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Cumulative Single-Pulse NMR Echoes in Cobalt

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Abstract

In this work the cumulative single-pulse echo effect in cobalt was studied when a train of single-pulse echoes generated by a repeating single RF pulse sequence, exhibits growth rather than damping. The phenomenon is observed below some threshold value of radio-frequency pulse power when the nonresonant mechanism of single-pulse echo excitation in cobalt becomes effective.

Keywords: NMR, magnets, single-pulse echo, nonresonant mechanism, cobalt, cumulative effect

1. Introduction

The single-pulse echo (SPE) is a resonance response of spin-system on the application of solitary exciting radiofrequency (RF) pulse arising at a time approximately equal to the pulse duration after its termination. The SPE was discovered by Bloom in 1955 soon after Hahn's discovery in 1950 of the two-pulse echo (TPE) phenomenon. The mechanism of its formation appeared to be far more complicated, as compared with the TPE one, and continues to attract the attention of researchers (Shakhmuratova et al., 1997; Prescott et al., 2008; Kuz'min & Kolesenko, 2004; Kuz'min & Kolesenko, 2012).

SPE formation mechanisms could be conditionally classified on co-called edge-type ones when RF pulse edges act like two RF pulses in the Hahn method – such as the nonresonant mechanism (Chekmarev et al., 1979; Ponti, 1998) and the distortion mechanism (Kiliptari & Tsifrinovich, 1998), and also internal mechanisms due to the presence in the spin-system dynamics particular nonlinearities, as example, connected with a strong dynamic frequency shift of the NMR frequency or with a nonlinear dynamics of nuclear spins due to the simultaneous presence of large Larmor and Rabi inhomogeneous broadenings of the NMR line (Shakhmuratova et al., 1997).

In this work we consider in more detail the so-called multiple pulse mechanism of cumulative SPE formation for systems with both types of inhomogeneous broadenings of NMR lines. An important example of such systems is multidomain magnets, for example, lithium ferrite. In work (Akhalkatsi & Mamniashvili, 1996) we investigated the peculiarities of SPE formation in this magnet. It was established that its properties sharply differ from SPE properties in cobalt where it was known (Kiliptari & Tsifrinovich, 1998) that it was formed by the distortion mechanism. Therefore, the conclusion was made on the possible effectiveness of new internal mechanism of the SPE formation in lithium ferrite. Then in works (Akhalkatsi et al., 2001; Akhalkatsi et al., 2002) the SPE formation mechanism in lithium ferrite was finally established where it was shown that the formation mechanism of SPE and its secondary signals in lithium ferrite were well described by the multiple pulse mechanism of SPE formation (Shakhmuratova et al., 1997).

Shakhmuratova et al. (1997) used the formalism of statistical tensors to perform a theoretical investigation of the formation of SPE and its secondary signals at periodical excitation by RF pulse series in the presence of large Larmor and Rabi inhomogeneous broadenings of the NMR line, which, e.g. takes place in multidomain ferromagnets, when the repetition period of RF pulse T satisfies the following inequality for the characteristic relaxation parameters:

$$T_3 \ll T_2 < T < T_1 \quad (1)$$

where T_1 is the spin-lattice relaxation time, T_2 is the transverse irreversible relaxation time, T_3 characterizes the transverse reversible relaxation time ($T_3 \sim 1/\sigma$, where σ is the half-width at half-maximum of the inhomogeneously broadened line).

Under these conditions, the RF cycles are applied to a nonequilibrium spin system, and in the end of each period T we should take into account only the longitudinal component of the nuclear magnetization as the initial condition for the consideration of the dynamics of the spin system.

It was shown that the dephasing of the spin system, which is accumulated in the course of n-fold repetition of the pulsed excitation, is recovered during a time interval following the (n+1)-th "read-out" pulse in the multiple pulse sequence, which leads to the formation of an SPE and its secondary signals at time moments multiple of the duration of the RF pulse τ after the termination of the "read-out" pulse.

