

High temperature mechanical field-cycling setup

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Received 20 December 2007; revised 11 February 2008

Available online 23 February 2008

Abstract

A new design of a mechanical field-cycling setup, operating in the wide temperature range up to 1200 K has been implemented. The sample is moved by a stepping motor in the stray field of a superconducting magnet inside a furnace of homogeneous temperature profile. For a field range from 0.75 to 7 T (transfer length 24 cm), the transfer time is less than 100 ms. The temperature profile is homogenized to better than 1% of the absolute set temperature. The main objective of this design is to extend the T_1 relaxation dispersion range covered by electronic field-cycling to higher frequencies.

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Keywords: FC NMR; Spin–lattice relaxation dispersion; High temperature

1. Introduction

For the investigation of field dependent nuclear spin relaxation effects field-cycling (FC) NMR is generally superior to conventional NMR. The reason is that the signal can always be detected at the maximum instrumentally available magnetic field. This is beneficial for the signal-to-noise ratio and it allows keeping the same receiver frequency. Important applications of FC NMR are studies of molecular dynamics via spin–lattice relaxation dispersion [1–3], double resonance NMR and Nuclear Quadrupole Resonance (NQR) experiments [4,5] as well as zero field spectroscopy [6–8].

There are two alternative implementations of a field-cycle: either the magnetic field itself is varied keeping the sample location fixed or the sample can be transferred in between positions of different field values. The first one is implemented in electronic [9–14] and the second is usually used in mechanical field-cycling [15–17]. Electronic field-cycling normally allows for fast field slew rates, but needs specially constructed magnets. Mechanical field-cycling can use standard superconducting magnets in order to

get high and homogeneous detection fields for the price of slower transfer rates. Various designs have been published [15–17]. Unfortunately none of these designs is appropriate for high temperatures.

The objective of this publication is to present our solution of mechanical field-cycling, able to operate at temperatures up to 1200 K and to shuttle the sample within less than 100 ms among any pair of magnetic fields in the range from 0.75 to 7 T. The presented setup has the goal to complement our home-built electronic field-cycling spectrometer which can provide magnetic fields up to 1 T [13] and temperatures of more than 1400 K [19]. The extended field range, gained using mechanical FC allows us to increase the sensitivity to faster dynamic processes.

2. Experimental setup

The spectrometer described in the present article performs the field-cycle by moving the sample in the stray field of a 300-MHz superconducting narrow (44 mm diameter) bore magnet (Oxford instruments). An overview of the mechanical field-cycling setup is shown in Fig. 1. The magnetic field profile along the z -axis is presented in Fig. 2. The field differences within the sample (length between 6 and 8 mm, diameter 3 mm) due to the field gradient in the stray field are

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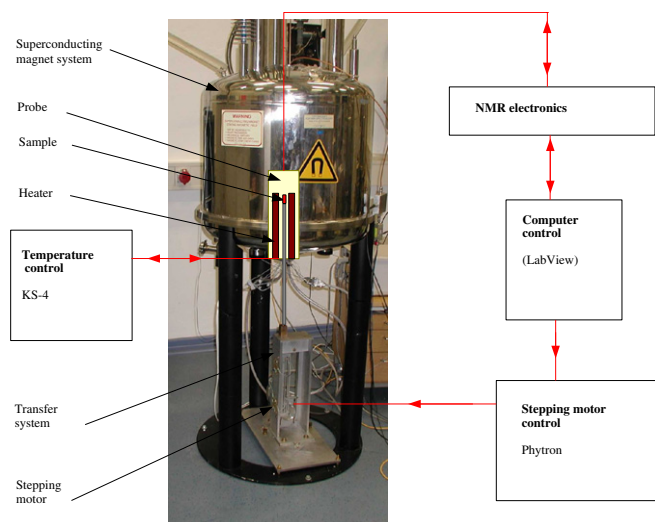


Fig. 1. Overview of the mechanical field-cycling setup.

