathrm{i}\omega'(t_1)/\Omega_2]\tan(\theta_2/2)\} \\
&a_2 = -[\mathrm{i}(\omega_1 \sin\theta_1)/2\Omega_1\Omega_2^2]\{\omega_2^2 + [\omega_2^2 + 2\omega'^2(t_1)]\cos\theta_2 + \mathrm{i}2\Omega_2\omega'(t_1)\sin\theta_2\} \\
&\qquad\qquad \times \exp(-\Gamma_1\tau)\{1 + [\mathrm{i}\omega'(0)/\Omega_1]\tan(\theta_1/2)\} \\
&\Gamma_j = \Gamma_0 + \Gamma_d[1 = \eta^2(t_j)]^{1/2} \qquad \omega'(t_j) = \omega - \omega_d\eta(t_j) \qquad \eta(t_j) = M_z(t_j)/M_0 \\
&M_z(t_1) = M_{z0}[\omega'^2(0) + \omega_1^2\cos\theta_1]/\Omega_1^2 \\
&M_z(t_2) = M_{z0}\{c_0 + c_1\cos[\omega'(t_1)\tau] + c_2\sin[\omega'(t_1)\tau]\} \\
&c_0 = (\Omega_1\Omega_2)^{-2}[\omega'^2(0) + \omega_1^2\cos\theta_1][\omega'^2(t_1) + \omega_2^2\cos\theta_2] \\
&c_1 = -(\omega_1\omega_2/\Omega_1\Omega_2)\exp(-\Gamma_1\tau)[\sin\theta_1\sin\theta_2 - [4\omega'(0)\omega'(t_1)/\Omega_1\Omega_2]\sin^2(\theta_1/2)\sin^2(\theta_2/2)] \\
&c_2 = (2\omega_1\omega_2/\Omega_1\Omega_2)\exp(-\Gamma_1\tau)\{[\omega'(t_1)/\Omega_2]\sin\theta_1\sin^2(\theta_2/2) \\
&\qquad\qquad + [\omega'(0)/\Omega_1]\sin^2(\theta_1/2)\sin\theta_2] \\
&\Omega_1^2 = \omega_1^2 + \omega'^2(0) \qquad \Omega_2^2 = \omega_2^2 + \omega'^2(t_1) \qquad \theta_j = \Omega_j t_j.
\end{aligned}
\tag{9}
$$

For further calculations we should simplify the expression for $\Gamma_2(M_z(t_2))$. The two following cases are of particular interest: first, $\eta_0^2 \ll 1$; second, η_0 is of the order of unity. Consider the first case. We have

$$
\Gamma_2 = \Gamma_0 + \Gamma_d [\![1 - (\eta_0^2/2)\{c_0 + c_1\cos[\omega'(t_1)\tau] + c_2\sin[\omega'(t_1)\tau]\}^2]\!]. \tag{10}
$$

Further, we can restrict our consideration by the resonant approximation, i.e. assume that $\omega'(0) = \omega'(t_1) = 0$ during the pulses. In this case, $c_2 = 0$ and we obtain from equation

(10)

$$\Gamma_2 \simeq \Gamma_2' - \Gamma_d \eta_0^2 c_0 c_1 \cos[\omega'(t_1)\tau] - (\Gamma_d \eta_0^2 c_1^2/4) \cos[2\omega'(t_1)\tau]$$
$$\Gamma_2' = \Gamma_0 + \Gamma_d[1 - (\eta_0^2/2)(c_0^2 + c_1^2/2)]. \tag{11}$$

Using the fact that ω_2 contains the term proportional to $\cos[\omega'(t_1)\tau]$, and Γ_2 additionally contains the term proportional to $\cos[2\omega'(t_1)\tau]$, one can make use of the expansion with respect to the Bessel functions of the first kind $J_n(q)$:

$$\exp(\mathrm{i}q \cos z) = \sum_{n=-\infty}^{\infty} \mathrm{i}^n J_n(q) \exp(\mathrm{i}nz). \tag{12}$$

