Edelweiss Applied Science and Technology
ISSN: 2576-8484
Vol. 9, No. 2, 1429-1438
2025
Publisher: Learning Gate
DOI: 10.55214/25768484.v9i2.4776

Comparative analysis of single-pulse and two-pulse echo signals in cobalt micropowders and nanowires

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Abstract: This study compares the behavior of two-pulse and single-pulse echo signals in cobalt micropowders and nanowires. In the first instance, the analysis focused on the influence of an additional magnetic video pulse on the echo signals in cobalt micropowders. The findings confirm the edge mechanism responsible for single-pulse echo formation in cobalt micropowders, where the fronts of the radio-frequency pulse act analogously to the radio-frequency pulses in the two-pulse Hahn echo technique. In the second instance, the radiofrequency resonant magnetometry method evaluated the coercive force of cobalt nanowires embedded in a polymer matrix and polarized by a magnetic field. The two-pulse and single-pulse echo signals were also examined during the magnetization and remagnetization of cobalt nanowires in this sample. The results also align with the conclusion that the edge mechanism underpins single-pulse echo signal formation in this context. Understanding the SPE formation mechanism is crucial for exploring phenomena such as multiple TPE signals, cumulative echoes, and the use of magnets as spin processors.

Keywords: *Cobalt, Distortion mechanism, Hyperfine field, Magnetic video-pulse, Multi-pulse mechanism, Nanowire. NMR, Single-pulse echo, Two-pulse echo.*

1. Introduction

The discovery of nuclear magnetic resonance (NMR) in ferromagnetic materials, enhanced by the hyperfine interaction, was made in 1959 [1]. Today, NMR remains one of the most effective techniques for investigating the structure and characteristics of magnetically ordered materials [2-5].

A key factor in NMR studies of magnetic materials is the electron-nuclear hyperfine interaction (HFI), which creates a strong local magnetic field, denoted as H_n, at the nuclear site [2]. The significant HFI in these materials makes the theory and approach to NMR quite different from those used for other materials. In a nuclear spin system, the HFI contributes significantly to H_n, primarily through a hyperfine field (HFF), HHFF, where HHFF = AM. Here, M represents the electron magnetization, and A is the hyperfine interaction factor. This interaction primarily influences nuclear magnetization, leading to the dominant contribution to Hn. In ferromagnetic materials, HHFF can reach magnitudes of 10^5 - 10^6 Oe. Consequently, the NMR resonant frequency in magnetic materials is mainly governed by Hn, unlike in non-magnetic materials.

Additionally, an external radiofrequency (RF) field with an amplitude H_1 and frequency near the NMR frequency causes the electron magnetization M to oscillate. Due to the HFF, this results in oscillating fields of greater intensity, denoted by ηH_1, at the nuclear sites. The factor η represents the enhancement of the RF field, typically around 10^2 - 10^3 in magnetic domains, but much greater amplification, on the order of 10^4 - 10^5, occurs in the domain walls (DWs) of magnets. As a result, the applied RF field and the observed NMR signals are both amplified by an enhancement factor of η. Because of this, NMR spectrometers for magnetic materials are generally simpler than standard NMR spectrometers, but they must be capable of covering a

History: Received: 9 December 2024; Revised: 17 January 2025; Accepted: 20 January 2025; Published: 14 February 2025
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broad frequency range. This is because the NMR line width in multi-domain magnets typically spans tens of MHz, and in some cases, ranges from tens to hundreds of MHz, with an average carrier frequency between 30 and 1000 MHz.

A notable aspect of NMR behavior in magnets is that, in many cases, the primary contribution to the intensity of resonant absorption originates from nuclei located within DWs. These DWs are highly responsive to magnetic video-pulses (MVPs), making them a practical tool for investigating the formation of additional echo signals induced by MVPs, [6].

The dynamics of DWs under the influence of MVPs were initially examined by Galt [7] in a single-crystal ferrite sample structured as a frame. In this study, the MVP was applied via a primary coil on one side of the frame, while the resulting induction signal, caused by DW motion, was recorded by a secondary coil on the opposite side and visualized on an oscilloscope.