In work (Akhalkatsi et al., 2002) the obtained in (Shakhmuratova et al., 1997) by the statistical tensors method expressions for the transverse components of nuclear magnetizations also obtained in the framework of the usual classical approach by solving the system of Bloch equations from (Chekmarev et al., 1979), where both types of inhomogeneous broadenings of NMR lines and condition (1) were allowed for. But the approach of work (Gegechkori & Mamniashvili 2001; Chigvinadze et al., 2004) using the Mims transformation matrix method (Mims et al., 1961), appeared to be more visual.

Let us consider the case when a local static magnetic field H_n is directed along **Z** axis and RF field is along **Y** axis of the rotating coordinate system (RCS) when an effective magnetic field modulus in RCS is given by the expression:

$$H_{eff} = \frac{1}{\gamma_n}\sqrt{\Delta\omega_j^{\,2} + \omega_1^{\,2}}$$

The angle between $\mathbf{H}_{effj} = \frac{1}{\gamma_n}(\Delta\,\omega_{nj}\hat{\mathbf{z}} + \omega_1\hat{\mathbf{y}})$ (2)

(where $\hat{\mathbf{z}}$, $\hat{\mathbf{y}}$ are unit vectors in RCS) and **Z** axis ψ_j is defined by the relation:

$$\sin\psi_j = \omega_1 / \Delta\omega'_j; \qquad \cos\psi_j = \Delta\omega_j / \Delta\omega'_j.$$

Where $\Delta\omega'_j = \sqrt{\Delta\omega_j^{\,2} + \omega_1^{\,2}}$

is the angular velocity of the precession of the j-th isochromate around $\mathbf{H}_{eff}$, $\Delta\omega_j=\omega_1-\omega_{RF}$ is the detuning for the j-th isochromate, ω_j is the isochromate frequency, $\omega_1 = \gamma_n\eta H_1$ is the pulse amplitude in frequency units, η is the gain of the RF field, γ_n is the nuclear gyromagnetic ratio

Time t characterizes time interval after a pulse termination and is counted from the back front of RF pulse. The transformation matrix describing the rotation of the magnetization vector around H_{eff} is Chigvinadze et al. (2004).

$$(R) = \begin{pmatrix} S_\psi^{\,2} + C_\psi^{\,2}C_\theta & -C_\psi S_\theta & S_\psi C_\psi(1-C_\theta) \\ C_\psi S_\theta & C_\theta & -S_\psi S_\theta \\ S_\psi C_\psi(1-C_\theta) & S_\psi S_\theta & C_\psi^{\,2} + S_\psi^{\,2}C_\theta \end{pmatrix}$$

Where C_ψ, S_ψ, C_θ and S_θ stand for cosψ, sinψ, cosθ and sinθ and $\Psi = tg^{-1}(\omega_1 / \Delta\omega_j)$

is an angle between the effective field $\mathbf{H}_{eff}$ and **Z** axis, θ is the angle by which the magnetization turns about during the pulse time τ: $\theta=\gamma_n H_{eff}\cdot\tau$, where H_{eff} is given by (2).

Let us consider firstly the case of single-pulse excitation. Let

$X_j=m_{xj}/m$; $Y_j=m_{yj}/m$; $Z_j=m_{zj}/m$ and $\boldsymbol{\mu}=(X_j\ Y_j\ Z_j)$,

where m is the magnetization modulus. If before the excitation by a RF pulse the nuclear spin system was at equilibrium condition, $\boldsymbol{\mu}_{eq}(0;0;1)$ then the result of RF pulse action $\boldsymbol{\mu}_{eq}$ is presented by the $\boldsymbol{\mu}_{eq} = (R)\ \boldsymbol{\mu}_{eq}$.

After the termination of RF pulse, the isochromates precess freely around the **Z** axis what is described by the matrix:

$$(R_\varphi) = \begin{pmatrix} C_\varphi & -S_\varphi & 0 \\ S_\varphi & C_\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

Where $\varphi=\Delta\omega_j t$ is the angle of rotation of an isochromate around **Z** axis, and t is the time elapsing from the trailing edge of pulse. Therefore, we have finally:

$$\boldsymbol{\mu}_1 = (\mathrm{R}_\varphi)(\mathrm{R})\boldsymbol{\mu}_{\mathrm{eq}} = \begin{pmatrix} \mathrm{C}_\varphi \mathrm{S}_\psi \mathrm{C}_\psi (1-\mathrm{C}_\theta) + \mathrm{S}_\varphi \mathrm{S}_\psi \mathrm{S}_\theta \\ \mathrm{S}_\varphi \mathrm{S}_\psi \mathrm{C}_\psi (1-\mathrm{C}_\theta) - \mathrm{C}_\varphi \mathrm{S}_\psi \mathrm{S}_\theta \\ \mathrm{C}_\psi^{\;2} + \mathrm{S}_\psi^{\;2}\mathrm{C}_\theta \end{pmatrix}$$

