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Nuclear magnetic resonance spectrometer based on a DC superconducting quantum interference device (SQUID)

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Abstract

We describe a system in which a DC superconducting quantum interference device (SQUID) is used as a detector in a zero-field pulse nuclear magnetic resonance (NMR) spectrometer, dedicated to the study of magnetic metals. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NMR; Spin echo; SQUID

In the present work, we describe a spectrometer involving a DC superconducting quantum interference device (SQUID). The system allows direct observation of spin echo nuclear magnetic resonance (NMR) [1] signals for frequencies up to 50 MHz. The SQUID is an ideal detector for low-field NMR, since its response does not depend on signal frequency as in conventional NMR spectrometers [2]. It is known, however, that at high frequency there are great technical difficulties [3] and signal-to-noise ratio for pulsed NMR is comparable with that obtained from pre-amplifiers based on semiconductors at low temperatures [2,4]. We use a low temperature demodulation circuit near the pre-amplifier (DC SQUID). This approach improves noise performance associated to the Johnson noise and as we reduce the distance between the pick-up coil and the demodulation stage and pre-amplifiers stage, there is reduced external interference, better impedance match, etc. [4]. The spectrometer shown in Fig. 1 is designed to detect zero-field NMR (ZFNMR) spectra, which arise from the interaction of a nuclear spin with the local hyperfine field [1], and is dedicated to the study of magnetic metals [5]. In ZFNMR all crystallites or equivalent sites have the same resonance frequencies. To the best of our knowledge this is the first example of such SQUID implementation in this frequency range. The setup is based on a commercial DC SQUID S165C (CONDUCTUS) coupled to a diode demodulation system shown in Fig. 1, both maintained at 4.2 K, and to a low pass filter through a transformer. One important aspect is the development of the demodulation system for small signals [6] at low temperature and the way to reduce the influence of radio frequency excitation on the SQUID input to an appropriate level. However, in magnetically ordered materials, the so-called enhancement factor [7] amplifies the RF field by a factor of 10^3–10^5, requiring pulses applied to the sample much smaller than those used for nonmagnetic samples. The pickup coil (L_{p1}) is a nonresonant gradiometer as shown in Fig. 1, consisting of a pair of coils, each one with ten turns of Cu wire, wound in opposition, 10 mm apart, on a mica tube. This coil is connected to a demodulator diode circuit. The diode is polarized with a polarization current of 2.0 mA, with a dynamic resistance of 1.75 Ω, the optimum operating point. Note that the system is sensitive to the value of the polarization. We estimate the total inductance of this coil to be $L_{\mathrm{p1}} = 0.70\,\mu\mathrm{H}$. The demodulation circuit is a standard diode demodulator [8] operating at He liquid temperature and consisting of a resistor ($R = 100\,\Omega$), one capacitor ($C_1 = 3.2\,\mu\mathrm{F}$), two capacitors ($C = 0.42\,\mu\mathrm{F}$), and an inductor of $L = 100\,\mu\mathrm{H}$. The two capacitors (C) and inductor (L) form a low-pass filter [8]. The capacitor (C_1) is intended to remove the DC level current. The transmitter coil is typically the same used for detecting ^{57}Fe in conventional ZFNMR in metallic iron [1]. The transmitter is composed of a Fluke 6061A synthesizer, a Tecmag Mini Pulse Kit pulse programmer, a ENI 100-W

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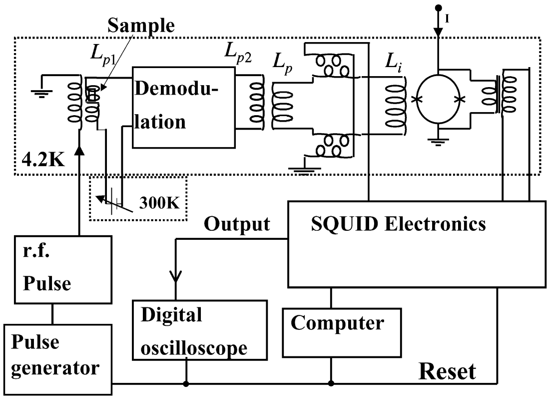

Fig. 1. Block diagram of the NMR spectrometer.

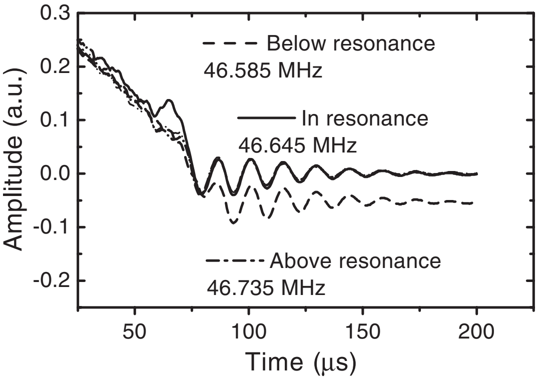

Fig. 2. Echo signal obtained from the oscilloscope.

