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RESEARCH ARTICLE

Inverse NMR echo in the rotating coordinate frame in cobalt micropowders and nanowires

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ABSTRACT

The first observation of an inverse nuclear magnetic resonance (NMR) echo in the laboratory coordinate system was recorded in cobalt nanofilms utilizing a nanosecond-scale magnetic video-pulse. This study extends that work by investigating a similar phenomenon, this time within the rotating coordinate frame in cobalt micropowders and nanowires. The nuclear spin system's response within the domain walls of these cobalt structures was analyzed under the combined influence of radio-frequency (RF) fields and a microsecond magnetic video-pulse. As a result, an echo signal analogous to an inversion echo in a rotating coordinate system was produced. The amplitude of the magnetic video-pulse required to generate this echo signal serves as an estimate of the domain wall pinning strength in the micropowders and nanowires. Additionally, this paper discusses the unique electroless synthesis method for cobalt nanowires within an external magnetic field utilized in this research. The experimental findings on domain wall pinning forces in these systems are presented, with potential applications including advances in logic and memory devices, sensors, rare earth magnets, medical hyperthermia, and beyond.

Keywords: Inverse NMR echo; magnetic video-pulse; cobalt micropowders; cobalt nanowires

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1. Introduction

The exploration of magnetism and magnetic materials is a significant area of interest in contemporary science and technology[1]. Gossard and Portis first observed nuclear magnetic resonance (NMR) in magnetically ordered materials within ferromagnetic cobalt[2]. Since this initial discovery, NMR has evolved into a powerful technique for probing magnetic materials, especially the static and dynamic properties of atomic systems in ferromagnetic micro- and nanoparticles—properties that are otherwise difficult to measure[3,4]. A key distinction between magnetic and non-magnetic materials is the presence of a strong local magnetic field acting on nuclei.

This local field is primarily influenced by the effective hyperfine field (HFF), which originates from the polarization of s-electrons by the spontaneous magnetization of the ferromagnet via the Fermi contact interaction. The presence of HFF on cobalt nuclei allows NMR to be observed 27 without an external magnetic field. In magnetic materials, the radio-frequency (RF) fields influence nuclei indirectly by altering electron magnetization, which then induces a resonant field at the nucleus, amplified by the gain factor $\eta_d \sim 10^2$ in domains and $\eta_w \sim 10^4$ at domain walls (DWs). Consequently, nuclei within DWs contribute significantly to resonant absorption due to the large η_w.

Given that DWs can be easily displaced by a magnetic video-pulse (MVP), this technique is an effective method for studying DW pinning and mobility[5].

The influence of MVP on DW displacement in ferromagnetic metals was first examined using NMR techniques[6]. When an MVP is applied simultaneously with a second RF pulse (symmetric action), the echo signal amplitude decreases, likely due to MVP-induced DW displacement, which reduces the number of nuclei exposed to both RF pulses. In contrast, when the MVP acts between RF pulses (asymmetric action), the echo signal diminishes proportionally to the MVP amplitude and duration, indicating a non-uniform shift in NMR frequencies due to HFF anisotropy. This method has since been applied to study the effects of MVP on nuclear spin echoes in various ferromagnetic materials, where it was determined that the critical MVP value needed to tear off DWs from pinning centers is also dependent on its area[7].

Under the applied MVP, DWs rapidly accelerate to speeds of several hundred m/s. Efforts are underway to further increase these speeds, which could enhance the performance of memory and logic systems. The dynamics of DWs in single-crystal ferrite samples subjected to MVP, were first explored by Galt[8]. The DW dynamics were characterized by a linear relationship between DW velocity (υ) and the MVP amplitude (H):

$$\upsilon = S(H - H_0), \tag{1}$$

where S represents DW mobility and H_0 is the critical field amplitude below which the DW remains pinned.

As the external RF field interacts with nuclei via the electron subsystem, the phenomena described here are explained by considering the displacement of electron magnetic moments (M) within the DW under MVP. Even minimal DW displacement results in substantial M rotation, which is proportional to the DW shift. This process alters the HFFs on nuclei, proportional to the DW displacement due to HFF anisotropy in magnetic materials[5].