Expressions for the magnetization compounds in $\boldsymbol{\mu}_1$ coincide with ones obtained in Shakhmuratova et al. (1997) and Chekmarev et al. (1979) for the case of single-pulse excitation.

Let us find now the effect of n-fold repetition of the pulsed excitation in the frameworks of model (Shakhmuratova et al., 1997) when before the next RF pulse of a train only the longitudinal component of nuclear magnetization remains. One could prove by successive matrix multiplication that the expression for equilibrium nuclear magnetization $\boldsymbol{\mu}_{\mathrm{eq}}$ before the final "read-out " (n +1)-th pulse is:

$$\boldsymbol{\mu}_n = \left(C_\psi^{\;2} + S_\psi^{\;2} C_\theta\right)^n \boldsymbol{\mu}_{\mathrm{eq}} .$$

Then the result of excitation by the read-out pulse and following free precession of magnetization is described directly as for the initial conditions:

$$\boldsymbol{\mu}_{\mathrm{n+1}} = (\mathrm{R}_\varphi)(\mathrm{R})\boldsymbol{\mu}_n = \left(\mathrm{C}_\psi^{\;2} + \mathrm{S}_\psi^{\;2}\mathrm{C}_\theta\right)^{\mathrm{n}} \begin{pmatrix} \mathrm{C}_\varphi \mathrm{S}_\psi \mathrm{C}_\psi (1-\mathrm{C}_\theta) + \mathrm{S}_\varphi \mathrm{S}_\psi \mathrm{S}_\theta \\ \mathrm{S}_\varphi \mathrm{S}_\psi \mathrm{C}_\psi (1-\mathrm{C}_\theta) - \mathrm{C}_\varphi \mathrm{S}_\psi \mathrm{S}_\theta \\ \mathrm{C}_\psi^{\;2} + \mathrm{S}_\psi^{\;2}\mathrm{C}_\theta \end{pmatrix}. \tag{2}$$

These expressions coincide with the ones obtained in (Shakhmuratova et al., 1997) using the formalism of statistical tensors. The n-th degree multiple has a simple physical meaning of a longitudinal nuclear magnetization created by the n elementary pulses of a multiple pulse train reflecting the spin system memory to the excitation. The expressions for the SPE and its secondary echo signals using similar expressions for nuclear magnetization vectors were obtained in (Shakhmuratova et al., 1997).

As it follows from (3) the intensity of the SPE formed by the (n+1)-th RF pulse is proportional to $\boldsymbol{\mu}_n=(C_\psi^2+ S_\psi^2 C_\theta)^n\cdot\boldsymbol{\mu}_{eq}$. If one supposes that in the intensity of multiple pulse SPE formed by the nonresonant mechanism the main contribution is caused by the nonresonant isochromates with small ψ_s then $\boldsymbol{\mu}_n \sim (1+n\psi^2 C_\theta)\cdot\boldsymbol{\mu}_{eq}$ and one could expect the possibility to observe the cumulative SPE effect when consecutive SPE amplitudes are linearly increase with number of RF pulses n during the excitation by a RF pulse train.

2. Experimental Results and Their Discussion

A standard phase-incoherent spin-echo spectrometer was employed for measurements in frequency range 40-400 MHz at temperature 77 K. In frequency range 40-220 MHz a standard self-excitation RF oscillator has been used. The frequency of oscillator could be gradually retuned by using a number of circuits with different inductance coils and adjustable capacities. In the frequency range 200-400 MHz it was used a commercial manufactured oscillator based on the two-wire Lekher-type line including two coils with different numbers of turns. For pulse lengths ranging between 0.1 and 50 μs a maximum RF field produced of the sample was estimated to be about 3.0 Oe, while the rise and fall times of RF pulse fronts were no more than 0.15 μs. The recovery time of the spectrometer characterizing the transient loss of its sensitivity following the RF burst, was about ~ 1 μs. For investigation of lithium ferrite the resonant system of spectrometer was modified similar to described in work (Zviadadze et al., 2015) allowing us to increase sharply its sensitivity as compared with one in work (Kiliptari & Tsifrinovich, 1998).