It was demonstrated that the DW velocity υ is linearly dependent on the MVP amplitude H according to the relationship:

$$\upsilon = S\,(H - H_0),$$

where S represents the mobility of the DW, and H0 is the pinning force—the critical field below which the DW remains stationary.

Even small displacements of the DW induced by the MVP can lead to significant rotations of the magnetization M. This rotation correlates with variations in the HFF and the NMR enhancement factor η due to the anisotropy of the HFF and the inhomogeneity of η within the DWs [8].

This paper presents a comparative analysis of single-pulse echo (SPE) and two-pulse echo (TPE) signals in cobalt micropowders exposed to MVPs [9]. Additionally, it examines the effects of external magnetic fields on SPE and TPE signals during the magnetization and remagnetization of cobalt nanowires. The SPE, a resonant response of a non-uniformly broadened nuclear spin system, is generated by applying a single RF pulse and forms approximately at the duration of the pulse after its termination, Figure 1.

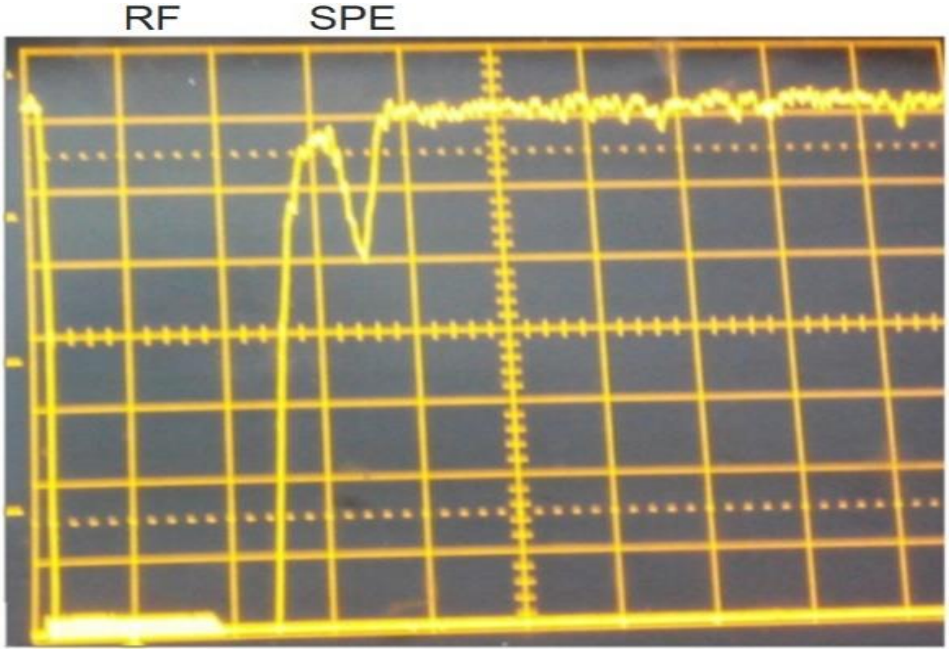

Figure 1.
The single-pulse echo signal of 59Co nuclei in cobalt is shown in the upper trace, while the RF pulse shape is displayed in the lower trace. The NMR frequency $\nu(\omega/2\pi) = 213$ MHz, with an RF pulse duration τR of 20 μs at a temperature of 293 K.

The formation mechanisms of the SPE can be classified into two categories [10]:

A. Edge-Type Mechanisms: These occur when the fronts of the RF pulse mimic two resonant RF pulses, as in the Hahn TPE method. The role of the RF pulse fronts in this mechanism is significant, as the direction of the effective magnetic field $H_{eff}=(\Delta\omega_j \cdot z+\omega_1 \cdot y)/\gamma_n$ in the rotating coordinate system (RCS) changes at these moments. Here, γ_n is the nuclear gyromagnetic ratio, z, and y are unit vectors in RCS, $\Delta\omega_j=\omega_{NMRj} - \omega_{rf}$ represents the detuning, $\omega_1=\gamma_n\eta H_1$ is the RF field amplitude in frequency units, and η is the RF field enhancement factor [2,3]. Such changes often arise due to non-resonant effects when the carrier frequency of an RF pulse is detuned by an amount ($\Delta\omega_0$ comparable to or exceeding the broadening of the NMR line $\Omega_{j,\,max}$ [10]. Distortions in the RF pulse fronts caused by non-ideal electronic components can also lead to similar effects [11].

