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Add-on extends the capability of a conventional NMR spectrometer

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Abstract

A spectrometer allowing the measurement of signals with spin–spin relaxation times as short as 0.5 μs has been developed. It consists of a transmitter based on a commercial spectrometer and a homemade receiver. The acquired signals are imported in the software of the commercial spectrometer. This is a simple and rather cheap way to transform a commercial rig into a spectrometer allowing measurements on systems with short T_2 such as found in magnetic systems.

Keywords: Spectrometer; Short recovery time; Magnetic materials; Short spin–spin relaxation times

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1. Introduction

The spin–spin relaxation times of nuclei of magnetic ions in magnetic materials are often short. This is particularly true if the nuclei are probed in the vicinity of a magnetic phase transition. The electronic dead time of the receiver of conventional spectrometers is usually too long to measure nuclei with T_2 of the order of 1 μs or shorter. To measure NMR signals with unusually short T_2's, we developed a spectrometer with a short recovery time. The spectrometer is based on a TecMag Apollo HF-1 commercial spectrometer. This instrument is controlled by computer using the NTNMR software delivered with the spectrometer. We had to add several components to improve the performance of the spectrometer. Most importantly, the recovery time had to be reduced to perform measurements using short delays between the excitation pulses. Furthermore, as a consequence of the short T_2's, the spin–echo of nuclei of magnetic ions tends to be short. The minimum dwell time of the receiver of the Apollo HF-1 is 0.3 μs. In the case of Eu resonance in EuO, for example, the echo might last for only about 0.4 μs (A. Comment, J.-Ph. Ansermet, C.P. Slichter, H. Rho, C.S. Snow, S.L. Cooper, Magnetic properties of pure and Gd doped EuO probed by NMR, unpublished). Thus, only a single point in the echo could be recorded with the commercial receiver. Therefore, a faster digitizer is needed. Finally, we transformed the transmitter to be able to reduce the delay between the excitation pulses and the length of the excitation pulses, the latter allowing to further decrease the delay between the excitation pulses.

2. Hardware design

A block diagram of the modified spectrometer is presented on Fig. 1. The RF pulses are provided at the output *F1* of the commercial TecMag spectrometer. The RF output is amplified and split (using a power splitter Mini-Circuits ZFSC 2-1W) into two channels [8], one that will be used to excite the sample, the other that will be used to demodulate the detected signal. The amplifier located in front of the power splitter is necessary to compensate the loss due to the splitters. The frequency range

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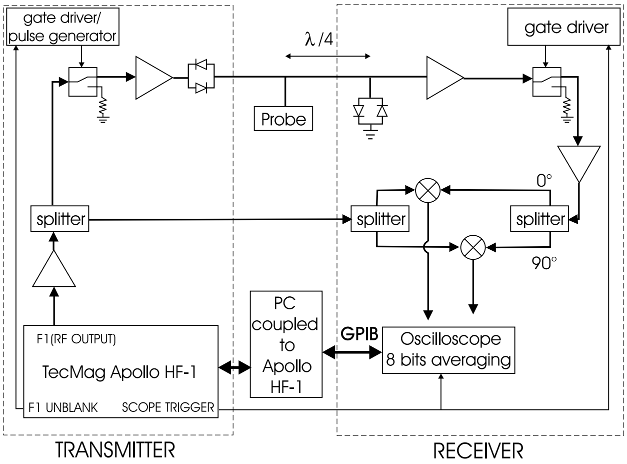

Fig. 1. Block diagram of the spectrometer. A circle containing a cross symbolizes a frequency mixer, and a large triangle symbolizes an amplifier.

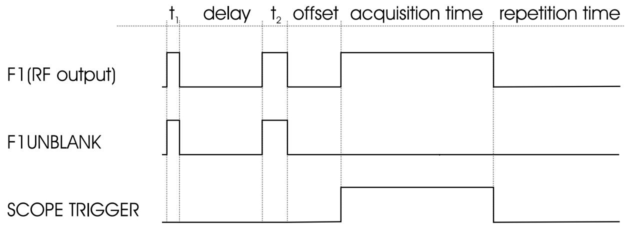

Fig. 2. RF output, *F1 UNBLANK* output and *SCOPE TRIGGER* output for one of the 16 phases of the sequence.

of the spectrometer is 80–500 MHz, the range being limited by the low frequency limit of the preamplifiers and by the high frequency limit of the gates. In principle it is possible to extend the range to 750 MHz by using fast gates adapted for higher frequencies [9].

A sketch of the RF output *F1* for a particular phase of a spin–echo experiment is shown in Fig. 2. It has two parts: the excitation part, composed of two short square pulses of time length t_1 and t_2 separated by a time denoted as *delay*, and the detection part consisting of a long pulse whose length is named *acquisition time*. In the following, we will refer to this last pulse as the demodulation pulse. The two parts are separated by a time called *offset*. Each phase of the sequence is followed by a waiting time denoted *repetition time*.