In Figure 1 the block-scheme of modernized pulsed NMR spectrometer for observation of cumulative SPE effect is presented. The spectrometer was supplemented by the ATMEGA328P-PU (1), where the formation of the required RF pulse package takes place. The number of RF pulses belonging to a packet could be arbitrary. The repetition rate of packet spans range from the single triggering to the hundreds kilohertz ones.

The controller controls the pulse generator G5-7A (2) by the trigger input. Video-pulses generated by generator (2) are supplied to the pulse-amplifier and modulator (3) which sends high-voltage pulses to RF generator (4) then to the sample under investigation. The NMR echo signals formed in the samples are supplied to the receiver of the NMR spectrometer (5) where the additional enhancement and detection of signals takes place. The detected echo signal is finally sent to the digital oscilloscope (6) LeCroy 9410 for the final processing of signal.

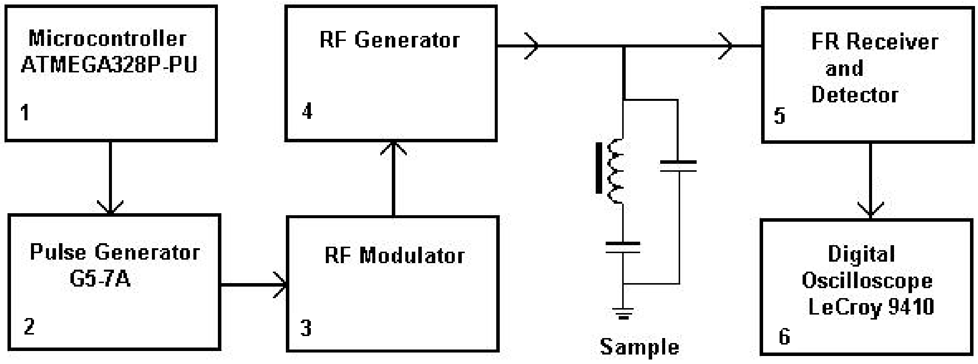

Figure 1. The block-scheme of noncoherent pulsed NMR spectrometer

The circular discs of dielectric lithium ferrite and its solid solutions with zinc $Li_{0.5}Fe_{2.5-x}Zn_xO_4$ ($0 \leq x \leq 0.25$) enriched by isotope ^{57}Fe (96.8 %) and polycrystalline cobalt power samples described in detail in (Kiliptari & Tsifrinovich, 1998) with the particle sizes less than 50 µs were also used.

Measurements were carried out at liquid nitrogen temperature T=77 K to obtain the intensive echo signals. The echo intensity values were taken directly from the oscilloscope screen.

Figure 2 shows the cumulative SPE effect at excitation by a series of six RF pulses, each of them with duration 3 µs, in lithium ferrite.

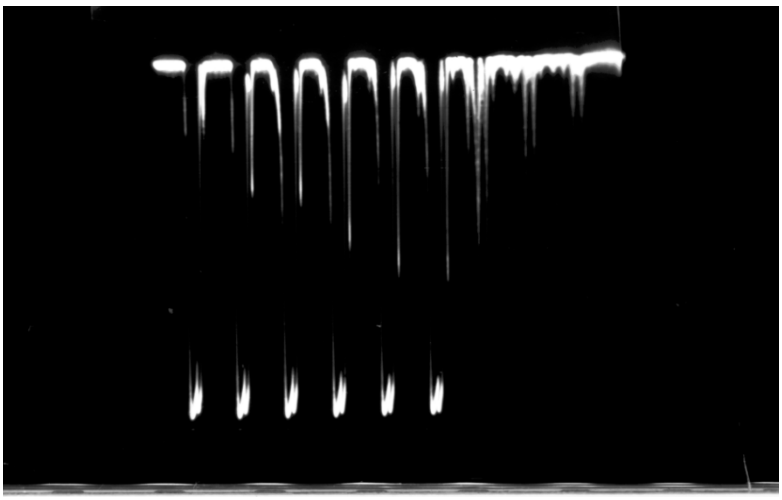

Figure 2. Cumulative single-pulse echo effect in lithium ferrite at excitation by series of six RF pulses (Zviadadze et al., 2015)