This facilitates transforming $M_+(t)$ in equations (9) into

$$M_+(t > \tau + t_2, \omega) = M_{z0} \sum_{n_1,n_2=-\infty}^{\infty} \mathrm{i}^{n_1+n_2}[\mathrm{i}a_0 J_{n_1+1}(q_1) + a_1 J_{n_1}(q_1)$$
$$- \mathrm{i}a_2 J_{n_1-1}(q_1)] J_{n_2}(q_2) \exp[-\Gamma_2'(t-\tau)] \exp\{\mathrm{i}\omega[t - (1 - n_1 - 2n_2)\tau]\}$$
$$\times \exp[-\mathrm{i}\omega_d \eta_0 c_0 (t-\tau) - \mathrm{i}(n_1 + 2n_2)\omega_d \eta(t_1)\tau] \tag{13}$$
$$q_1 = -c_1[\omega_d \eta_0 + \mathrm{i}\Gamma_d \eta_0^2 c_0](t-\tau) \qquad q_2 = -(\mathrm{i}/4)\Gamma_d \eta_0^2 c_1^2 (t-\tau).$$

The result obtained describes an isochromat with difference frequency ω. In principle, the absorption line may be inhomogeneously broadened for two reasons: the spread of the unshifted frequency Ω_0, and the spread $\Delta\omega_d$ of the parameter ω_d. When the spread ω_d is neglected, equation (13) shows that echoes are generated at times

$$t_e = (-n_1 - 2n_2 + 1)\tau \tag{14}$$

the selection rule $-n_1 - 2n_2 = N$ corresponding to the Nth echo signal. According to the definition of q_1 and q_2, one can see that $|q_i| < 1$. Thus, $n_1 = -1$, $n_2 = 0$, and $n_1 = 1$, $n_2 = -1$, are the terms which are responsible for a substantial contribution to the first echo signal $(t = 2\tau)$.

In the case of intense pulses when $\theta_j = \omega_j t_j \sim 1$, one should take into consideration the contribution from both the above terms. In this case the expression for the signal becomes excessively long, resulting in laborious analyses. The dependence of the echo on τ does not exhibit any distinct pecularities.

In the case of weak pulses, i.e. when $\theta_j \ll 1$, we have $|q_2| \ll 1$, and one should retain only the term for $n_1 = -1$, $n_2 = 0$, in the expression for $M_+(t = 2\tau)$. The dependence of the echo amplitude $V(2\tau)$ on τ can be written as

$$V(t = 2\tau) \sim |M_+(2\tau)| \sim M_{z0}|a_0 J_0(q_1) + \mathrm{i}a_1 J_1(q_1) - a_2 J_2(q_1)| \exp(-\Gamma_2'\tau)$$
$$a_0 \simeq \mathrm{i}\sin\theta_1 \sin^2(\theta_2/2)\exp(-\Gamma_1\tau) \qquad a_1 \simeq -\mathrm{i}\cos\theta_1 \sin\theta_2$$
$$a_2 \simeq -\mathrm{i}\sin\theta_1 \cos^2(\theta_2/2)\exp(-\Gamma_1\tau) \qquad c_0 \simeq \cos\theta_1 \cos\theta_2 \tag{15}$$
$$c_1 \simeq -\sin\theta_1 \sin\theta_2 \exp(-\Gamma_1\tau).$$

According to this expression, the term $a_0 J_0(q_1)$ describes the contribution in the echo signal of the Hahn type, the other two terms being responsible for the Gould-type echo in agreement with the qualitative consideration.

Consider now the dependence of parameters of the echo on τ. The parameter q_1, being a function of τ, increases its modular value from zero (when $\tau = 0$), attaining its maximum at $\tau = 1/\Gamma_1$. A further increase in τ results in a gradual decrease in the parameter q_1. Under the approximation $|q_1|^2 \ll 1$, one finds that $V(2\tau)$ has a minimum when $\tau = \tau_{\min}$, and a maximum when $\tau = \tau_{\max}$ (figure 3), where

$$\tau_{\min(\max)} = (1/4\Gamma^*)[1 - \alpha(\Gamma_d/\omega_d)\eta_0 c_0 \pm (1-\alpha^2)^{1/2}]$$
$$\Gamma^* = \Gamma_0 + \Gamma_d\{1 - (\eta_0^2/4)[\cos^2\theta_1(1+\cos^2\theta_2) + \tfrac{1}{2}\sin^2\theta_1\sin^2\theta_2\exp(-2\Gamma_1\tau)]\} \quad (16)$$
$$\alpha = 2\Gamma^*\omega_d\eta_0/[\omega_d^2 + \Gamma_d^2\eta_0^2c_0^2]\eta_0^2\cos\theta_1\cos^2(\theta_2/2).$$

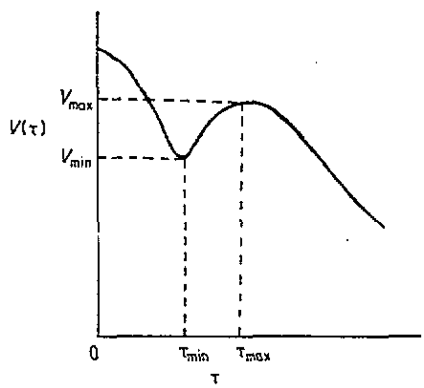

Figure 3. Amplitude of the two-pulse echo ($t = 2\tau$) versus interval τ between pulses.