B. Internal Mechanisms: These are driven by nonlinearities in spin systems. For example, in weakly anisotropic magnets at low temperatures, large dynamic frequency shifts can lead to a frequency-modulated SPE formation [3]. Another internal mechanism, the "multi-pulse mechanism," arises in systems with significant Larmor and Rabi inhomogeneous broadenings of NMR lines and spin system non-equilibrium prior to the RF pulse sequence [12]. This mechanism is observed in materials like lithium ferrite and cobalt at low RF pulse power, where SPE signals may not appear during single-pulse excitation but are replaced by two-pulse stimulated echoes (TPSE) [13].

The SPE in cobalt was first experimentally observed by Stearns [14] despite theoretical predictions suggesting its absence. Particularly strong SPE signals were identified in the hexagonal close-packed (hcp) phase, characterized by significant anisotropy of the HFF. Subsequent studies Tsifrinovich, et al. [11] attributed the SPE formation to RF pulse front distortions caused by transient electronic processes during pulse generation. A comparative analysis with lithium ferrite [10] clarified that the SPE in cobalt is predominantly formed by the distortion of RF pulse fronts within DWs, facilitated by the HFF anisotropy. Below a critical RF power threshold, SPE formation aligns with the multi-pulse mechanism, as seen in lithium ferrite [10, 15].

Recent research Mamniashvili, et al. [16] has further validated these conclusions. For instance, controlled RF pulse front distortions created by two magnetic MVPs highlighted their influence on SPE amplitude. Additionally, comparisons of SPE and TPE enhancements in cobalt nanowires under external magnetic fields during remagnetization reinforce the edge mechanism of SPE formation.

This paper presents a comparative analysis of single-pulse echo (SPE) and two-pulse echo (TPE) signals in cobalt micropowders exposed to MVPs. Additionally, it examines the effects of external magnetic fields during the magnetization and remagnetization of cobalt nanowires.

The primary goal of this work is to compare SPE and TPE signals in cobalt micropowders and nanowires to provide further experimental confirmation of the edge mechanism of SPE formation.

2. Experimental Observations and Analysis

NMR measurements on cobalt micropowders were performed using a phase-incoherent spin echo spectrometerg in the 200–400 MHz range at a temperature of 77 K [17]. A commercial Lecher-type generator with a two-wire line and variable inductors produced RF pulses with durations between 0.1 and 50 μs, generating a maximum RF field amplitude of approximately 3.0 Oe. The RF pulse fronts had a steepness of 0.15 μs, and the receiver's dead time was about 1 μs.

The experimental setup is shown in Figure 2, where a gated current stabilizer generated magnetic field pulses of up to 500 Oe in a copper coil were used for samples approximately 10 mm in size.