In work (Mamniashvili et al., 2015) the role of the hyperfine field anisotropy in the formation of a single-pulse NMR spin echo in cobalt was studied. It was shown that the single-pulse echo in cobalt is formed by the distortion of the exciting RF pulse edges according mainly due to hyperfine field anisotropy beginning with a certain value of RF pulse power. Before this threshold RF power, the single-pulse echo is formed by nonresonant mechanisms as in lithium ferrite.

So, in cobalt also one could expect appearance of the cumulative single-pulse echo effect at excitation by a series of RF pulses with sufficiently low power.

In Figures 3, 4, 5 we show the oscillograms for three different increasing RF pulse powers confirming this supposition.

The cumulative single-pulse echo effect was observed at excitation by pulse packets consisting of 6 RF pulses with duration 4.5 µ and time intervals between them in 23 µs. The repetition rate of packets is F_p=1 Hz.

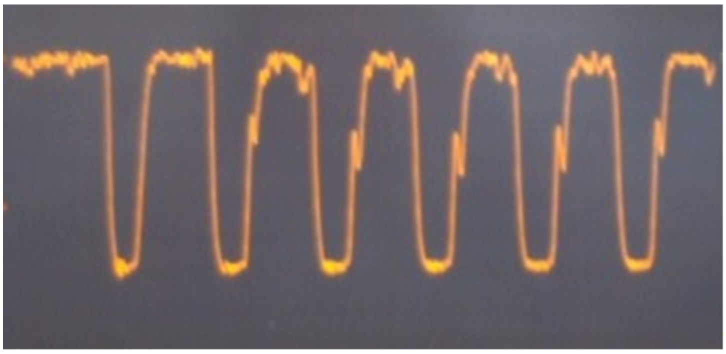

Figure 3. Cumulative echo effect in cobalt during excitation by six 4.5 μs duration RF pulses with intervals between them τ_I =23 μs, f_{NMR} = 216,8 MHz, T = 77 K, RF pulse amplitude is H_1=0.1 mOe.

In Figures 4 and 5 we show evolution of this picture at increasing RF power.

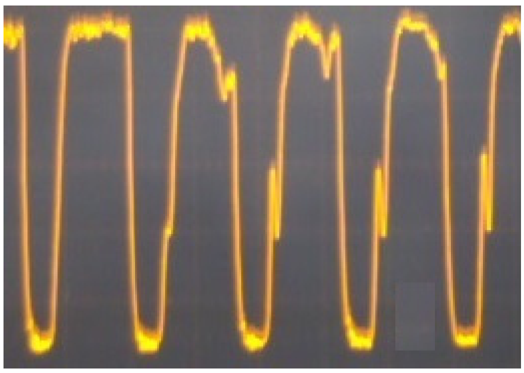

Figure 4. The response of nuclear spin-system to the excitation by RF pulses with amplitude H_1=0.3 mOe and the same τ and τ_1

In Figure 5 we present the case when distortion mechanism is effective, so one can see single-pulse echo formed after the first pulse in the packet.

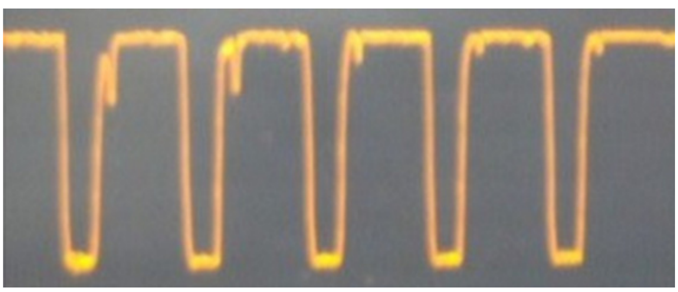

Figure 5. The response of the spin-system to the excitation by a packet of RF pulses when the distortion mechanism of single-pulse echo is effective: τ=14 μs; τ_I =50 μs, F_p=3.3 Hz, H_1=0.3 mOe

In Figure 6 we present the SPEs dependences after the second – E_2, the third – E_3 and the fourth – E_4 RF pulses on RF amplitude H_1.