400 MHz broadband RF power amplifier, and double balanced mixers (DBMs) used for pulse modulation. The output power is controlled through a Wavetek P556 programmable attenuator. The relative positions of the pickup and transmitter coils are adjusted empirically. Between the demodulating circuit and the DC SQUID there is a superconducting flux (system input) transformer (Fig. 1). The transformer that couples the demodulator and the input circuit consists of two coils, one made of Cu with four turns (L_{p2}), with an estimated inductance of $L_{p2} = 36$ nH and a coil of five turns of Pb (L_p) with estimated inductance of $L_p = 65$ nH. The SQUID operates in a flux-locked loop (FLL) with a flux modulation frequency of 256 kHz, which means that the output is linear with a wide dynamic range, which is in turn limited by the slew rate of the whole circuitry. Since in pulsed NMR applications large magnetic pulses are applied to the sample, this creates considerable technical problems [2]. TTL pulses are provided by a computer-controlled pulse generator. They are used for timing the radio frequency transmitter pulse, resetting the FLL during the application of the pulses (the FLL is disabled and output is forced to be close to 0 V). Signals are captured and averaged on an oscilloscope (Tektronix TDS 520A) which in turn is controlled by a PC with LabView software. We present an example of an ^{57}Fe NMR spectrum in metallic iron, taken at 4.2 K, averaged 256 times. Fig. 2 shows the echo signal from the oscilloscope. The formation of the spin echo occurs after a sequence of two pulses is applied to the sample. The first is a $\pi/2$ pulse (3 μs), and the second a π pulse (6 μs), separated by a time interval of 70 μs, with a recycle rate of 50 Hz. Fig. 3 shows the result, after subtracting a baseline (signal outside resonance) and also the free induction decay after the second pulse; it is evident the formation of a spin echo after 70 μs. The amplitude of the echo signal is shown at several frequencies. The integrated signal is shown in Fig. 4, as a function of frequency. Line position (46.64 MHz) and linewidth (0.06 MHz) are in good agreement with those measured in a conventional ZFNMR spectrometer [5,7], as shown in Fig. 4. Data acquisition and data treatment, such as baseline subtraction and signal integration are not straightforward, but can easily be implemented by software. Our major difficulty in detecting ZFNMR has been the noise in the diode and the resistor, and the influence of the RF pulses on the SQUID. We had to reduce the inductances of the coils that couple the demodulating system with the flux superconductor transformer, which led to a loss in

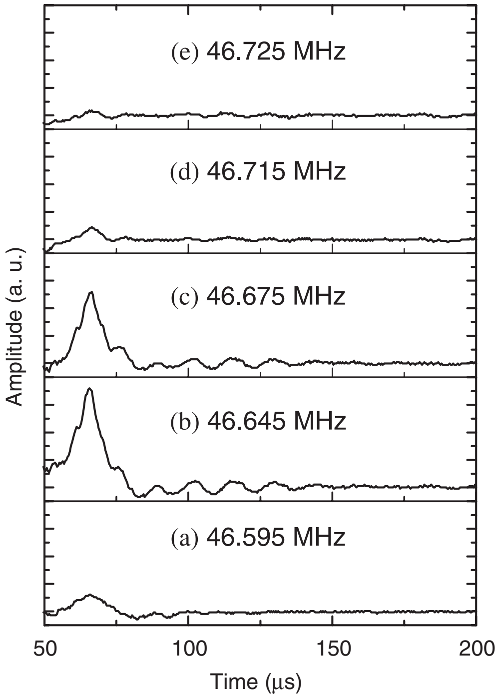

Fig. 3. Echo signal after treatment of noise and subtraction of the baseline.

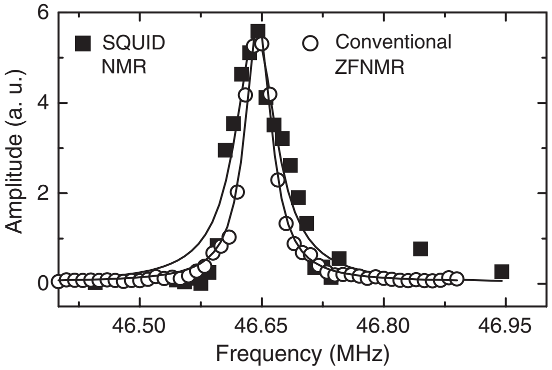

Fig. 4. Spectrum of ^{57}Fe at 4.2 K using a DC SQUID and spectrum using conventional ZFNMR.

sensitivity. This restriction can be overcome by implementing a Q-Spoiler, improving the demodulation stage, and using a SQUID having a wider range of frequency.

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