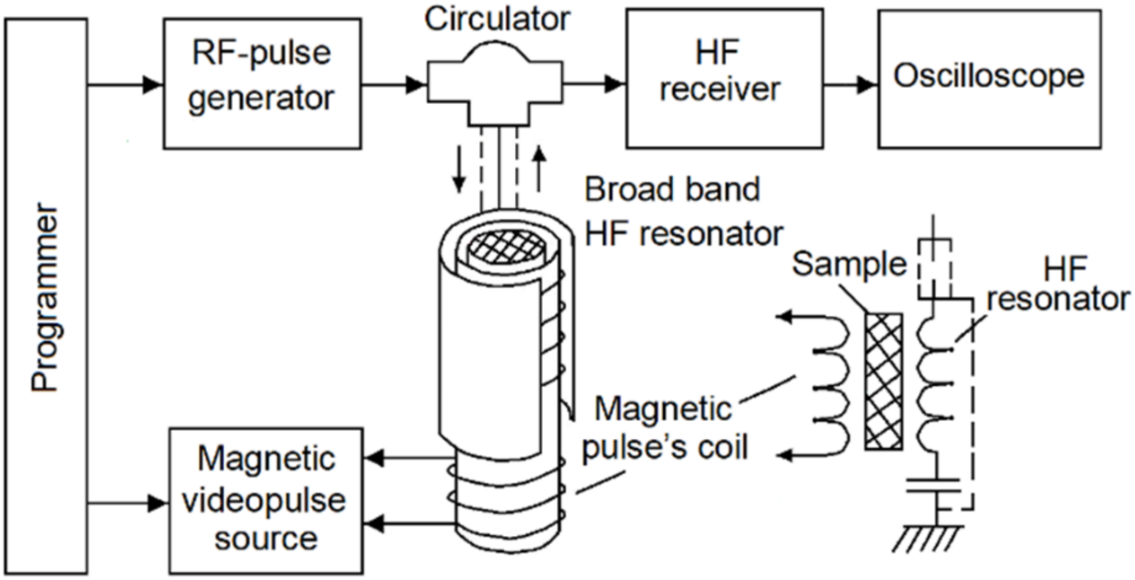

Figure 2.
Experimental setup.

Polycrystalline cobalt micropowders, with average grain sizes under 50 μm, were synthesized via induction furnace melting. The NMR spectrum^{59}Co nuclei in the DWs of the face-centered cubic (FCC) phase is presented in Figure 3 at optimal RF pulse power and 77 K [17, 18].

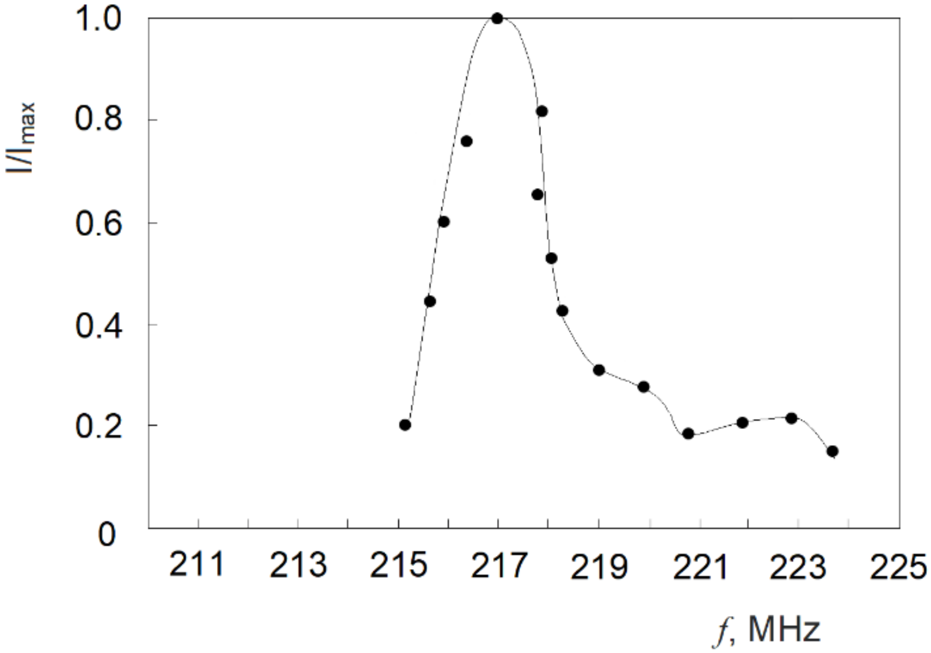

Figure 3.
The ^{59}Co NMR spectrum recorded at T=77K under optimal RF pulse power conditions.

Time diagrams illustrating the effects of an additional MVP on TPE and SPE signals are shown in Figure 4*a* and 4*b*. The MVP-induced structural changes in these diagrams appear only when its amplitude surpasses the pinning force of DWs, displacing them from their pinning centers [19].