The upper sign (+) applies to $\tau_{\max}$, and the lower sign (−) to $\tau_{\min}$. These expressions express the parameters of interest, namely α and Γ^*, through the measurable value $\Delta\tau = \tau_{\max} - \tau_{\min}$:

$$\Delta\tau = (1-\alpha^2)^{1/2}/2\Gamma^*. \quad (17)$$

As the definition of α suggests, it is easier to observe the extrema at low values of θ_1 and θ_2. They disappear on increase in θ_j.

One finds for the intensity of the echo at the extrema (16)

$$V_{\min} = V_0\sin\theta_1\sin^2(\theta_2/2)(\omega_d/\alpha\Gamma^*)^{1/2}[1-(1-\alpha^2)^{1/2}]^{1/2}\exp(-2\Gamma^*\tau_{\min})$$
$$V_{\max} = V_0\sin\theta_1\sin^2(\theta_2/2)(\omega_d/\alpha\Gamma^*)^{1/2}[1+(1-\alpha^2)^{1/2}]^{1/2}\exp(-2\Gamma^*\tau_{\max}). \quad (18)$$

This readily yields another relationship for the unknown values:

$$V_{\min}^2/V_{\max}^2 = \{[1-(1-\alpha^2)^{1/2}]/[1+(1-\alpha^2)^{1/2}]\}\exp[2(1-\alpha^2)^{1/2}] \quad (19)$$

or, making use of equation (17),

$$V_{\min}^2/V_{\max}^2 = [(1-2\Gamma^*\Delta\tau)/(1+2\Gamma^*\Delta\tau)]\exp(4\Gamma^*\Delta\tau). \quad (20)$$

When $\theta_1 = \pi/2$, $\theta_2 = \pi$, i.e. when the Gould mechanisms do not operate, one observes a purely exponential decay of the echo signal, the parameters Γ_2' and Γ^* exhibiting the maximum values

$$\Gamma_2'(\pi/2, \pi) = \Gamma^*(\pi/2, \pi) = \Gamma_0 + \Gamma_d. \tag{21}$$

Inflection points are the other characteristic points of the time dependence of the 2τ echo. In the more interesting limit $\Gamma_d \ll \omega_d$ (see below),

$$\tau_{1,2}^{\inf} = (1/4\Gamma_0)[\![1 + (\tfrac{3}{2})^{1/2} \pm \{[1 + (\tfrac{3}{2})^{3/2}]^2 - 4\alpha^2(\Gamma_d = 0)\}^{1/2}]\!]. \tag{22}$$

Here the lower sign $(-)$ applies to $\tau_1^{\inf}$, and the upper sign $(+)$ to $\tau_2^{\inf}$. The intensities of echoes at these points are related by

$$(V_1/V_2)^2_{\inf} = \{1 + [4\Gamma_0^2/\alpha^2(\Gamma_d = 0)](\tau_1^{\inf})^2\}\{1 + [4\Gamma_0^2/\alpha^2(\Gamma_d = 0)](\tau_2^{\inf})^2\}$$
$$\times \exp(4\Gamma_0 \Delta\tau_{\inf}) \tag{23}$$

$$= [1 + (1 + \tfrac{3}{2} - 2\Gamma_0\Delta\tau_{\inf})^2/\alpha^2(\Gamma_d = 0)]/[1 + (1 + \tfrac{3}{2} + 2\Gamma_0\Delta\tau_{\inf})^2/\alpha^2(\Gamma_d = 0)]$$
$$\times \exp(4\Gamma_0 \Delta\tau_{\inf}) \tag{24}$$

$$\Delta\tau_{\inf} = \tau_2^{\inf} - \tau_1^{\inf} = (1/2\Gamma_0)\{[1 + (\tfrac{3}{2})^{1/2}]^2 - 4\alpha^2(\Gamma_d = 0)\} \tag{25}$$

and finally we arrive at

$$\Delta\tau/\Delta\tau_{\inf} = (1 - \alpha^2)/\{[1 + (\tfrac{3}{2})^{1/2}]^2 - 4\alpha^2\} \qquad \Gamma_d = 0. \tag{26}$$