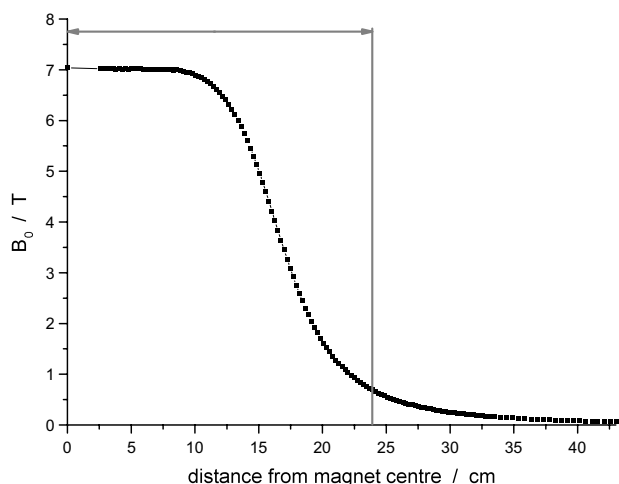


Fig. 2. Magnetic field profile of the 300 MHz narrow bore superconducting magnet as measured by a Hall probe.

always less than $\pm 10\%$ of the centre field for all used samples. Such field differences ΔB lead to an inhomogeneous distribution of the relaxation rates T_1^{-1} . The width of this distribution can be approximated by $\frac{\delta(T_1^{-1})}{\delta B} \Delta B$, i.e. it depends on the—a priori unknown—relaxation dispersion. Strictly speaking, this leads to a non-exponential magnetization recovery curve; and it is a matter of data precision whether we are able to see this non-exponentiality. For the experiments presented in this paper, we can, according to our limited statistical accuracy, safely parametrize the data by a mean relaxation rate and its corresponding error bar.

Different from other published designs [15], only the sample is moved—the tank circuit stays at rest. This design avoids eddy currents, because all moving parts are either non-conducting, are placed outside the high field gradients or are generally unresponsive with respect to the development of eddy currents due to a small inductivity-to-resistance ratio.

We are using a Phytron ZSH 87 stepping motor, allowing for a fast transfer and an exact positioning. Since the reproducibility of the position is 0.1 mm and the detection field is homogeneous to 10^{-5} over the sample a reproducible NMR spectrum is provided. The transfer time for the maximum displacement of 24 cm is 100 ms. In comparison with pneumatic designs [16,17] the use of a stepping motor reduces the mechanical oscillations after deceleration since the deceleration rates are controlled and kept comparatively moderate ($< 150 \text{ m/s}^2$). The stepping motor control operates autonomously according to computer control, but is synchronized with the pulse program to provide an accurate timing. As a reference and in order to avoid positions which are out of range, light barriers are placed at the edges of the positioning range.

The sample is air-tightly enclosed in a sample tube. This sample tube is the mechanically most stressed part of the probe. It has to be non-magnetic with a small thermal expansion coefficient and has to withstand temperatures up to 1200 K. There must be no moveable part within the sample tube, because otherwise it could get destroyed by the permanent vibrations. Also the sample itself has to be carefully fixed. Our solution for the sample tube is a quartz–stainless-steel composite construction which combines the mechanical stability of stainless-steel with the small thermal expansion coefficient of quartz (Fig. 3). The sample tube has a length of 44 cm and a maximal thermal expansion of 0.2 mm within the operating temperature range. The total weight of all transferred parts (sample, tubes, adapters ...) is approximately 225 g. The sample is encapsulated in an evacuated quartz tube, the remaining space inside this tube is filled with a quartz stick that secures the sample's position. This sample capsule is welded on top of another quartz stick (length 40 cm, diameter 4 mm), which is well protected inside a stainless-steel tube (outer diameter 6 mm), which is well protected inside a stainless-steel tube. It stays out of the heated area, thus ordinary adhesives can be used. Inside the heated area the two elements are not connected to prevent damage caused by the different thermal expansions of both when heated up to 1200 K. The sample tube is attached to the transfer device via a stainless-steel adapter, secured by a screw on either side.

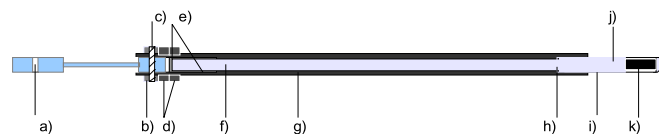


Fig. 3. Sample tube. (a) Adapter to transfer system, (b) stopper (brass ring), (c) screw, fixing adapter to (g), (d) stopper (rubber), (e) adhesive area for (g) and (f), (f) quartz stick, (g) stainless-steel tube, (h) melting point connecting (f) and (i), (i) evacuated quartz tube containing the sample, air-tightly closed by short quartz stick (j), (k) sample.

Two rubber rings damp any unwanted vibrations if the sample tube touches by accident the lower surface of the probe.

