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Two-Pulse Echo in Solids Containing Isolated Three-Spin Systems

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The response of an isolated three-spin system in solids to the pulse sequence $90°$–τ–β_φ is investigated theoretically and experimentally. It is shown that in this system an echo occurs both in the case of $90°$–τ–$90^{\circ}_{90^{\circ}}$ ("solid" echo) and in the case of $90°$–τ–β_{0° pulse sequences. In contrast to the "solid" echo the $90°$–τ–β_{0° echo is observed not at 2τ but is shifted. The value and sign of this shift depend both on τ and on parameters characterising the geometry and orientation of the three-spin system in a magnetic field. The experiments on polycrystalline $(CH_3)_4NBr$ are in good agreement with theory.

Теоретически и экспериментально исследуется отклик от изолированной трехспиновой системы в твердых телах на действие двухимпульсной последовательности $90°$–τ–β_{φ°. Показано, что в такой системе возникает эхо как в случае $90°$–τ–$90^{\circ}_{90^{\circ}}$ („солид" эхо) так и в случае $90°$–τ–β_{0° импульсной последовательности. В отличие от „солид" эха это эхо наблюдается не на 2τ, а сдвинуто. Величина и знак сдвига зависят как от τ так и от параметров, характеризующих геометрию и ориентацию трехспиновой системы относительно внешнего магнитного поля. Эксперименты, проведенные на поликристаллическом образце $(CH_3)_4NBr$, дают хорошее согласие с теорией.

1. Introduction

It is well known what important role is played by magnetic dipole interactions in processes proceeding in nuclear paramagnetics [1, 2]. In many cases just these interactions determine the mechanism of spin–lattice relaxation. The magnetic dipole interactions determine also the spin–spin relaxation and lead to the loss of phase memory by the spin system.

In 1962 Powles and Mansfield [3] discovered that dipole–dipole interactions in solids on the contrary in some cases can lead to refocussing of the collective phase memory of the spin system which reveals experimentally in signals of the so-called "solid" echo. This echo is quite different from the spin echoes in liquids [4] and "quadrupole" echoes in solids [5] which depend on refocussing the spin dephasing caused by static inhomogeneous interactions. Later Mansfield [6], Siegle [7], and others have shown that the resonance response R to the radio frequency (RF) pulse sequences $90°$–τ–β_{0° (XX sequence) and $90°$–τ–β_{90° (XY sequence) in solids containing single identical spins is [8]:

XX sequence

$$R_{XX} = a \cos \omega_0 t \cos \beta[F(t) + k_1] , \tag{1}$$

XY sequence

$$R_{XY} = a \cos \omega_0 t[\cos^2 \beta F(t) + \sin^2 \beta F(t - 2\tau) + k_2] , \tag{2}$$

where β_φ is the nutation angle of the second pulse applied at $t = \tau$ along an axis in the XY plane of the frame rotating at Larmor frequency $\omega_0 = \gamma H_0$ making an angle φ with the Y-axis. (The first 90° pulse is applied along the Y-axis at $t = 0$); a is a function of the nuclear constants and external magnetic field H_0, k_i are error terms; $F(t)$ is the free induction decay (FID) determined by the expression

$$F(t) = \frac{1}{\mathrm{Tr}\,\{I_x^2\}} \mathrm{Tr} \left\{ I_x^2 + \frac{t^2}{2!}\left[\frac{\mathcal{H}_\mathrm{d}^0}{\hbar}, I_x\right]^2 + \frac{t^4}{4!}\left[\frac{\mathcal{H}_\mathrm{d}^0}{\hbar}, \left[\frac{\mathcal{H}_\mathrm{d}^0}{\hbar}, I_x\right]\right]^2 + \dots \right\},$$

where $\mathcal{H}_\mathrm{d}^0$ is a truncated Hamiltonian of dipole–dipole interactions [1].

As a consequence of (1) and (2) one expects an echo only following the XY pulse sequence in the case of solids containing single identical spins [6 to 9].

Recently in [10, 11] an echo was observed following the XX pulse sequence in solids containing isolated mobile three-spin groups of magnetically equivalent spin-1/2 nuclei (CH_3, NH_3). The results obtained were explained by treating the tunnelling [10] and classically rotating [11] three-spin system as a single quasiparticle of spin 3/2 whose Hamiltonian is analogous to the Hamiltonian of a real quadrupole particle of spin 3/2 in a high magnetic field H_0. In the case of a rigid three-spin system this treatment is not applicable.