Recent advancements in controlling magnetization switching at micro- and submicron scales have opened new avenues for understanding magnetization reversal processes. These studies are particularly relevant for magnetoresistive random access memory (MRAM) systems. DW displacement remains one of the most promising techniques for switching local magnetization. The dynamics of DWs in enclosed structures are of fundamental interest and have significant technological implications for modern magnetic logic systems, particularly as the width of magnetic structures approaches that of the DW[9].

In an earlier study[10], during the rapid magnetization reversal of polycrystalline ferromagnetic cobalt thin films, inverse echo (IE) signals were observed at an NMR frequency of 218 MHz. In this case, the first RF pulse shifts nuclear magnetization from equilibrium, causing nuclear isochromates to dephase due to HFF inhomogeneity. Then, at time $t = \tau$, the magnetic film is remagnetized over $t_R \approx 10^{-9}$ s by the action of a nanosecond-long MVP, leading to the formation of an inverse nuclear spin echo via a novel mechanism involving the reversal of isochromate precession direction, **Figure 1*a***.

Given that the nuclear spins precess with a period $T=2\pi/\omega_j$ is $T = 5 \cdot 10^{-9}$ s, it's reasonable to assume that the spins remain stationary during the interval $t_R << T$. Once the magnetization is reversed, both the hyperfine field (HFF) and the direction of isochromatic precession invert, causing rephasing and the emergence of the IE signal. To successfully detect the IE signal, the reversal time $t_R << T$ must be significantly shorter than T, necessitating an MVP duration in the nanosecond range. As noted in[5], it's technically simpler to alter the direction of the effective magnetic field $H_{eff} = (\Delta\omega_j\, z + \omega_1\, y)/\gamma_n$ in a rotating coordinate frame (RCF), where γ_n represents the nuclear gyromagnetic ratio, and **z**, and **y** are unit vectors in the RCF. The detuning for the j-th isochromate is $\Delta\omega_j = \omega_j - \omega_{RF}$, and $\omega_1 = \gamma_n\, \eta\, H_1$ is the amplitude of the RF field in frequency units, with η is the gain factor of the RF field[3]. In this scenario, the time required for changing H_{eff}'s direction should be much shorter than the precession period $T' = 2\pi/\Delta\omega'_j$ in the RCF, for which $T' >> T$ holds true because, $\omega_j >> \Delta\omega'_j$, where $\Delta\omega'_j = (\Delta\omega^2_j + \omega^2_1)^{1/2}$.

This research aims to simplify the IE method by incorporating an additional MVP targeting the nuclei in the domain wall (DW), combined with the RF pulse field, to investigate the formation of the rotational inversion echo (RIE), an analog of IE in the RCF, as illustrated in **Figure 1*b***.

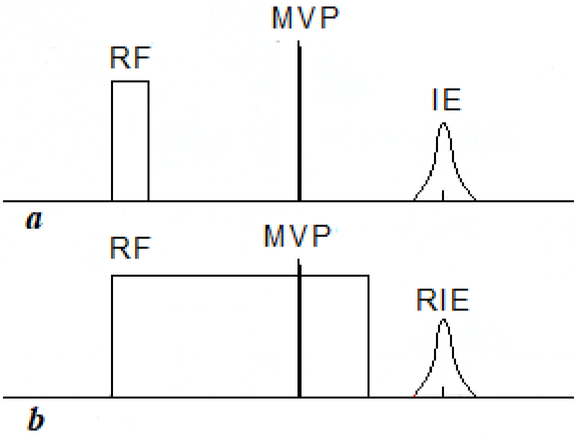

Figure 1. Time diagrams for the excitation of the inverse echo (IE) (a) and the rotational inverse echo (RIE) (b) at combined excitation by RF and an additional magnetic video-pulse (MVP).