The NMR signal is always measured in the homogeneous field, at the geometrical centre of the magnet by a saddle-shaped RF coil. This coil is made of massive flat platinum wire to withstand high temperatures (diameter: 11 mm, length: 10 mm, one winding). The RF coil is self-supporting but electrically isolated by a thin alumina tube.

In order to control the temperature over the entire positioning length, the sample tube moves inside a cylindrical furnace with a homogeneous temperature profile. The heater consists of a central solenoid-like coil and two additional coils at the edges to compensate the temperature gradient at the ends (see Fig. 4). The coils are wound bifilarly using $\text{Ni}_{0.8}\text{Cr}_{0.2}$ alloy wire on alumina tubes. The heating currents are controlled separately for each coil by a “KS-4” temperature controller (Prozess- und Maschinen-Automation GmbH (PMA)). The feedback for the temperature controller is provided by three thermo-couples at the edges and in the centre of the furnace (see Fig. 4). The temperature profile in the leading tube has been measured by another thermo-couple before the start of operation. This design provides temperature homogeneity of better than $\pm 1\%$ of the absolute set temperature.

The total heating power of up to 750 W limits the maximum temperature to 1200 K. The outer mantle is water cooled. A protection circuit evaluates the temperature of the mantle. During the recording of the NMR signal, the heating currents are switched off to avoid magnetic influence on the detection field. The assembled probe is presented in Fig. 4.

The field-cycle used for the FC NMR measurements is sketched in Fig. 5. First, the magnetization is destroyed by a saturation pulse sequence in order to establish reproducible initial conditions. Then the spin system is prepolarized during the time t_{pol} . For high evolution fields this period is skipped. Then the sample is transferred in the evolution field B_{ev} . There, the magnetization relaxes towards the equilibrium magnetization according to the evolution field B_{ev} during the time t_{ev} . Finally, the sample is transferred back to the high field where the magnetization is read out by a 90° pulse. By varying the evolution time t_{ev} the magnetization decay curve can be traced. Due to the

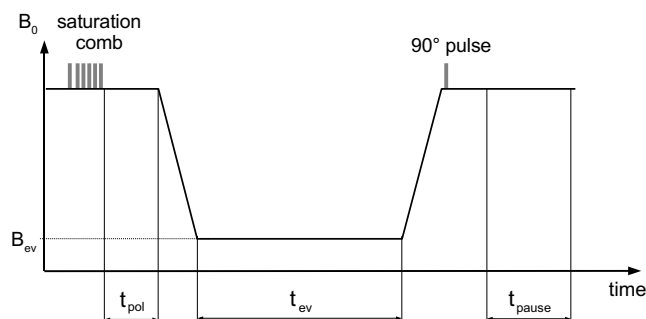


Fig. 5. Field-cycle, see text for detailed explanation.

movement of the sample tube the temperature profile is destabilized. Therefore, the waiting time t_{pause} is introduced before the next experiment in order to allow the system to restore its equilibrium temperature profile.

3. Test results

Due to the intention to use the new mechanical field-cycling spectrometer mainly for the investigation of the molecular dynamics in superionic conductors, the spectrometer has been tested by measuring the spin–lattice relaxation dispersion of LaF_3 doped with 3% SrF_2 and CaF_2 . The resonant nucleus is ^{19}F . In both samples the spin–lattice relaxation is expected to be due to translational motion in the fluorine sublattices. For a detailed account of the motional model and the involved physics we refer to previous electronic field-cycling results in pure and doped LaF_3 [18,20]. Our present spin–lattice relaxation rates obtained by mechanical FC are compared with those previous electronic FC data (in the case of doped LaF_3) and with own unpublished electronic FC data (in the case of CaF_2). Fig. 6 shows that the relaxation rates measured with both, mechanical and electronic FC, are well consistent to each other. Analysis of LaF_3 T_1^{-1} dispersion presented in [18,20] thus can be extended to higher frequencies, enhancing the sensitivity of relaxometry to faster ion dynamics.