In the present work the resonance response of an isolated three-spin system both rigid and mobile to the RF pulse sequence $90°$–τ–β_φ is investigated theoretically and experimentally. It is shown that parallel with an expected "solid" echo according to (2) an echo occurs also in the case of the XX pulse sequence.

2. Theory

The Hamiltonian of a three-spin system (CH_3, NH_3 groups in solids) in a high static magnetic field H_0 is [1]

$$\hbar\mathcal{H} = \hbar(\mathcal{H}_0 + \mathcal{H}_\mathrm{d}^0),$$

where

$$\mathcal{H}_0 = -\omega_0 \sum_{i=1}^{3} I_{zi}$$

is the Zeeman term,

$$\mathcal{H}_\mathrm{d}^0 = \sum_{i<j} (\boldsymbol{I}_i \boldsymbol{I}_j - 3 I_{zi} I_{zj}) A_{ij}$$

is the term describing dipole–dipole interactions between identical nuclei of spin 1/2 in a three-spin system.

$$A_{ij} = \gamma \frac{\mu}{r_{ij}^3} (3\cos^2\theta_{ij} - 1),$$

where $\mu = \gamma\hbar/2$, γ is the proton gyromagnetic ratio, r_{ij} is the length of a vector joining nuclei i and j, θ_{ij} is the angle between this vector and the direction of the applied magnetic field H_0.

In the present work we assume that the Hamiltonian describing the effect of a resonant RF pulse on the spin system $\mathcal{H}_\mathrm{rf} \gg \mathcal{H}_\mathrm{d}^0$, so that during the pulse the dipole interaction may be ignored. In this case the RF pulse acts as a simple rotation operator R.

The mean value of the x-component of the full magnetization $I_x(t)$ after the application of j short coherent pulses R_j each separated by a time interval t_j

within a time of the order of the spin–spin relaxation time T_2 is [12]

$$\langle I_x(t)\rangle = \frac{a\cos\omega_0 t}{\mathrm{Tr}\,\{I_x^2\}}\,\mathrm{Tr}\left[\left(\prod_j O_j^*\right)^+ I_z\left(\prod_j O_j\right) I_x\right],$$

where $O_j = R_j \exp(i\mathcal{H}_d^0 t)$; $\sum_{i=1}^{n} t_j \lesssim T_2$.

For a 90° pulse ($j = 1$) along the Y-axis we obtain the expression for the free induction decay:

$$\langle I_x(t)\rangle = \frac{a\cos\omega_0 t}{\mathrm{Tr}\,\{I_x^2\}}\,\mathrm{Tr}\,[\exp(-i\mathcal{H}_d^0 t)\, I_x \exp(i\mathcal{H}_d^0 t)\, I_x] = a\cos\omega_0 t F(t)\,,$$

where

$$F(t) = \tfrac{1}{2}\alpha^2\cos\omega_1 t + \tfrac{1}{2}\delta^2\cos\omega_2 t + \tfrac{3}{2}\alpha^2\delta^2\cos\omega_3 t + \tfrac{1}{2}(1 - 3\alpha^2\delta^2)\,,$$

$$\alpha^2 = \frac{1}{2}\left(1 + \frac{x}{y}\right), \qquad \delta^2 = \frac{1}{2}\left(1 - \frac{x}{y}\right),$$

$$\omega_1 = 3x + y\,, \qquad \omega_2 = 3x - y\,, \qquad \omega_3 = 2y\,,$$

$$x = \tfrac{1}{4}(A_{12} + A_{13} + A_{23})\,, \qquad y^2 = x^2 + a^2 + b^2\,,$$

$$a = \frac{\sqrt{6}}{4}(A_{13} - A_{23})\,, \qquad b = \frac{\sqrt{2}}{4}(2A_{12} - A_{13} - A_{23})\,.$$

It is evident that $F(t)$ is the Fourier transform of the tree-spin system NMR spectrum calculated by Andrew and Bersohn [13]. This fact reflects the well-known theorem of Lowe and Norberg [14].