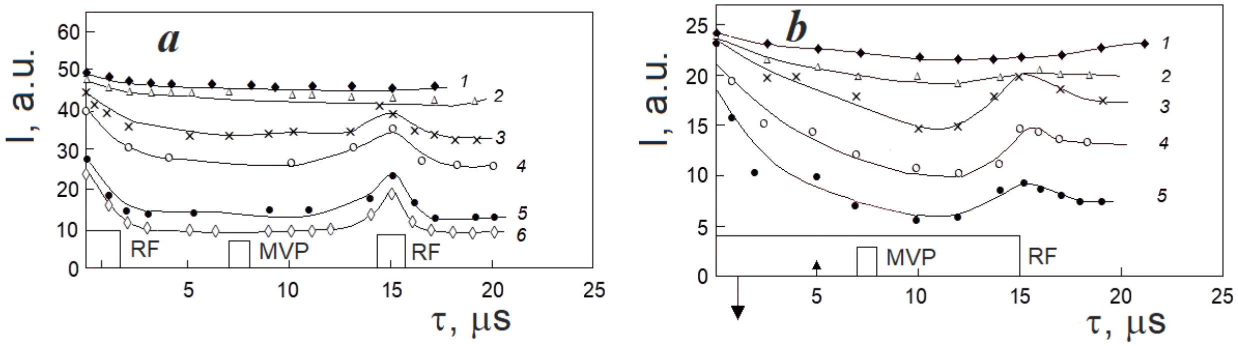

Figure 4.
Time diagrams of the effect of the additional magnetic video pulse on the signals of the two-pulse echo (1-6) at the amplitude of H=27, 51, 107, 139, 293, 320 Oe, respectively (*a*). Time diagrams of the effect of the additional magnetic video pulse on the signals of the single-pulse echo (1-5) at H=32, 53, 127, 139, and 293 Oe, respectively (*b*). NMR frequency f_{NMR}=217 MHz.

A comparison of the MVP effect on the TPE signal, depending on whether it acts during RF pulse intervals or concurrently, reveals analogous behavior in SPE signals when MVPs coincide with RF pulse fronts or occur within the pulse duration (Figure 5*a* and 5*b*).

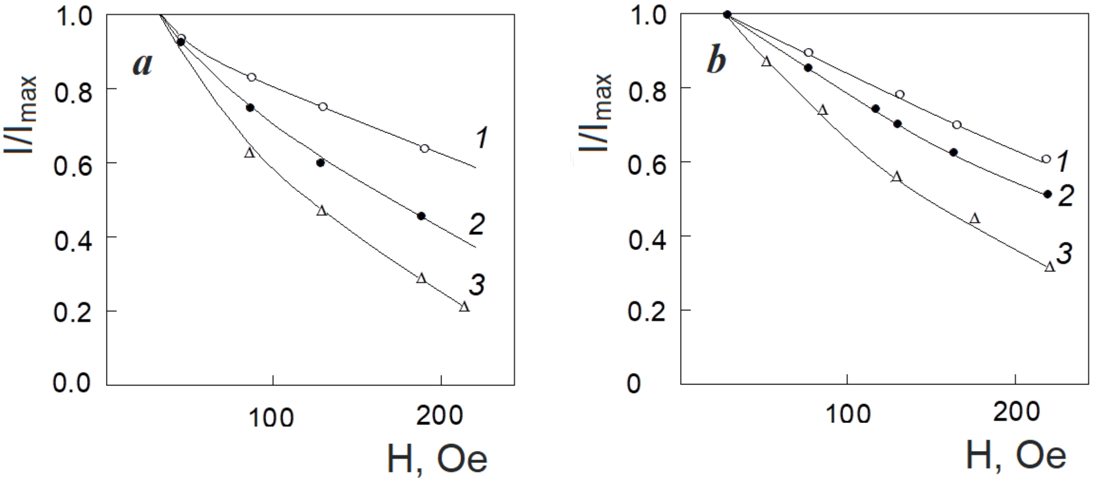

Figure 5.
Time diagrams of the magnetic video-pulse effect on the single-pulse echo (*a*) and two-pulse echo (*b*) depending on the time position of the magnetic video-pulse with a length of τ_m = 1 μs and coincidence with the fronts of the RF pulses (1, 2), respectively, and in the middle of the interval between them (3) at the optimal power of the RF pulses, f_{NMR} = 217 MHz.

In TPE signals, MVPs acting simultaneously with RF pulses induce abrupt DW displacements, while MVPs between RF pulses attenuate SPE signals by causing non-uniform frequency shifts in nuclear isochromates [8].

Figure 6 demonstrates the MVP effect on SPE signals at optimal RF pulse power (*1*) and reduced power (*2*), where the signal intensity decreases fourfold. Lower RF power amplifies MVP effects, as nuclei in more mobile DWs contribute dominantly to SPE signals. This observation aligns with previous studies [10].