2.1. Transmitter

The output of the power splitter is connected to a fast RF gate that truncates the demodulation pulse of the RF signal (cf. Fig. 1). The TTL signal sent to the driver piloting the gate is coming out of the *F1 UNBLANK* output of the Apollo HF-1. A sketch of the TTL signal is shown in the second line of the diagram of Fig. 2. Then, the RF signal is amplified by a power amplifier (Kalmus model LP1000 for frequencies lower than 165 MHz, and various Amplifier Research models for higher frequencies) and filtered by crossed diodes before being sent to the probe. We typically worked with power of the order of few hundred watts at the output of the crossed diodes.

2.2. Receiver

The receiver of the spectrometer is protected during the excitation sequence by a $\lambda/4$ cable followed by crossed diodes connected to the ground. In addition, a gate (Watkins–Johnson model S1) has been incorporated between the two preamplifiers (Doty model LN-2H) used to amplify the NMR signal coming from the probe. The TTL signal driving the gate is coming out of the *SCOPE TRIGGER* output of the Apollo. A sketch of the TTL signal is shown in Fig. 2. At the output of the second amplifier, the signal is split into two channels, one of them which is phase shifted by 90°. Both channels are demodulated by two frequency mixers (Mini-Circuits model ZAD-1W) connected to the amplified *F1* output. The mixers multiply the amplified *F1* signal by the signal detected by the coil of the resonance circuit, giving an output signal with a frequency corresponding to the difference between the frequency of the detected signal and *F1*. This allows a comparison between the frequency of the excitation signal *F1* and the actual resonance frequency of the studied nuclei. The resulting signals are sent to a digital oscilloscope (Tektronix model TDS 224) triggered by the TTL signal coming from the *SCOPE TRIGGER* output. This oscilloscope also plays the role of averager. It has a sampling rate of 1 gigasample/s which means a maximum time resolution of 1 ns.

To have a short recovery-time receiver, every component must be broadband. The Doty LN-2H preamplifiers have a recovery time of 0.3 μs. Since the gates have a switching time of 1 ns, they will not alter the recovery time. The maximum bandwidth of the oscilloscope is 100 MHz but we limited it to 20 MHz to remove the high-frequency noise. The bandwidth of the receiver is determined by the minimum bandwidth of all the components, and therefore it is equal to the bandwidth of the preamplifiers. The recovery time of the receiver described above is thus 0.3 μs. Karlicek and Lowe [1] previously developed a broadband NMR spectrometer with a recovery time of about 0.5 μs by using blocking gates.

It is important to mention that the Apollo HF-1 does not have the capability to produce pulses with different phases if the delay between the pulses is shorter than 0.3 μs. Therefore, the minimum delay between the two excitation pulses was limited to 0.3 μs. Also, the time *offset* described in Fig. 2 was always set to this minimum value 0.3 μs because the demodulation pulse also needs to have a different phase than the excitation pulses. Therefore, even if the recovery time of the receiver was

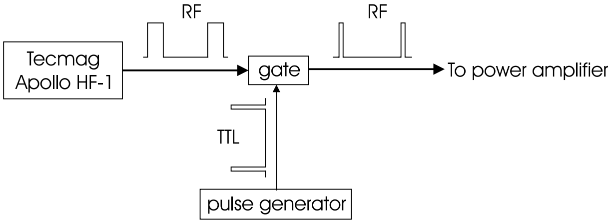

Fig. 3. Block diagram of the modified transmitter.

faster than 0.3 μs, the performance of the Apollo HF-1 would limit the spectrometer to the same value of *delay*.

2.3. Modification of the transmitter: how to create very short RF pulses

The TecMag Apollo HF-1 is not capable of producing pulses shorter than 0.1 μs. In most cases this is short enough, but if T_2 is very short, it is necessary to use spin–echo sequences with very short delays (typically, we worked with delays of the order of 0.5 μs). By reducing the length of the excitation pulses, we reduce the time between the end of the second pulse and the echo. Consequently, for a given recovery time, it is possible to detect echoes using shorter delays.

To reduce the pulse length, we replaced the gate driver connected to the output *F1 UNBLANK* by a pulse generator (Hewlett–Packard Model 8015A) that can produce pulses as short as 10 ns (cf. Fig. 1). The RF pulses coming out of the *F1* output of the Apollo HF-1 can be truncated by adjusting the length of the pulses generated by the HP 8015A (Fig. 3). Note that the pulse generator model 8015A is only able to produce a sequence consisting of two pulses of the same length.

3. Software

The spectrometer is controlled by the NTNMR software. However, it was necessary to develop a program to acquire the data from the oscilloscope. For convenience purposes, we also developed a script to load the data into the NTNMR graphics environment. To perform these two tasks we developed a Visual Basic script. The choice of the Visual Basic language was suggested by TecMag as Visual Basic commands are predefined within the NTNMR environment.

The resolution of the digitizer of the oscilloscope is only 8-bit. To increase the resolution of the signal, the averaging process is made in two steps: first, 64 curves (4 times the 16 echoes produced by a 16 phases pulse sequence) are acquired and averaged in the memory of the oscilloscope. Then, the resulting curve is transferred through a GPIB connection to the computer where it is stored in an array. Once the required number of arrays has been acquired, this number being defined by the user, the Visual Basic script process them to obtain the averaged curve. The resulting curve is then exported to the graphics environment of the NTNMR software that controls the pulse sequences.