For the two-pulse sequence 90°–τ–β_φ^0 ($j = 2$) we have

$$\langle I_x(t)\rangle = \frac{a\cos\omega_0 t}{\mathrm{Tr}\,\{I_x^2\}}\,\mathrm{Tr}\,[\exp\left(-i\mathcal{H}_d^0(t-\tau)\right) R_2^+ \exp(-i\mathcal{H}_d^0\tau) \times$$
$$\times\, I_x \exp(i\mathcal{H}_d^0\tau)\, R_2 \exp\left(i\mathcal{H}_d^0(t-\tau)\right) I_x]\,. \tag{3}$$

The rotation operator R_2 has the form

$$R_2 = \exp(i\varphi I_z)\, R \exp(-i\varphi I_z)\,,$$

where

$$R = \exp(-i\beta I_y)\,.$$

R_2 describes the rotation of the magnetisation by an angle β about an axes in the XY plane which makes an angle φ with the Y-axis in a frame rotating at frequency ω_0.

The calculation of expression (3) is conveniently performed in a representation in which $\mathcal{H}_d^0$ is diagonal.

In the basis of eigenwave functions I_1^2, I_2^2, I_3^2, $\vec{\mathcal{J}}^2$, $\vec{I}^2$, and I_z, where $\vec{\mathcal{J}} = \vec{I}_1 + \vec{I}_2$, $\vec{I} = \vec{\mathcal{J}} + \vec{I}_3$, and $I_z = I_{1z} + I_{2z} + I_{3z}$ the matrix of the rotation operator R is determined by the Wigner coefficients [15]:

For quartet state ($I = 3/2$)

$$\langle \tfrac{3}{2}, m|\, R\,|m', \tfrac{3}{2}\rangle = D^{3/2}_{mm'}(0, \beta, 0)\,; \tag{4}$$

for two doublet state ($I_1 = 1/2$; $I_2 = 1/2$)

$$\left\langle \left(\frac{1}{2}\right)_{\mathrm{I,II}}, m|\, R\,|m', \left(\frac{1}{2}\right)_{\mathrm{I,II}}\right\rangle = D^{1/2}_{mm'}(0, \beta, 0)\,. \tag{5}$$

In the representation diagonalising $\mathcal{H}_d^0$ the matrix of the rotation operator R is found by using (4) and (5). The calculation of (3) leads to the following result:

$$\langle I_x(t)\rangle = a\cos\omega_0 t\,\{\tfrac{1}{2}(1+\cos 2\varphi)\,[\cos\beta\,F(t) - \sin^2\beta\cos\beta V_{XX}] + \\ + \tfrac{1}{2}(1-\cos 2\varphi)\,[\cos^2\beta F(t) + \sin^2\beta F(t-2\tau) - \sin^2\beta V_{XY}]\}\,.$$

The expressions for V_{XX} and V_{XY} are given in the Appendix.

For $\varphi = \pi/2$ (XY pulse sequence) we have

$$\langle I_x(t)\rangle = a\cos\omega_0 t[\cos^2\beta F(t) + \sin^2\beta F(t-2\tau) - \sin^2\beta V_{XY}]\,. \tag{6}$$

Expanding V_{XY} up to the fourth power in t, τ we find

$$V_{XY} = \frac{6}{4!}M_{4\varepsilon}(t-\tau)^2\tau^2 + \cdots,$$

where

$$M_{4\varepsilon} = 2M_4 - 3M_2^2 = \frac{9}{N}\left(\frac{3}{8}\sum_{i\neq j\neq k}A_{ij}^2A_{jk}^2 + \frac{3}{4}\sum_{i\neq j\neq k}A_{ij}^2A_{ik}A_{jk}\right).$$

M_2 and M_4 are the second and fourth moments of the NMR absorption spectrum of the rigid three-spin system [13].

The results obtained for the XY pulse sequence coincide fully with the known results for "solid" echo [6 to 9].

For $\varphi = 0$ (XX pulse sequence) we have

$$\langle I_x(t)\rangle = (a\cos\omega_0 t\cos\beta[F(t) - \sin^2\beta V_{XX}]\,. \tag{7}$$