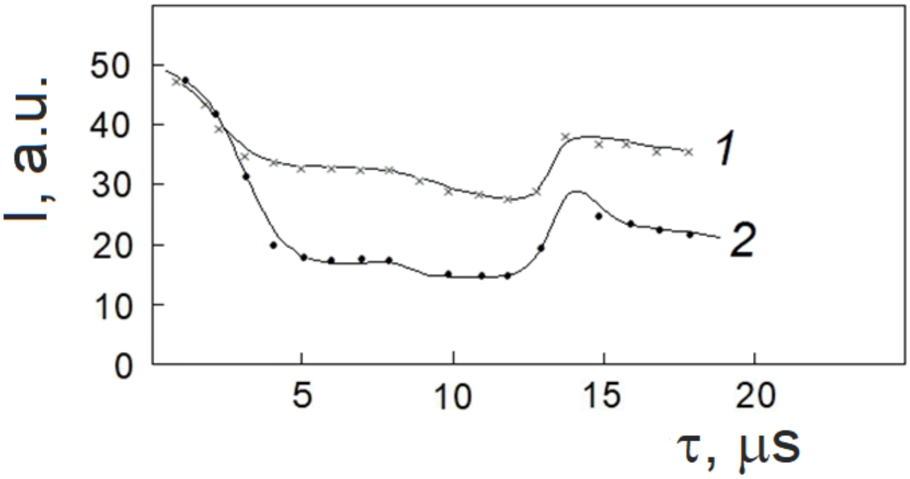

Figure 6.
Time diagrams of the magnetic video-pulse exposure with an amplitude of H=214 Oe on the single-pulse echo at the optimal RF pulse power (*1*) and reduced power (*2*) corresponding to a 4-fold decrease in the single-pulse echo intensity, f_{NMR}=217 MHz.

As shown in Figure 7, varying the RF pulse duration does not alter the shape of the effective RF pulse fronts responsible for SPE signal formation. However, reducing the RF pulse duration further may lead to overlapping fronts, resulting in a shift in the SPE formation mechanism and a subsequent decrease in SPE intensity. This behavior contrasts with lithium ferrite, where reduced RF pulse duration increases SPE intensity [13].

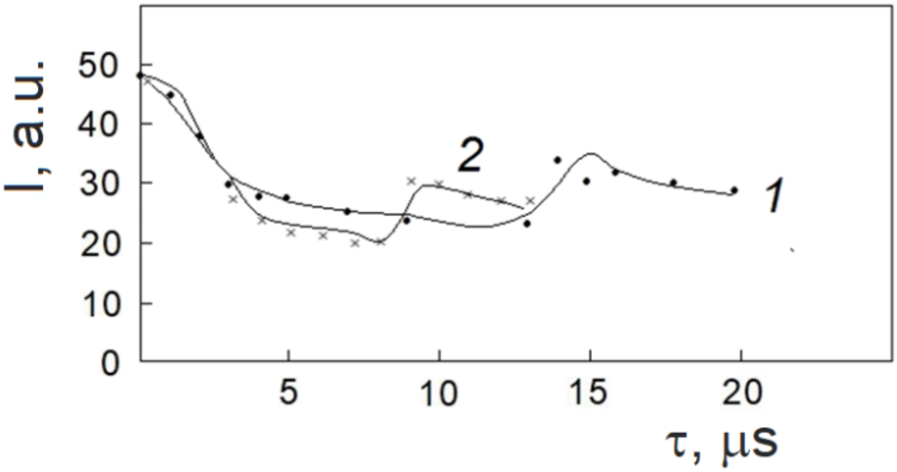

Figure 7.
Time diagrams of the effect of magnetic video-pulse with an amplitude of H = 293 Oe and τ_m = 1 μs at RF pulse durations of τ = 15 μs (*1*) and τ = 10 μs (*2*) on the single-pulse echo signals. f_{NMR}=217 MHz

Previous studies have explored various mechanisms underlying SPE formation in magnets. However, these studies failed to establish a definitive mechanism. In Mamniashvili, et al. [16] a novel method was proposed, utilizing two MVPs to induce controlled distortions in the effective RF pulse fronts, thereby generating additional SPE signals. The local RF field on nuclei distorts as DWs shift under MVP influence, driven by HFF anisotropy and RF field gain factor inhomogeneity.