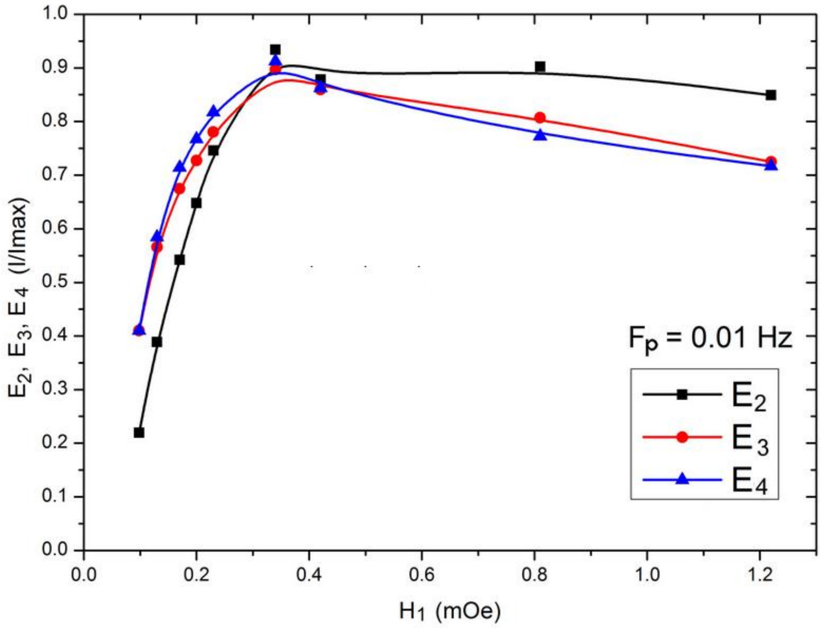

Figure 6. The consecutive SPEs (E_2, E_3, E_4) intensities dependences on RF pulse amplitude H_1 at τ=5 μs; τ_I=23 μs, F_p=0.01 Hz, f_{NMR} = 216,8 MHz; T = 77 K

Let us note that E_2 is the so-called two-pulse stimulate echo studied in detail in (Zviadadze et al., 2012).

In Figure 7 it is shown its dependences on F_p at different RF pulse amplitudes H_1:

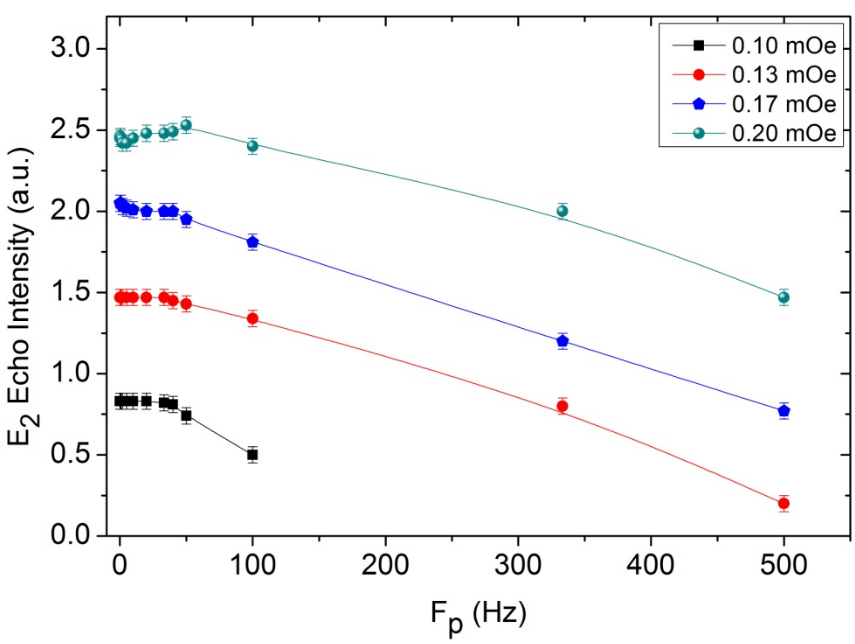

Figure 7. The two-pulse stimulated echo E_2 dependence on the RF pulse pocket repetition frequency F_p at different RF pulse amplitudes H_1: RF pulse duration τ=5 μs; time interval between RF pulses τ_I=23 μs, f_{NMR} = 216,8 MHz, T = 77 K.