Comparing (7) and (1) we can see that

$$k_1 = -\sin^2\beta V_{XX}\,.$$

Expanding V_{XX} up to the sixth power in t, τ we obtain

$$V_{XX} = \frac{3}{4}\frac{(t-\tau)^2\tau^2}{2!\,2!}\left[M_{4x} - \frac{M_{6x}}{12}\left((t-\tau)^2+\tau^2\right)\right] + \cdots, \tag{8}$$

where

$$M_{4x} = (\alpha^2\omega_1^2 + \delta^2\omega_2^2 - 3\alpha^2\delta^2\omega_3^2)^2$$

and

$$M_{6x} = (\alpha^2\omega_1^2 + \delta^2\omega_2^2 - 3\alpha^2\delta^2\omega_3^2)\,(\alpha^2\omega_1^4 + \delta^2\omega_2^4 - 3\alpha^2\delta^2\omega_3^4)\,.$$

Therefore, V_{XX} has for a given τ in the limits of application of (8) an maximum at t_e which is determined by the equality

$$2(t_e-\tau)^2 + \tau^2 = \frac{12M_{4x}}{M_{6x}} \equiv 3C^2 \tag{9}$$

that leads to the experimentally observed echo in the case of the XX pulse sequence [10, 11]. It is easy to see from (9) that at $\tau < C$, $t_e > 2\tau$ and at $\tau > C$, $t_e < 2\tau$. The echo following the XX pulse sequence is observed at $t_e = 2\tau$ when the condition $\tau = C$ is fulfilled. As it can be seen from (8) the τ dependence of the echo amplitude has a maximum at $\tau = C$, i.e. this echo achieves its maximum amplitude when $t_e = 2\tau$.

Hence, in contrast to the XY pulse sequence following which a "solid" echo occurs at $t_e = 2\tau$ for a given τ in the case of the XX pulse sequence an echo occurs at time t_e which is determined by both τ and parameters depending on the interspin separations and the orientation of the three-spin system relative

to the external magnetic field H_0. The estimates indicate that approximation of V_{XX} by the expansion (8) is valid at $(t-\tau), \tau < C$. For longer τ and $(t-\tau)$, the dependence of $(t_e-\tau)^2$ on τ must deviate from the dependence predicted by (9).

The expressions (7) and (8) have been obtained for the rigid three-spin system. If an isolated three-spin system performs the reorientational motion around the normal to the plane of the triangle with the frequency $\omega_r \gg \mathcal{H}_d^0$ then calculating the response to the $90°$–τ–β_φ sequence it is necessary to use the Hamiltonian of dipole–dipole interaction averaged over all reorientational states as it was shown in [11]. In this case in (8) $M_{4x} = \omega_2^4$ and $M_{6x} = \omega_2^6$, where $\omega_2 = 4x$. The echo maximum t_e must shift then to the side of longer τ.

If $A_{13} = A_{23} = 0$, the three-spin system considered above turns into a two-spin system and an isolated proton. It follows from Appendix A that in this case $V_{XX} = 0$ for any t and τ and therefore the XX pulse sequence does no produce the echo for an isolated two-spin system. This result was obtained for the first time by Metzger and Gaines [16]. In real solids containing two-spin systems ($>CH_2$, H_2O), however, it is possible to observe an echo and in the case of the XX pulse sequence due to the presence of the intermolecular dipole–dipole interactions [17, 18].

3. Experimental

The experiments were carried out on a chemically pure sample of polycrystalline tetramethylammonium bromide $(CH_3)_4NBr$ (TMA-Br). For removing the adsorbed water the sample was pumped under vacuum for about 20 h at 80 °C and then sealed off in a glass tube.

The study of wide line spectra of proton magnetic resonance (PMR) and spin–lattice times T_1 at various temperatures in this compound [19 to 21] indicates that in TMA-Br there are two types of internal mobility: the reorientation of the methyl group CH_3 around its threefold axis C_3 and the isotropic tumbling of the $(CH_3)_4$ cation.

The analysis of the second moment (M_2) results [19 to 21] indicates that the second moments of the PMR spectra are determined completely by the proton–proton dipole interactions. The contribution to the total value of M_2 from the interaction of protons with nitrogen and bromine nuclei in TMA-Br is negligible.

For the determination of the temperature regions of rigid and reorientating CH_3 groups in the TMA-Br sample used the wide line PMR spectra were recorded at 46.6 MHz on a JNM 3H-60 spectrometer with the wide line attachment BL-2 in the temperature range -150 to $+20$ °C. The line widths ΔH were measured between points of maximum and minimum deflection of the derivative spectrum. In the low-temperature region the PMR spectra consist of multiplets and the line width was determined from the two extreme peaks. In the low-temperature region the PMR spectra were recorded at low values of RF field H_1 for avoiding the saturation effects due to long T_1 at these temperatures.