This study aimed to validate the SPE formation model proposed in Mamniashvili, et al. [16] using an alternative experimental approach. The results showed that the additional MVP's effect on SPE and TPE echo signals supports the edge mechanism, where RF pulse fronts mimic the role of two RF pulses in the Hahn TPE method.

Understanding the formation mechanism of the SPE in cobalt is crucial for explaining phenomena such as multiple signals of the TPE in magnets, cumulative echo effects, and related behaviors [20, 21]. Additionally, it holds significance for employing magnets as the active medium in spin processors using the NMR TPE method [22].

The SPE method offers nearly the same insights into the spin system as the TPE method. When designing spin processors based on spin-echo NMR, it is essential to consider the characteristics of SPE and the conditions required for its detection. Furthermore, if the signal intensity is sufficient, it becomes possible to develop a device for processing RF pulses using the SPE phenomenon. A key advantage of such a system is that it eliminates the need to read pulses within the RF sequence, thereby overcoming challenges related to synchronization between recording and reading pulses.

The findings of this study build upon and extend the results of previous research [16] enabling a more comprehensive interpretation of earlier works in this field [10-16]. Specifically, works [10, 16] highlight the conditions under which the internal multi-pulse mechanism responsible for SPE formation, investigated in studies [12, 15] transitions to a mechanism involving RF pulse front distortion [11, 12]. This shift occurs when the RF pulse power surpasses a critical threshold determined by the pinning force of DWs in cobalt.

The experimental findings also extend to cobalt nanowires. Samples were prepared using cobalt nanowires from PlasmaChemGmbH 200–300 nm with a diameter, up to 200 μm length, embedded in epoxy resin capsules. The process involved placing 0.4 g of cobalt nanowires in a polyethylene tube with liquid epoxy resin, mixing to ensure homogeneity, and curing under a magnetic field.

To characterize the magnetic properties of the obtained samples, in addition to the NMR method, the RF magnetometry method is used [12].

For this purpose, an RF resonance magnetometer was used based on an LC resonance generator assembled according to a standard circuit using field-effect transistors. The essence of the method lies in monitoring the magnetic susceptibility of the sample by measuring the change in the resonance frequency $\Delta f(H_e)$ of the LC generator with the sample in its resonance circuit under the action of an external magnetic field H_e.

This paper presents a comparative study of the NMR data of the SPE and TPE signals and magnetometry in the study of the specified samples of a polymer composite based on cobalt nanowires.

Figure 8 shows the dependences of the change in the resonance frequency $\Delta f(H_e)$ of the LC generator under the action of an external magnetic field H_e (initial resonance frequency f_0 = 10 MHz) directed along or across the magnetization of the sample.