In Figure 8 similar dependences are obtained for the second SPE signal E_3:

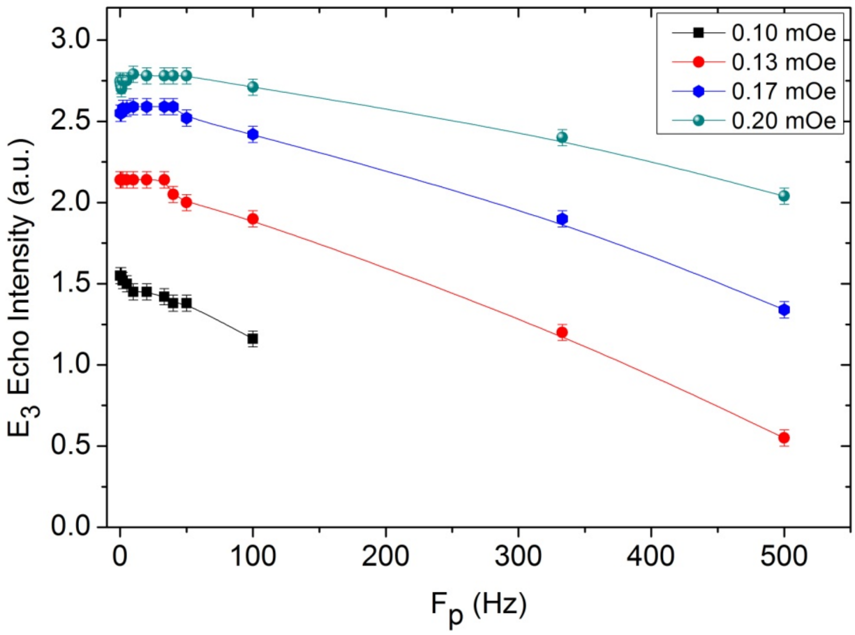

Figure 8. The SPE (E_3) after the third RF pulse dependence on the RF pulse pocket repetition frequency F_p at different RF pulse amplitudes H_1; τ=5 μs; τ_I=23 μs, f_{NMR} = 216,8 MHz, T = 77 K

The nuclear spin-system in cobalt could be considered at equilibrium before the application of each pulse packet at the used repetition frequency of RF pulse packets F_p and known spin-lattice relaxation times in cobalt.

As seen from Figure 3a single-pulse echo signal after the first RF pulse is absent what should be in the case when the nonresonant mechanism of single-pulse echo formation is active but two-pulse stimulated echo signal following the second RF pulse and subsequent stimulated signals (E_3, E_4 …) have definite increasing values due to their common stimulated nature just as it is takes place in lithium ferrite (Mamniashvili et al., 2015; Zviadadze et al., 2015) where the nonresonant mechanism of single-pulse echo formation is effective in agreement with the considered by us theoretical model.

Figures 6, 7 and 8 show common stimulated nature of investigated echo signals E_2 and E_3 (we restricted ourserves with F_p frequencies up to 500 Hz because at higher frequencies echo signals we gradually saturated).

From presented experimental results one could conclude that the cumulative SPE effect in cobalt is observed when the nonresonant mechanism is effective just as in lithium ferrite (Mamniashvili et al., 2015)

3. Conclusion

We report an unusual spin-echo phenomenon in cobalt when a train of echoes, generated by a repeating single RF pulse sequence, exhibits growth rather than damping. Similar effect was earlier observed for photon-echoes generated by a repeating two-pulse sequence (Schenzle et al., 1984). The effect in cobalt is observed below some threshold value of RF pulse power when the nonresonant mechanism of SPE formation is effective. At higher values of RF pulse powers the distortion mechanism of SPE formation caused by the hyperfine field anisotropy is effective (Mamniashvili et al., 2015) and the cumulative SPE effect is not observed.

Acknowledgments

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References

Akhalkatsi, A. M., & Mamniashvili, G. I. (1996). On the role of pulse edges in the single-pulse spin echo technique. *Physics of Metals and Metallography, 81*, 632-635.