The pulse experiments were carried out at 30 MHz using a home-made phase coherent pulse spectrometer with phase-sensitive and diode detection. The long time stability of the electromagnet used was 10^{-6}. The spectrometer dead time was equal to 8 μs. The typical signal to noise ratio was larger than 100 at maximum signal amplitude.

The value of the rotating component of the RF field H_1 in a sample coil of 10 mm diameter was 12 to 30 G. The rotation angle of the magnetisation by the

second pulse was found from the comparison of its length and the length of a 90° RF pulse with ±3%. For decreasing the RF inhomogeneity the sample whose volume was equal to ≈70% of the RF coil volume was placed in the centre of the coil.

The change of the interval between two pulses τ was performed by a program unit [22] in 1 μs steps with accuracy better than 1%.

The detected FID and echo signals were displaced on a storage oscilloscope S8-1 and recorded photographically. The initial value of the magnetisation during the application of the first pulse M_0 was found with the help of a "solid" echo $90°$–τ–$90^{\circ}_{90°}$ sequence at $\tau \gtrsim t_d$ ($\tau = 10$ μs) which restored the initial magnetisation M_0 not observed after the first pulse due to the dead time of the receiver, t_d, and the finite pulse width [9] with an error determined by a fourth-moment term $M_{4\varepsilon}\tau^4$ [3, 6].

The measurement of the echo shift relative to 2τ was performed using the program unit and a box-car integrator of a quadrupolar pulse spectrometer IS-3. The echo signal and time marks corresponding to the moments of the first pulse beginning and $t = 2\tau$ were displayed simultaneously on the oscilloscope from the output of the box-car integrator (Fig. 4).

The temperature control was carried out with accuracy of ±1 deg.

4. Experimental Results and Discussion

4.1 Wide line measurements

The values of the line widths ΔH of TMA-Br PMR spectra are given as a function of temperature in Fig. 1. It can be seen that ΔH changes considerably in two narrow temperature regions. The obtained ΔH-temperature dependence of the TMA-Br sample used is in a good agreement with the results of [19 to 21]. In accordance with their analysis the low-temperature values of ΔH (below −120 °C) correspond to the rigid structure of TMA-Br and the ΔH plateau in the temperature region −50 to −32 °C corresponds to the methyl group reorientation around the C_3-axis with frequency exceeding the rigid PMR line width. In accordance with these results all pulse experiments were performed in general at two temperatures: at −145 °C (in the rigid structure region) and at −40 °C (in the middle of the ΔH plateau of methyl reorientation).

4.2 $90°$–τ-$\beta_{90°}$ pulse sequence

Following the XY sequence $90°$–τ–$90^{\circ}_{90°}$ an echo is observed both at −145 and −40 °C. At short τ this "solid" echo reproduces the full FID after a single

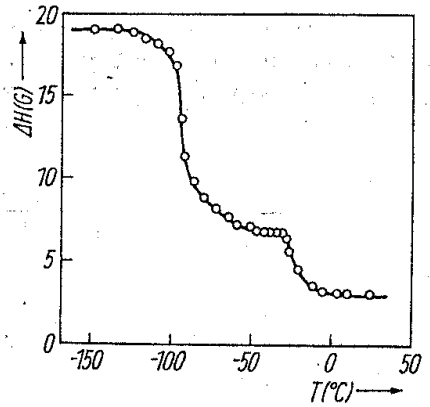

Fig. 1. The temperature dependence of the line width of the PMR spectra of polycrystalline TMA-Br

90° pulse. The β dependence of the echo amplitude indicates (for examples for $\tau = 15\,\mu s$ at -145 °C and for $\tau = 30\,\mu s$ at -40 °C) that the echo amplitude depends on β as $\sin^2\beta$ in agreement with (6). Increasing τ leads to a decrease of the echo amplitude from its maximum value M_0 to zero at τ corresponding to the full decay of FID following the first pulse.

4.3 $90°$-τ-$\beta_{0°}$ pulse sequence

The application of two phase-coherent pulses with $\beta \neq 90°$ in TMA-Br produces an echo both in the rigid case and the case of the reorientating CH_3 group. The phase of this echo is shifted relative to the phase of FID and the "solid" echo on 180° (see Fig. 2) at the phase-sensitive detection. In contrast to the "solid" echo the echo produced by the XX pulse sequence is equal to zero at short τ in the cases of rigid and reorientating CH_3 groups, then the amplitude of this echo reaches its maximum and decreases to zero again at τ corresponding to the full decay of FID following the first pulse.