4. Performances

As an example of the kind of measurements that are possible with this modified spectrometer, we show in Fig. 4 a spin–echo measurement of ^{153}Eu in EuO doped with Gd. Gd doped EuO is a ferromagnetic material and at temperature well below its Curie temperature of about 120 K, the 4f-shell electron spins are the source of an effective magnetic field of the order of 30 T acting on the nuclear spins and leading to Larmor frequencies around 140 MHz without any applied external field. The zero-field measurement shown in Fig. 4 was performed at 20 K and the frequency of the excitation pulses was 140 MHz. The pulses have a length of about 20 ns and are separated by a delay of about 500 ns. We are therefore at the limits of feasibility for pulsed NMR since the pulses length corresponds to only a few periods of the Larmor frequency. In ferromagnetic materials, the excitation RF field H_1 acting on the nuclear spins is greatly amplified by a factor η via the magnetic susceptibility of the unpaired electron spins. This amplification factor η is at the origin of the fact that we can flip the nuclear spins of this system with such short pulses [2–5]. This and other issues specific to NMR in magnetically ordered materials have been reviewed recently [6].

The pulses shown in Fig. 4 correspond to the pulses recorded at the output of the HP pulse generator, i.e., to the pulses at the gate. The fact that the echo maximum seems to occur later than *delay* after the second pulse on Fig. 4 is simply due to the signal propagation through the whole

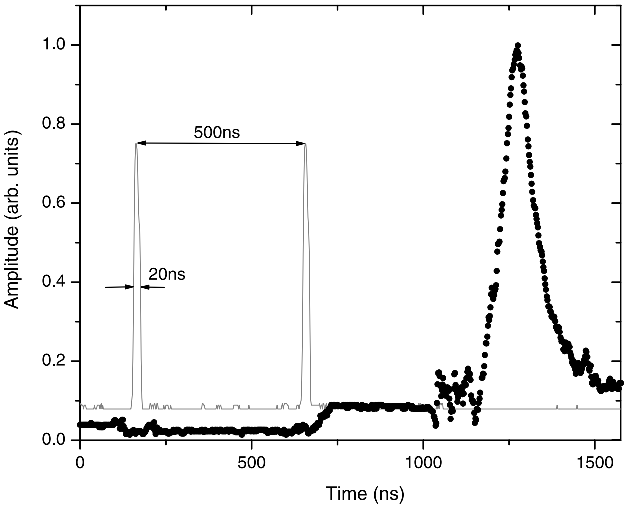

Fig. 4. Echo in 4.3% Gd doped EuO after 20 ns pulses. Sum of two screenshots of the oscilloscope set on average 64.

spectrometer. Also, note that the spurious noise just before the echo is due to non-cancelled ringing that can be cancelled by increasing the averaging.

4.1. The need for low Q resonance circuit

The recovery time of the receiver is the technical limitation that needed to be improved, but to be able to use short delays between the excitation pulses, the ring-down of the resonance circuit has to be at least as short as the recovery time of the receiver. That means that the quality factor Q of the resonance circuit has to be small. Let us approximate the maximum Q value corresponding to a recovery time of 0.3 μs. Typically, the recovery time needs to be equal to about 20 times the time constant of the resonance circuit to measure a NMR signal after sending a excitation RF pulse in the resonance circuit [7]. The straightforward relationship between the time constant τ and the quality factor of a resonance circuit resonating at ω_0, $Q = \omega_0 \tau$, gives us the value of Q (at 100 MHz)

$$Q = \omega_0 \frac{T_{\text{recovery}}}{20} \cong 10. \tag{1}$$

With this value of Q, the bandwidth of the resonance circuit is about 10 MHz, which allows to cover a broad frequency range in excitation. A simple way to obtain a resonance circuit matched at 50 Ω with a low value of Q is to use a serial circuit composed by a resistor of about 50 Ω, a low Q coil and a capacitor. Typically, we used a coil of inductance $L = 1$ μH and a capacitor of capacitance $C = 10$ pF. Note that the excitation range of a 20 ns long pulse is larger than the bandwidth of a resonance circuit with $Q = 10$. Lowering the value of Q would increase the bandwidth of the circuit, but it would also reduce the power of the pulse, thus reducing the flipping of the spins. We therefore have to find a compromise between the pulse length and the value of Q.

5. Conclusions

We developed a spectrometer allowing to measure spin–echo of nuclei of magnetic ions with delays as short as 0.5 μs. Such performances are expected to open a wide range of new NMR studies of magnetic materials in which relaxation times are very short. We presented the example of Eu resonance in Gd doped EuO.

Acknowledgments

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[9] It is possible to use the spectrometer in the 20–80 MHz frequency range by using Doty LN-2M preamplifiers, although this will increase the recovery time of the rig since the recovery time of the LN-2M is 1 μs instead of 0.3 μs for the LN-2H.