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# NMR shift and relaxation measurements in pulsed high-field magnets up to 58 T

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ABSTRACT

Nuclear magnetic resonance (NMR) experiments at fields up to 58 T in pulsed magnets at the Dresden High Magnetic Field Laboratory are reported. The challenge to resolve NMR shifts in these time-dependent fields is addressed for the first time, and it is shown that this can indeed be accomplished with high precision with an internal reference. As a result, signal averaging is possible during a single magnetic field pulse, but also for multiple pulses. Thus, even very weak signals can in principle be recorded and their shifts can be determined. In a second set of experiments, the measurement of nuclear relaxation is investigated. Using adiabatic inversion with the inherent time dependence of the magnetic field and small-angle inspection, it is shown that relaxation measurements are possible, as well. The shift experiments were performed with $^{27}$Al NMR on a mixture of aluminum metal and a Linde type A zeolite. For the relaxation studies, $^{27}$Al NMR and $^{69}$Ga NMR on the metals aluminum and gallium were preformed, respectively.



## 1. Introduction

High magnetic fields are important for modern materials science since they can induce new electronic phases that may not be reached otherwise and the field dependence of observables can help in understanding and developing theories for describing new electronic phenomena. In order to generate the highest fields, pulsed magnets with resistive wire must be used, which are available only in a few dedicated facilities worldwide [1–4]. Recently, fields up to 100 T have been reported with non-destructive coils. Not only are these fields inherently time dependent, but also rather inhomogeneous, and available only for fractions of a second. Furthermore, since the magnet heats up during the field pulse, it has to cool down for some time before one can apply another field pulse that is similar but not exactly the same as the previous one. Despite these disadvantages, pulsed magnets are of great importance in materials science [5,6].

An example of the field's time dependence in a real experiment is shown in Fig. 1. With the discharge of a capacitor bank at time $t = 0$ into the magnet coil, the current and with it the magnetic field ($B$) rises and crests about 34 ms after the discharge began [4]. The field maximum, cf. upper right inset in Fig. 1, is not well reproduced in successive experiments.

Nuclear magnetic resonance (NMR) experiments seem particularly difficult in such a time dependent field since the resonance frequency is not well defined, cf. Fig. 1. Nevertheless, efforts to perform NMR experiments in pulsed magnetic fields are being pursued in facilities in Germany [7], Japan [8], and France [9], recently. For a number of applications, NMR appears feasible, and the very high accessible fields may give unprecedented insight into new phenomena. The mere gain in signal-to-noise ratio (SNR) from the higher field is readily wiped out by the loss of efficient signal averaging available with highly stable static magnets, and the resolution is expected to be poor in these small unshimmed magnet coils. Therefore, the usual NMR reasoning for high magnetic fields does not apply to pulsed magnets. In fact, even the highest static fields, created with hybrids of superconducting and resistive magnets suffer from poor stability and low resolution, as well [10,11].

In a more recent set of NMR experiments in pulsed magnets, Meier et al. [12] showed that the field variation near its maximum is rather smooth, so that the field's time dependence can be measured with NMR and removed numerically. After such a procedure, the NMR signals appear as if recorded at constant field with a stability better than a few ppm. As a consequence, even coherent signal averaging during a single field pulse is possible. However, with such experiments, one cannot determine the field precisely on an

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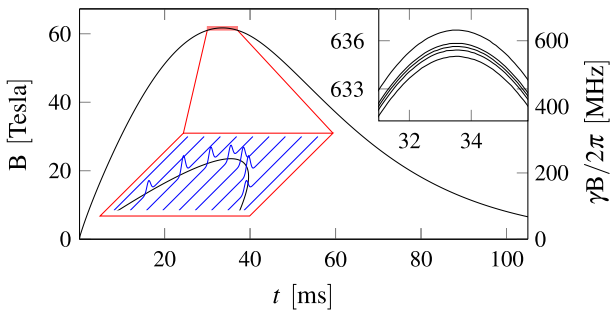


**Fig. 1.** Magnetic field as a function of time in a typical pulsed magnet (estimated from shunt voltage). Near the field maximum, a small time window of several ms can be used for NMR experiments. Within this window, the center frequency of the NMR signal is different at different times (red box). Upper right: Actual field maxima for five subsequent field pulses obtained during one day (shunt voltage calibrated by NMR). Frequencies are for metallic aluminum (for main plot axis to the right and for inset axis to the left). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

absolute scale, i.e., with respect to a reference so that shift measurements become possible. With the importance of shift measurements in NMR, the question arises whether this obstacle can be removed.

Shift measurement in high-field static magnets that use resistive coils also suffer from temporal instabilities, as well, and methods were proposed to measure the shifts properly by following the phase of a reference signal [13,14]. However, since the overall field variations are small in those fields, the time-dependence of the difference frequency (shift multiplied by field) between both signals was neglected. Such procedures cannot be adopted in pulsed magnets since the changes in field during the NMR experiments are much larger. Here, we introduce a correction that allows for field-dependent changes in the frequencies between both signals.