The τ dependence of the $90°$–τ–$55°_{0°}$ echo amplitude is shown in Fig. 2 at -145 and $-40°$ C. The distinctive feature of this echo is revealed most clearly in the case of methyl reorientation in which the echo occurs at 16 μs only and the echo maximum is observed at 42 μs in contrast to the rigid structure case where the echo maximum is observed at $\tau = 12\,\mu s$. It is noteworthy that temperature decrease below $-40°$ C leads to a shift of the echo maximum of the τ dependence towards shorter τ (at -56 °C it is observed at 24 μs) and temperature increase shifts this echo maximum towards longer τ (at $+20$ °C it equals $\approx 52\,\mu s$).

In the case of methyl reorientation the signal of FID following the second pulse of the XX sequence is observed at short τ ($\tau < 16\,\mu s$). The β dependence of the FID amplitude at $\tau = 10\,\mu s$ is shown in Fig. 3. It agrees sufficiently well with the theoretically predicted β dependence of $F(t)$ (7) $\cos\beta$. The deviation of the experimental points at $\beta > 110°$ from the theoretical β dependence is connected probably with long length of the second pulse and with effects of RF inhomogeneities.

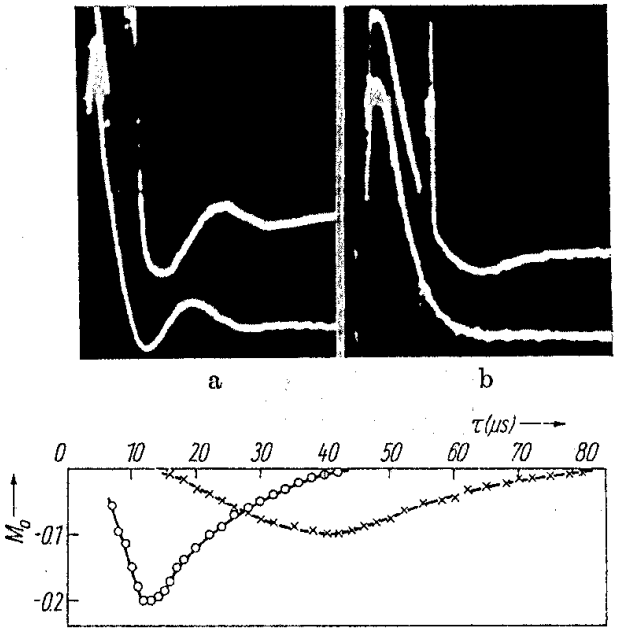

Fig. 2. The τ dependence of the echo amplitude following a $90°$–τ–$55°_{0°}$ RF pulse sequence at resonance in polycrystalline TMA-Br at -145 °C (○) and -40 °C (×). It is shown also FID (lower signal) and $90°$–τ–$55°_{0°}$ echo (upper signal) for the cases of a) the rigid structure and b) methyl reorientation in TMA-Br at -145 °C, $\tau = 12\,\mu s$ and at -40 °C, $\tau = 42\,\mu s$, respectively

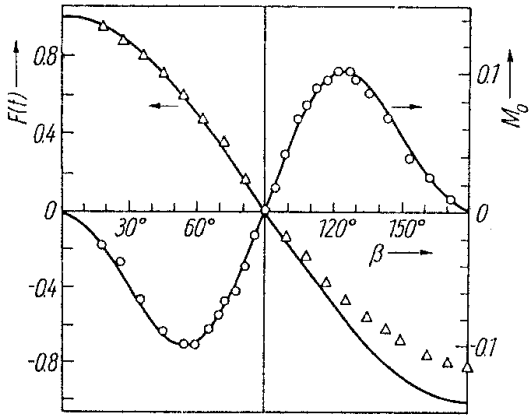

Fig. 3. The β dependence of FID ($\triangle$) and echo amplitude ($\circ$) following the second pulse of the $90°$–τ–$\beta_{0°}$ sequence in polycrystalline TMA-Br at $\tau = 10$ and 42 μs, respectively. $t° = -40$ °C, $t_\omega^{90°} = 5$ μs. The full lines are curves of $\cos\beta$ and $-\sin^2\beta\cos\beta$ fitted to the experimental points at $\beta = 45°$ (FID) and at $\beta = 55°$ (echo)