2. Experimental results and discussion

The experiments were conducted using a phase-incoherent spin-echo spectrometer[11] operating in the 200-400 MHz frequency range at a temperature of 77 K and 217 MHz frequency.

The experimental setup is depicted in **Figure 2.** The MVP field was generated by a strobed current stabilizer producing MVP field pulses around 500 Oe for a sample size of ~10 mm

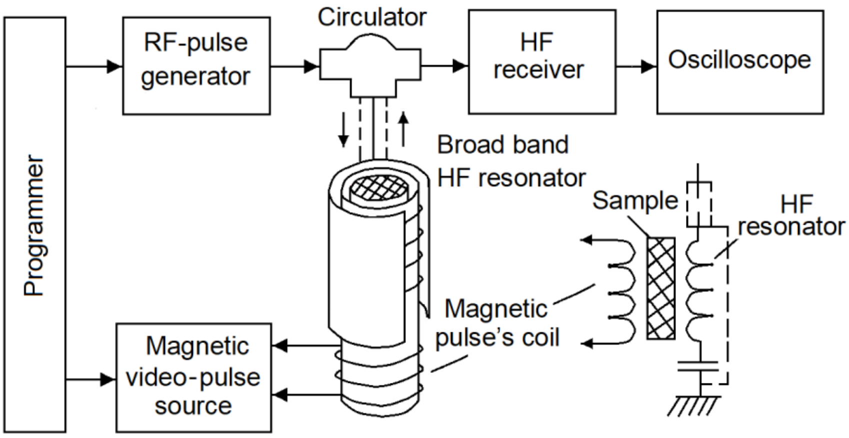

Figure 2. Experimental setup.

The measurements were performed using polycrystalline cobalt micropowders obtained through induction furnace melting with an average grain size under 50 µm[11], as well as synthesized and commercial nanowires.

Figure 3 displays the electron diffraction patterns of the synthesized and commercial cobalt nanowire samples, obtained using an SEM TESCAN VEGAS XMU scanning microscope. The commercial cobalt nanowires, provided by PlasmaChem GmbH, had an average diameter of 200-300 nm and a length up to 200 µm, while the synthesized nanowires were created via chemical deposition under an external magnetic field of 500 Oe[11,12].

The analysis of the electron diffraction patterns revealed that while the average diameters of both nanowire types were similar, the synthesized nanowires were approximately five times shorter on average.

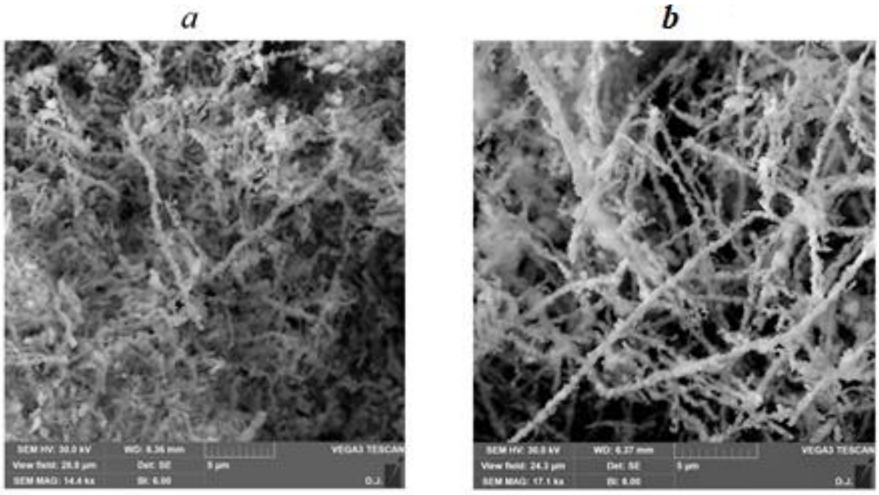

Figure 3. Synthesized (a) and commercial (b) cobalt nanowires.

In practical applications, the RIE signal can be observed under the combined influence of RF and MVP pulses.