The larger statistical error in the mechanical FC data for 600 K is due to the fact that the spin–lattice relaxation times become comparable to or even shorter than the transfer times. This results in a poorer data quality since a significant fraction of the magnetization difference already

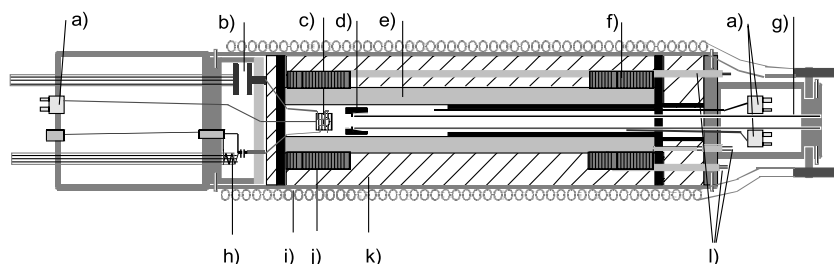


Fig. 4. Probe used for mechanical field-cycling NMR. (a) Thermo-couples, (b) tuning capacitor, (c) saddle-shaped RF coil with insulating tube, (d) centring piece, (e) main heating coil, (f) lower additional heating coil, (g) leading tube (stainless-steel), (h) matching coil, (i) cooled mantle, (j) upper additional heating coil, (k) thermal isolation, (l) electrical contacts for heating coils.

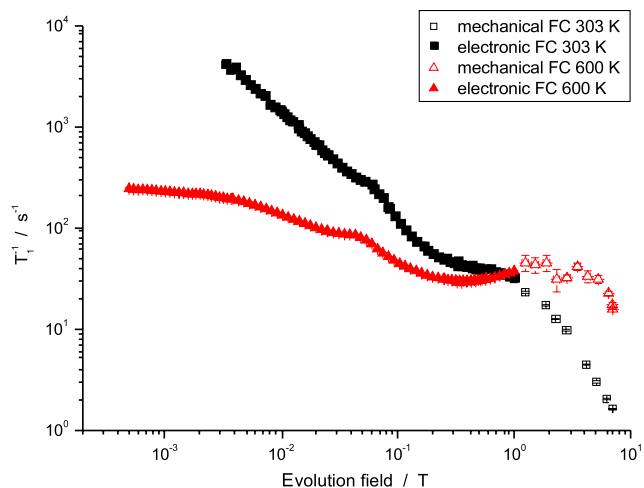


Fig. 6. Spin–lattice relaxation dispersion of $\text{La}_{0.97}\text{Sr}_{0.03}\text{F}_{2.97}$ for 303 and 600 K. The ^{19}F -resonance frequency of the detection field was 280.5 MHz. The electronic FC data have been taken from [20].

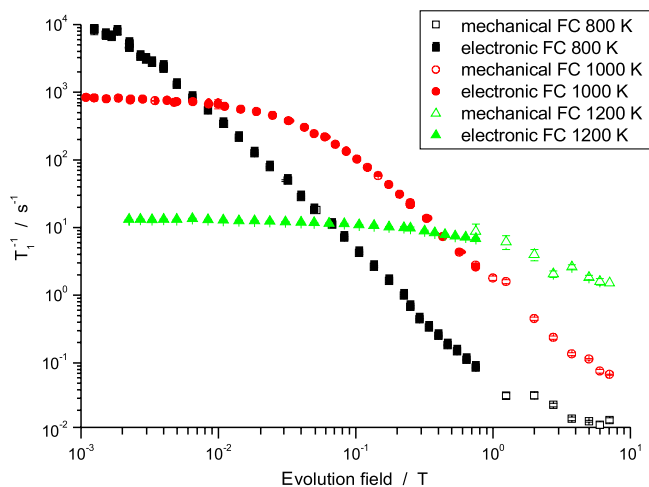


Fig. 7. Spin–lattice relaxation dispersion of CaF_2 at 800, 1000 and 1200 K measured by the mechanical FC spectrometer and by an electronic FC spectrometer. Ten accumulations have been used in the mechanical FC experiment.

decays during the transfer time. Instead, the measurements at higher temperatures have been performed on CaF_2 . Here, the spin–lattice relaxation times at higher temperatures are longer, and their dispersion is expected to be due to the anionic mobility [21]. Again, we can compare the mechanical with electronic FC data (see Fig. 7). The sample has been annealed at temperatures above 1000 K during several hours before the measurement. It can be seen from Fig. 7, that for all temperatures under consideration both, the mechanical and the electronic FC data are in good consistency with each other.

4. Conclusions

A new setup for mechanical FC NMR has been presented. This setup combines comparatively short transfer

times of less than 100 ms with quite high temperatures up to 1200 K. Together with the field range from 0.75 to 7 T these features render it a valuable tool for investigating the molecular dynamics of superionic conductors in the high field range. It can be used complementarily to an electronic FC spectrometer.

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