In their experiments, Meier et al. [12] used the time evolution of the phase ($\phi_j(t)$) of the free induction decay (FID) excited multiple times during a single field pulse to determine $B_j(t)$ for each FID ($j$) ($\gamma B_j(t) = d\phi_j(t)/dt$). The obtained set of field values was fitted to a simple polynomial. Clearly, such a procedure fails if one has multiple NMR lines as the phase derivative oscillates, i.e., with the beat frequency in case of two signals. In addition, while demodulation is precise for one signal the shifts between various signals cannot be retrieved with high precision by such a procedure. However, the question of whether two signals can be measured at the same time in pulsed magnets is a crucial one since any reference signal must be recorded during the same period of time as the unknown signal for high-precision shift measurements.

Here, we will show that if proper filtering of a particular signal can be implemented, one can use a sufficiently strong signal for determining the relative time dependence of the field. This allows one to analyze another, even much weaker signal. The presented results demonstrate that high-precision shift measurements, only limited by the linewidth, are indeed possible in pulsed magnets.

In another set of experiments, we investigate the feasibility of measuring the nuclear spin relaxation ($1/T_1$) in pulsed fields. Using adiabatic inversion created by the time-dependent magnetic field in the presence of a weak radio frequency (RF) field, followed by short inspection pulses, $T_1$ can be measured in time-dependent fields, as well, for sufficiently strong signals.

## 2. Experimental

The experiments were performed at the Hochfeld-Magnetlabor Dresden (HLD) of the Helmholtz-Zentrum Dresden-Rossendorf using the magnets *KS3* and *LP* [4,15]. By setting the proper charging voltage, a chosen set of modules of the capacitor bank was energized [16]. Shortly thereafter, a discharge into the magnet coil was triggered to create the field pulse. In order to obtain similar maximum field values in successive experiments, cf. Fig. 1, the actually measured, previous maximum field value as well as the magnet coil resistance measured immediately before the experiment were used for empirical estimates.

A small RF coil fit to a sample of several microliter volume was used for the experiments. This limits the spatial inhomogeneity of the main field and allows for short RF excitation pulses. Details of the home-built probe that fits the inner diameter (16 mm) of the cryostat (for variable temperature investigations), as well as the spectrometer can be found elsewhere [16].

For the shift measurements, some milliseconds after triggering the discharge of the capacitor bank, a train of about 100 RF pulses is sent to the probe. Since the actual Larmor frequency, i.e., the field, is unknown prior to successful NMR experiments, this train of pulses ensures that the Larmor frequency will be close to the RF carrier for some subset of the 100 pulses. Due to the inherent off-resonance excitation to varying degree, the signal intensities have to be calculated numerically. Typically, on-resonance flip-angles of only about 25° were used.

The pulses are derived from the same carrier frequency and have the same amplitude. The delay between the pulses is fixed (in the range between 0.1 and 1 ms) and used for data acquisition. The resonance frequency of a broadband RF tank circuit, and with it the RF carrier frequency were set to the resonance frequency at the predicted field maximum. After each RF pulse, the receiver is unblanked for the duration of the delay between pulses. After the total experiment, we have a complex signal trace that consists of about 100 digitized segments (I/Q-demodulated). Depending on the particular experiment, this trace can contain many FIDs (recorded with a sampling rate of 10 MHz, totaling a few megabytes of data).

For the relaxation studies, the excitation and signal recording was similar, except for an additional long, low-power RF pulse during which the pulsed field sweeps through resonance and adiabatically inverts the population of the nuclear Zeeman levels.

For data analysis, we select the set of digitized segments that contain FIDs. Each FID is subjected to the same left shifts and baseline correction as with regular NMR experiments before further processing. The more detailed data analysis is discussed in the main body of this paper.

We investigated a mixture of metallic aluminum powder (Alfa Aesar, 99.97% purity, $T_1 \approx 7.4$ ms) and standard Linde type A zeolite for shift measurements. For the hydrated zeolite we determined a $T_1$ of about 1.4 ms. The volume density of Al nuclei in the zeolite was about an order of magnitude smaller (≈14%) compared with the metal. The relaxation measurements were performed on metallic aluminum powder set in epoxy glue, and liquid gallium (ESPI Metals, 5 N purity) that was heated and emulsified in epoxy glue, as well.

## 3. Results and discussion

To illustrate the consequences of a time-dependent magnetic field for the NMR signals, we display two computer-simulated FIDs in Fig. 2, in order to exemplify the consequences without noise. Given the apparent Fourier transform (FT) distortions and resonance shifts, it is obvious that reliable shift and intensity (relaxation) measurements must be corrected for the field's time dependence, which we will discuss now.