Rapid changes in the direction of the effective field in the rotating coordinate frame (RCF) occur when the DW is displaced due to the action of a MVP. This is a result of the anisotropy of the effective field and the inhomogeneity of the η factor within the DW. The magnetic echo (ME) signal, as investigated in[5], arises from the combined effects of two RF pulse fronts and the MVP on the nuclear spin subsystem in the DW, analogous to the three-pulse stimulated Hahn echo (**Figure 4**).

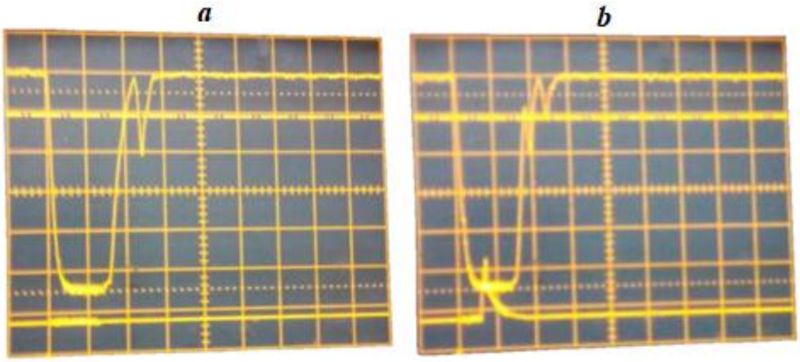

Figure 4. Oscillogram of the single-pulse echo (SPE) signal (a) and oscillogram of the exciting RF pulse with an additional ME (b), generating an additional ME signal, $\nu = 217$ MHz, $\tau_m = 1.0$ μs, $T = 77$ K. The lower trace indicates the MVP's position within the RF pulse and its duration.

ME signal is generated when the MVP amplitude surpasses the pinning force of the DW (**Figure 5**).

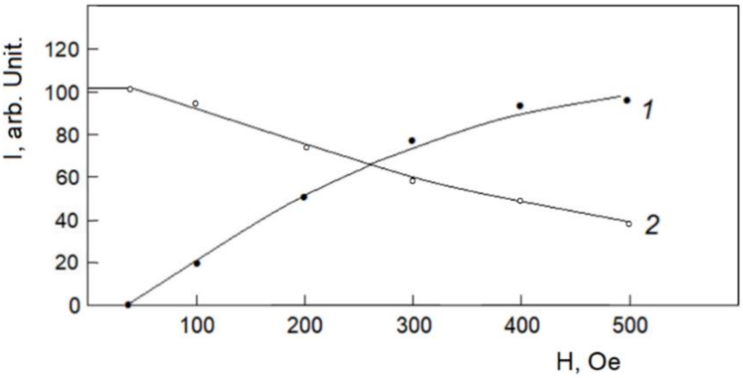

Figure 5. ME (1) and SPE (2) signals in cobalt micropowder as a function of MVP amplitude, $\nu = 217$ MHz, $T = 77$ K.

According to the edge mechanism of SPE formation[13], a portion of the transverse nuclear magnetization induced by the leading edge of the RF pulse is refocused by the MVP pulse, acting similarly to the second RF pulse in the stimulated Hahn echo technique. The ME signal appears when the MVP amplitude exceeds the DW pinning force.

Similarly, the RIE signal is produced by the combined action of the MVP and the trailing edge of a sufficiently long RF pulse, at a point when the SPE signal is no longer detectable, as illustrated in **Figure 6**.

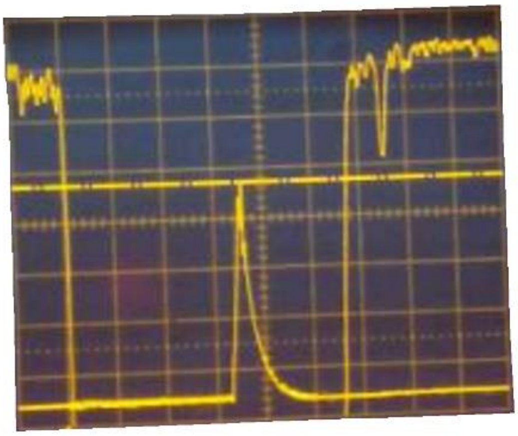

Figure 6. Oscillogram of the RIE signal in cobalt micropowder formed by the combined action of the MVP and the trailing edge of a long RF pulse, ν = 217 MHz, T = 77 K.