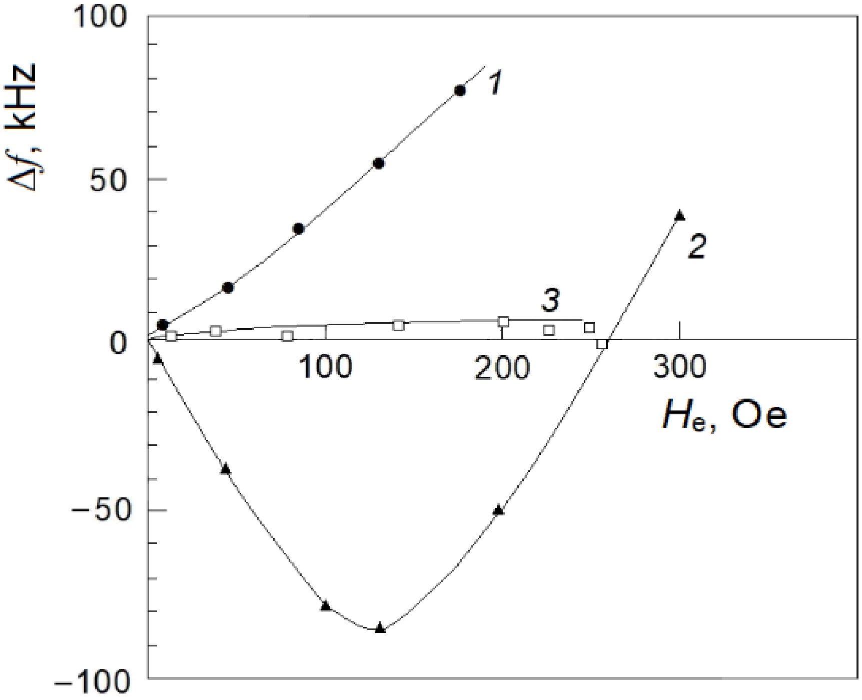

Figure 8.
Variation in the resonant frequency of the LC generator when a cobalt composite sample is included in its resonant circuit, as the magnetic field H_e increases: (*1*) along the sample's magnetization direction, (*2*) opposite to the magnetization direction, and (*3*) perpendicular to the magnetization.

The minimum of the $\Delta f(H_e)$ dependence, observed at an external magnetic field value of $H_e \sim 130$ Oe, corresponds to the maximum of the susceptibility χ_{DIS} associated with the displacement of DWs, and, according to Shakhmuratova, et al. [12] this value of He also gives an estimate of the coercive force of the sample H_c.

Amplification of SPE signals during the magnetization reversal of these nanowires, as shown in Figure 8, demonstrates a similar effect observed with TPE signals [18].

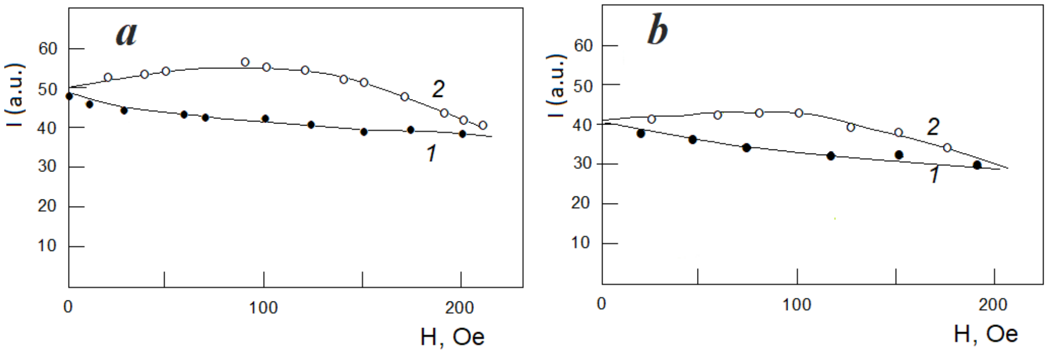

Figure 9.
Intensity dependence of TPE signals on external magnetic fields aligned (*1*) or opposing (*2*) the nanowire magnetization (*a*); Intensity dependence of SPE signals under similar conditions (*b*).

The enhancement of the TPE signal intensity χ_{DIS} corresponds to a rise in magnetic susceptibility, attributed to the displacement of the DW. This, in turn, results in an increased gain factor η_{eff} for the transverse RF field h interacting with the nuclei, expressed as $\eta_{eff} = A\chi_{DIS}$, where A represents the hyperfine coupling constant. Consequently, this leads to a greater absorption of NMR power, given by $P \sim \eta_{eff}^2 h^2$ [2].

3. Conclusion

This study confirms that SPE signals in cobalt are formed through distortions in RF pulse fronts caused by DW displacement. The RF pulse fronts act similarly to the two pulses in the Hahn TPE technique.

Key contributions of this work include:

1. Direct comparison of MVP effects on SPE and TPE signals in cobalt micropowders;
2. First-time observation of time diagrams illustrating MVP effects on these signals;
3. Validation of the edge mechanism as a dominant SPE formation pathway;
4. Extension of the findings to cobalt nanowires, where magnetization reversal amplifies SPE and TPE signals, further supporting the proposed mechanism;
5. Understanding the SPE formation mechanism is crucial for exploring phenomena such as multiple TPE signals, cumulative echoes, and the use of magnets as spin processors.

Transparency:

The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

Acknowledgments:

This work was supported by the Shota Rustaveli National Science Foundation of Georgia (SRNSFG) [FR-22-7899].

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