Akhalkatsi, A. M., Mamniashvili, G. I., & Ben-Ezra, S. (2001). On mechanism of single-pulse echo formation in multidomain magnetic materials. *Physics Letters, A291*, 34-38. http://dx.doi.org/10.1016/S0375-9601(01)00698-3

Akhalkatsi, A. M., Mamniashvili, G. I., Gegechkori, T. O., & Ben-Ezra, S. (2002). On the mechanism of formation of a single-pulse echo of ^{57}Fe nuclei in lithium ferrite. *Physics of Metals and Metallography, 394*, 33-40.

Chekmarev, V. P., Kurkin, M. I., & Goloshchapov, S. I. (1979). Mechanism of formation of single-pulse echo in Hahn spin systems. *Soviet Physics JETP, 49*, 851-855.

Chigvinadze, J. G., Mamniashvili, G. I., & Sharimanov, Yu. G. (2004). Single-pulse and secondary echoes in systems with a large inhomogeneous broadening of NMR lines. *Low Temperature Physics, 30*, 799-804. http://dx.doi.org/10.1063/1.1808198

Gegechkori, T. O., & Mamniashvili, G. I. (2001). On formation mechanisms of single-pulse and secondary echoes in systems with a large inhomogeneous broadening of NMR lines. *Proceedings of Ivane Javakhishvili Tbilisi State University, Physics, 36*, 12-18.

Kiliptari, I. G., & Tsifrinovich, V. I. (1998). Single-pulse nuclear spin echo in magnets. *Physical Review, B57*, 11554-11564. http://dx.doi.org/10.1103/PhysRevB.57.11554

Kuz'min, V. S., & Kolesenko, V. M. (2004). Dynamics of single-pulse echo signals under the conditions of Zeeman switching. *Journal of Applied Spectroscopy, 71*, 14-21. http://dx.doi.org/10.1103/PhysRevB.57.11554

Mamniashvili, G., Gegechkori, T., Akhalkatsi, A., & Gavasheli, T. (2015). On the role of the hyperfine field anisotropy in the formation of a single-pulse NMR spin echo in cobalt. *Journal of Superconductivity and Novel Magnetism, 28*, 911-916. http://dx.doi.org/10.1007/s10948-014-2812-9

Mims, W. B., Nassau, K., & McGee, J. D. (1961). Spectral diffusion in electron resonance lines. *Physical Review, 123*, 2059–2069. http://dx.doi.org/10.1103/PhysRev.123.2059

Ponti, A. (1998). Single-pulse echo and oscillatory free induction decay; the importance of rephasing. *Molecular Physics, 95*, 943-955. http://dx.doi.org/10.1080/00268979809483228

Prescott, D. W., Miller, J. B., Tourigny, C., & Sauer, K. I. (2008). Nuclear quadrupole resonance single-pulse echoes. *Journal of Magnetic Resonance, 194*, 1-7. http://dx.doi.org/10.1016/j.jmr.2008.05.020

Shakhmuratova, L. N., Fowler, D. K., & Chaplin, D. H. (1997). Fundamental mechanisms of single-pulse NMR echo formation. *Physical Review, A5*, 2955-2967. http://dx.doi.org/10.1103/PhysRevA.55.2955

Schenzle, A., DeVoe, R. G., & Brewer, R. G. (1984). Cumulative two-pulse photon echoes. *Physical Review, A30*, 1866-1872. http://dx.doi.org/10.1103/PhysRevA.30.1866

Zviadadze, M., Mamniashvili, G., Akhalkatsi, A., & Menabde, M. (2015). Investigation of the interaction of series of RF pulses of arbitrary length with nuclear spin systems of magnets. *Journal of Superconductivity and Novel Magnetism, 28*, 927-934. http://dx.doi.org/10.1007/s10948-014-2757-z

Zviadadze, M. D., Mamniashvili, G. I., Gegechkori, T. O., Akhalkatsi, A. M., & Gavasheli, T. A. (2012). Two-pulse stimulated echo in magnets. *Physics of Metals and Metallography, 113*, 849-854. http://dx.doi.org/10.1134/S0031918X12090165

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