RIE is analogous to the SPE echo signal, resulting from the interaction of an additional MVP and the trailing edge of a long RF pulse. Up to this point, the ME signal, formed by the stimulated mechanism due to the combined action of the MVP and two RF pulse edges, has been studied[5]. The next focus will be on the properties of the RIE signal.

In **Figure 6**, the RIE signal is depicted. The RIE is formed by a distortion mechanism since it persists even when there is a single excitation by the combined RF and MVP, unlike the RIE signal in cobalt micropowder when the RF pulse power is below the threshold value[13]. The RIE intensity dependence on the MVP amplitude for cobalt micropowder, synthesized, and commercial cobalt nanowire samples is shown in **Figure 7**.

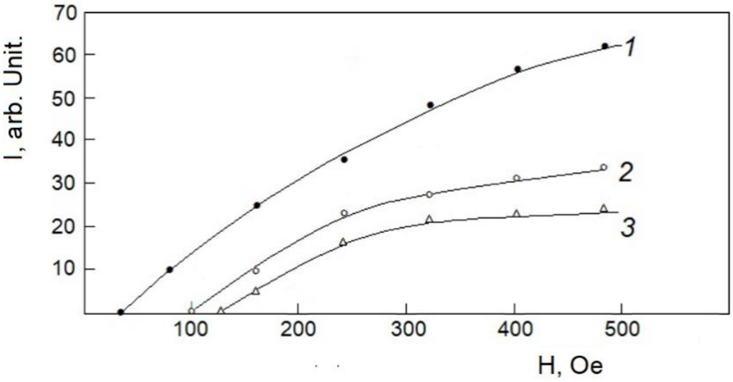

Figure 7: Dependence of RIE intensities on the MVP amplitude for cobalt micropowder (1), synthesized (2), and commercial (3) cobalt nanowires, ν = 217 MHz, T = 77 K.

The RIE signal emerges when the MVP amplitude exceeds a threshold value defined by the pinning force, corresponding to the pinning force value when MVP acts on two-pulse echo (TPE), **Figure 8*a***. As demonstrated in **Figure 7**, the commercial cobalt nanowire sample exhibits the highest pinning force. In this study, the effect of MVP on the development of RIE was examined alongside its impact on TPE, particularly when MVP acts between two RF pulses during TPE observation. When the MVP amplitude surpasses the DW pinning force, the TPE signal diminishes due to the partial loss of coherence among the nuclear isochromates. This loss occurs because of the inhomogeneous frequency shifts within the DW, attributed to the HFF anisotropy[5]. As shown in **Figure 8*a***, the DW pinning forces determined by these two methods are consistent.

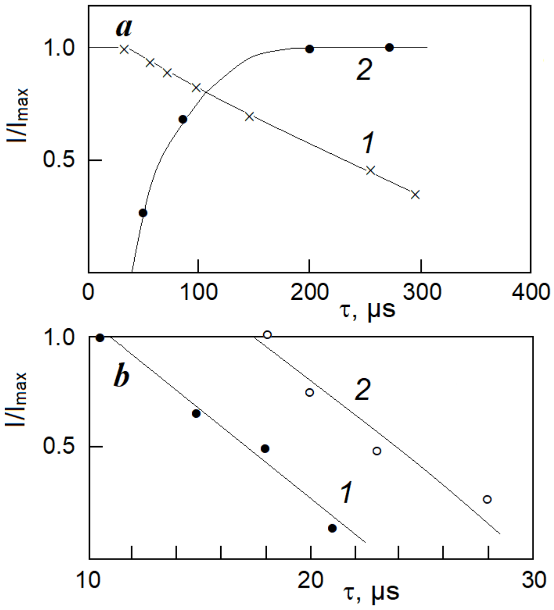

Figure 8. 1 - TPE signal dependence on MVP amplitude H with an RF pulse duration of τ_m = 1 μs; 2 - RIE signal dependence on MVP amplitude H with an RF pulse duration of τ_m = 1 μs (a); 1 - SPE signal amplitude dependence on RF pulse duration, and 2 - RIE signal amplitude dependence on the interval between MVP and the RF pulse trailing edge (b).