For $\beta = 90°$ the signal following the second pulse is equal to zero at any τ in both cases, rigid and reorientating CH_3 group. The echo produced by the XX sequence reaches its maximum for a given τ at $\beta \approx 55°$ and 135°. The β dependence of this echo amplitude is given in Fig. 3 for the case of methyl reorientation at $\tau = 42$ μs. It can be seen that the experimental echo amplitudes agree well with a theoretically predicted $\sin^2\beta\cos\beta$ dependence (equation (7)). The $\sin^2\beta\cos\beta$ dependence is observed also in the case of the rigid three-spin system.

An interesting feature of the $90°$–τ–$\beta_{0°}$ echo consists in the presence of a shift of the echo maximum t_e from $t = 2\tau$, in constrast to the well-known Hahn [4] and "solid" echoes [6 to 9] which are centered at $t = 2\tau$. At τ shorter than $\tau = 12$ μs (the rigid structure case) and $\tau = 42$ μs (the methyl reorientation case) the echo occurs far later than 2τ (for example at $\tau = 21$ μs, $t_e = 70$ μs, $t = -40$ °C). $t_e = 2\tau$ when the τ dependence of the echo amplitude reaches its maximum. At longer τ the echo occurs earlier than 2τ.

In Fig. 4 an experimental τ^2 dependence of $2(t_e - \tau)^2$ in the case of methyl reorientation is shown. It can be seen that at τ up to 49 μs the τ^2 dependence is in good agreement with a theoretical linear dependence $2(t_e - \tau)^2 + \tau^2 = \text{const}$ (equation (9)). At longer τ a deviation is observed from this linear dependence. This deviation is caused probably by higher terms of the V_{XX} expansion.

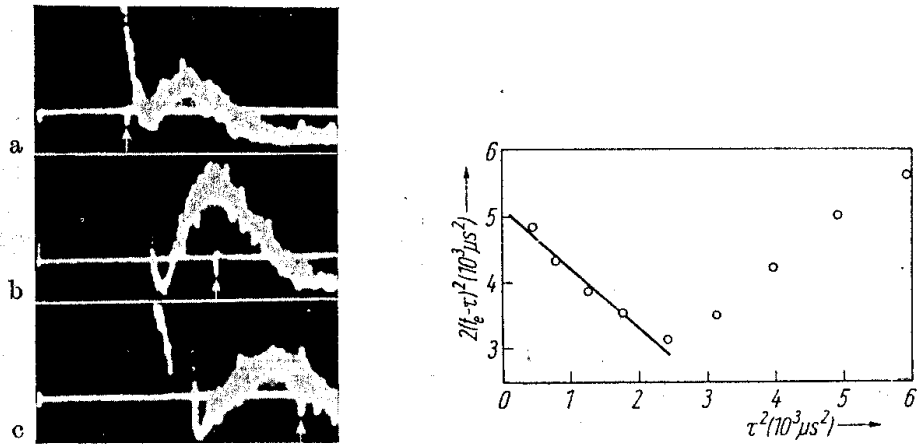

Fig. 4. The dependence of $2(t_e - \tau)^2$ on τ^2 in polycrystalline TMA-Br at -40 °C, $t_\omega^{90°} = 4$ μs, $t_\omega^{\beta} = 2.5$ μs. The photos show the shift of the echo centre t_e relatively to 2τ: a) $\tau = 21$ μs, b) $\tau = 42$ μs, and c) $\tau = 56$ μs. The arrows indicate the 2τ time marks of a box-car integrator. Diode detection was used

The theoretical treatment of the response of an isolated three-spin system to the XX pulse sequence permits to estimate the position of the echo maximum as a function of τ. Averaging M_{4x} and M_{6x} over all orientations of the angle between H_0 and the normal to the triangle plane for a polycrystalline sample we obtain that for a rigid three-spin system the echo maximum is expected at $\tau = 14\,\mu s$ and for a reorientating three-spin system at $45\,\mu s$ that agree well with the obtained experimental values $(12 \pm 1)\,\mu s$ and $(42 \pm 1)\,\mu s$.