According to the definition of $\tau_{\min}$ in equations (16), the minimum value can be obtained only when

$$1 - \alpha(\Gamma_d/\omega_d)\eta_0 c_0 > (1 - \alpha^2)^{1/2}. \tag{27}$$

Consider now some limiting cases. If $\Gamma_d \simeq 0$, condition (26) holds and the minimum takes place when $\tau_{\min} > 0$. In the case $\omega_d \simeq 0$ the echo intensity attains its maximum value at

$$\tau_{max} \simeq (1/4\Gamma^*)[2 - \alpha(\Gamma_d/\omega_d)\eta_0 c_0]$$

with an increase in τ followed by a further gradual decrease. From the physical viewpoint the increase in the signal over the interval $\Delta\tau$ implies that the contribution of the Gould mechanisms dominates the exponential decay there.

Let us briefly dwell on the case of polarization of spins with $\eta_0 \sim 1$, which may take place at sufficiently low temperatures. Again, let us confine our consideration to the case $\theta_j \ll 1$, so that $c_0 \simeq 1$, $c_1 \ll 1$. Under these conditions, we have

$$\begin{aligned} \Gamma_2 &\simeq \Gamma_2'' - [\Gamma_d \eta_0^2 c_0/(1 - \eta_0^2 c_0^2)^{1/2}] c_1 \cos[\omega'(t_1)\tau] \\ \Gamma_2'' &= \Gamma_0 + \Gamma_d(1 - \eta_0^2 c_0^2)^{1/2} \end{aligned} \tag{28}$$

instead of equation (11) if $1 - \eta_0^2 c_0^2 \gg 2\eta_0^2 c_0 c_1$. Further calculations are similar to those made above.

4. Three-pulse echoes

Let the third pulse (H_3, t_3) arrive after time τ_1 following the first pulse. In the case of the Hahn echo we have single signals at times $\tau_1 + \tau$, $2\tau_1 - 2\tau$, $2\tau_1 - \tau$ and $2\tau_1$. In our case they are replaced by signals of four infinite sequences, the above signals being the leading ones. In mathematial terms, each specific response of the system is described by infinite series with terms proportional to the product of four Bessel functions under the resonant approximation. Owing to the excessively long nature of the respective formulae we omit here the explicit expressions for these signals. Let us dwell only on the first stimulated echo $t = \tau_1 + \tau$, whose major part can be expressed as

$$V(t = \tau_1 + \tau) \sim M_{z0} \sin\theta_3 |\{1 - \exp[-(\tau_1 - \tau)/T_1](1 - \cos\theta_1 \cos\theta_2)\} J_1(q_3) + (\mathrm{i}/2) \sin\theta_1 \sin\theta_2 \exp[-\Gamma_1 \tau - (\tau_1 - \tau)/T_1]\, J_0(q_3) - (\mathrm{i}/2) \sin\theta_1 \sin\theta_2 \exp[-\Gamma_1 \tau - (\tau_1 - \tau)/T_1]\, J_2(q_3)| \exp(-\Gamma_3 \tau) \tag{29}$$

$$q_3 = -c_1 \cos\theta_3 \exp[-(\tau_1 - \tau)/T_1]\,(\omega_d \eta_0 + \mathrm{i}\Gamma_d \eta_0^2 c_3)(t - \tau_1)$$

$$c_3 = \cos\theta_3\,\{1 - (1 - c_0) \exp[-(\tau_1 - \tau)/T_1]\}.$$

One can easily show that, in this case, one may expect to observe the minimum or maximum of the echo as well. From equations (29), one can find the values $\tau'_{\min}$ and $\tau'_{\max}$ under which the stimulated echo attains its minimum or maximum value:

$$\begin{aligned} \tau'_{\min(\max)} &= (1/2\Gamma_3^*)[1 - \alpha'(\Gamma_d \eta_0 c_3/\omega_d) \pm (1 - \alpha'^2)^{1/2}] \\ \Gamma_3^* &= \Gamma_0 + \Gamma_1 + \Gamma_d[1 - (\eta_0^2 c_3^2/2)] \\ \alpha' &\simeq [2\Gamma_3^* \omega_d/(\omega_d^2 + \Gamma_d^2 \eta_0^2 c_3^2) c_3 \eta_0] \exp(\tau_1/T_1) \\ \Delta\tau' &= \tau'_{\max} - \tau'_{\min} = (1/\Gamma_3^*)(1 - \alpha'^2)^{1/2}. \end{aligned} \tag{30}$$