Figure 8*b* illustrates the relationship between the RIE amplitude and the time interval between the MVP and the RF pulse trailing edge. It is evident that the SPE signal relaxation time matches the relaxation time of the SPE formed via the distortion mechanism in cobalt: T_2(RIE) = T_2(SPE) = 30 μs. Our experimental findings suggest that the RIE, like the SPE, arises from the distortion mechanism of the effective RF pulse formed by the MVP and the RF pulse trailing edge. The observed experimental dependencies of the RIE and TPE signals can be explained by considering that under MVP influence, the DW is reversibly displaced by a distance Δx ~ $\upsilon\ \tau_m$=S(H-H_0) τ_m, which is proportional to the MVP amplitude and RF pulse duration. Nuclei within the Δx layer, subjected to the combined RF and MVP pulses, experience a stepwise alteration in the effective magnetic field H_{eff} within the RCF, due to corresponding changes in the HFF and the factor η. According to the non-resonant SPE formation model [13], the MVP effect is analogous to the leading edge effect of the effective RF pulse during SPE formation, with RIE amplitude being proportional to the number of nuclei in the Δx layer: I_{RIE} ~ Δ*x*/L, where L is the width of the excited DW section under RF pulse action.

In this context, the stepwise NMR frequency shifts in the RCS must satisfy the condition $\Delta\omega'_j\ \tau_m$ <<1, ensuring the precession period of the nuclei in the RCS $T=2\pi/\Delta\omega'_j=2\pi/(\Delta\omega^2_j+\omega^2_1)^{1/2}$ exceeds τ_m During TPE formation, nuclei precess between RF pulses in the laboratory coordinate frame with a frequency of $\omega_j=\gamma_n H_{nj}$ in the local field. To observe an additional ME signal, the condition $\omega_j\ \tau_m$ <<1 must be met, requiring a nanosecond-long MVP duration τ_m, similar to IE [10], which is not applicable in this scenario. Consequently, MVP's effect on TPE results in TPE attenuation, proportional to the wall displacement Δx: I_{TPE} ~ (L-Δx)/L, caused by the loss of phase coherence among nuclei in this layer. These qualitative insights help explain the experimental dependencies of RIE and TPE signals under MVP influence.

3. Conclusion

By examining the combined effects of MVP and RF pulses on nuclear spin systems within domain walls of micropowders and cobalt nanowires, the study demonstrates the formation of a rotating inverse echo (RIE) signal in the rotating coordinate frame—analogous to the inverse echo signal observed in cobalt nanofilms in the laboratory coordinate frame. A comparative analysis of DW pinning forces obtained via this method was conducted, using commercial cobalt nanowires, synthesized ones under an applied magnetic field, and cobalt micropowders.

In this study, the leading edge of the corresponding effective RF pulse is generated under MVP's influence, causing a stepwise change in the effective magnetic field's direction and amplitude in the rotating coordinate system when the domain wall (DW) is displaced due to MVP pulse action, owing to local hyperfine field anisotropy and gain factor inhomogeneity η, at MVP amplitudes exceeding the pinning force determined by MVP's effect on TPE. The MVP amplitude, which induces RIE, also provides an estimate of DW pinning force for nuclei at different local sites in cobalt micropowders and nanowires. This precise microscopic NMR technique may prove valuable in optimizing the DW pinning force in cobalt nanowires for use in memory and logic devices, sensors, medical hyperthermia, and related applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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