5. Conclusion

The treatment of the response of a three-spin system to the two pulse XX sequence considered above explains the appearance of an echo in this case, its phase sign relative to FID, its dependence on the second pulse length and on the pulse separation τ, the position of the echo maximum as a function of τ, and an observed shift of the echo position relative to 2τ.

We note in conclusion that as far as a reorientating three-spin system in solids behaves like a quadrupolar particle of spin 3/2 in a high magnetic field H_0 [11] then the features of an echo following the XX pulse sequence mentioned above must be observed and for real quadrupole particles of spin 3/2.

Appendix A

$$V_{XX} = \tfrac{3}{4}\,[\alpha^2 \cos\omega_1(t-\tau) + \delta^2 \cos\omega_2(t-\tau) - 3\alpha^2\delta^2 \cos\omega_3(t-\tau) + \\ + (3\alpha^2\delta^2 - 1)]\,[\alpha^2 \cos\omega_1\tau + \delta^2 \cos\omega_2\tau - 3\alpha^2\delta^2 \cos\omega_3\tau + (3\alpha^2\delta^2 - 1)]\,.$$

Appendix B

$$V_{XY} = F(t-\tau) + F(\tau) + F(t) + F(t-2\tau) - 1 - 3F(\tau)\,F(t-\tau) + \Phi(t,\tau)\,,$$

where

$$\Phi(t,\tau) = \tfrac{3}{4}\,[-\cos\omega_1(t-\tau) - \cos\omega_2(t-\tau) - \cos\omega_3(t-\tau) - \\ - \cos\omega_1\tau - \cos\omega_2\tau - \cos\omega_3\tau - \\ - \cos\omega_1 t - \cos\omega_2 t - \cos\omega_3 t + \\ + \cos(\omega_2 t + (\omega_1 - \omega_2)\tau) + \cos(\omega_1 t + (\omega_2 - \omega_1)\tau) + \\ + \cos(\omega_1 t + (\omega_3 - \omega_1)\tau) + \cos(\omega_3 t + (\omega_1 - \omega_3)\tau) + \\ + \cos(\omega_2 t - (\omega_3 + \omega_2)\tau) + \cos(\omega_3 t - (\omega_2 + \omega_3)\tau) + 3]\,\alpha^2\delta^2\,.$$

References

[1] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961.
[2] M. Goldman, Spin Temperatures and Nuclear Magnetic Resonance in Solids, Oxford University Press, Oxford 1970.
[3] J. G. Powles and P. Mansfield, Phys. Letters 2, 58 (1962).
[4] E. L. Hahn, Phys. Rev. 80, 580 (1950).
[5] I. Solomon, Phys. Rev. 110, 61 (1958).
[6] P. Mansfield, Phys. Rev. 137, A961 (1965).
[7] G. Siegle, Dissertation, Stuttgart 1967.
[8] R. Hausser and G. Siegle, Phys. Letters 19, 356 (1965).
[9] J. G. Powles and J. H. Strange, Proc. Phys. Soc. 82, 6 (1963).
[10] P. S. Allen, W. Harding, and P. Mansfield, J. Phys. C 5, L89 (1972).
[11] Yu. N. Moskvich, N. A. Sergeev, and G. I. Dotsenko, Fiz. tverd. Tela 15, 2854 (1973).

[12] P. Mansfield and D. Ware, Phys. Rev. 168, 318 (1968).
[13] E. R. Andrew and R. Bersohn, J. chem. Phys. 18, 159 (1950).
[14] I. J. Lowe and R. E. Norberg, Phys. Rev. 107, 46 (1957).
[15] M. E. Rose, Elementary Theory of Angular Momentum, Wiley, New York 1957.
[16] D. S. Metzger and J. R. Gaines, Phys. Rev 147, 644 (1966).
[17] G. Siegle, Z. Naturf. 23a, 1194 (1968).
[18] N. Boden, Y. K. Levine, and R. T. Squires, Chem. Phys. Letters 28, 523 (1974).
[19] J. Dufourcq and B. Lemanceau, J. Chim. phys. et Physico-Chim. biol. 67, 9 (1970).
[20] M. Mahajan and B. D. Nageswara Rao, J. Phys. Chem. Solids 33, 2191 (1972).
[21] M. Polak and M. Sheinblatt, J. magn. Res. 12, 261 (1973).
[22] G. I. Dotsenko, B. I. Cherkasov, and Yu. N. Moskvich, Prib. i Tekh. Eksper. 2, 139 (1974).

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