The upper sign (+) applies to $\tau'_{\max}$ and the lower sign(−) to $\tau'_{\min}$. Extremal values of the intensity of the stimulated echo are determined by the expression

$$V^2_{\max(\min)} = V^2(\tau_1 + \tau'_{\max(\min)}) = V_0'^2[(\omega_d^2 + \Gamma_d^2 \eta_0^2 c_3^2)\eta_0^2/\Gamma_3^{*2}] \times \sin^2(2\theta_1) \sin^2(2\theta_2) \sin^2(2\theta_3)[1 \pm (1 - \alpha'^2)^{1/2}] \exp[-2\Gamma_3^* \tau_{\max(\min)}] \tag{31}$$

where the upper sign (+) applies to $V_{\max}$ and the lower sign (−) to $V_{\min}$. This readily yields another relationship for unknown parameters:

$$V^2_{\min}(\tau_1 + \tau)/V^2_{\max}(\tau_1 + \tau) = [1 - (1 - \alpha'^2)^{1/2}]/[1 + (1 - \alpha'^2)^{1/2}] \exp(2\Gamma_3^* \Delta\tau') \tag{32}$$

or

$$V^2_{\min}/V^2_{\max} = [(1 - \Gamma_3^* \Delta\tau')/(1 + \Gamma_3^* \Delta\tau')] \exp(2\Gamma_3^* \Delta\tau'). \tag{33}$$

Equations (30)–(33) also provide information concerning the parameters Γ_0, Γ_d, ω_d, etc. However, the situation is complicated by the presence of the new parameter T_1. Therefore, while determining Γ_0, Γ_d and ω_d the 2π echo is preferable to the stimulated echo. On the other hand, these relationships enable one to evaluate T_1. Indeed, in the case of the small angles $\theta_{1,2,3}$, c_3 and Γ_3^* are weak functions of τ_1. Therefore, one can assume that $\alpha'(\tau_1) \sim \exp(\tau_1/T_1)$, as soon as $|\alpha'| < 1$. Assume that the values α' are obtained from equations (30)–(33) for times $\tau_1 = \tau_1'$ and $\tau_1 = \tau_1''$. Then one has

$$T_1 = (\tau_1' - \tau_1'')/\ln[\alpha'(\tau_1')/\alpha'(\tau_1'')]. \tag{34}$$

5. Discussion

The two new mechanisms introduced play an important role in controlling the properties of echoes as a function of time τ between pulses. This role is especially important for weak pulses when the echo may exhibit a maximum or minimum value within this interval. On increase in the intensity of pulses the points of extrema approach each other, merging at $\alpha = 1$ in the case of the 2τ echo and at $\alpha' = 1$ in the case of the stimulated echo. Subsequently the decay of the echo $V(\tau)$ becomes gradual but non-exponential.

It is difficult to compare this modulation effect with the existing experiments [2,3]. Indeed, strong pulses (e.g. $\theta_1 = \theta_2 = 2\pi/3$) are used in these experiments, when the effect is absent. We should note, however, that the decay pictures of two-pulse and three-pulse echoes [9], at least qualitatively, are described by equations (13) and (29) quite correctly.

The amplitude dependence of $T_2(M_z) = \Gamma^{-1}$ has been observed experimentally for ruby [10]. As should be expected, T_2 at $\theta_1 = \theta_2 = 2\pi/3$ is smaller than at $\theta_1 = \theta_2 = \pi/12$. Perhaps the modulation effect, which in the last case was to take place at $\tau \leqslant 1\ \mu s$, simply remained unnoticed.

In conclusion, we may say that the evolution of electron spins in solids is described by the Bloch equations as usual, but the transverse relaxation parameter T_2 and the precession frequency Ω depend on the amplitudes of the excitation pulses. The modulation effect predicted in this paper permits us to determine the relaxation parameters Γ_0, Γ_d, T_2 and T_1 and the dispersion paramater ω_d through data from experiments on ESEs.

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