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Cryogen-free superconducting magnet system for multifrequency electron paramagnetic resonance up to 12.1 T

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Multifrequency and high field/high frequency (HF) electron paramagnetic resonance (EPR) is a powerful spectroscopy for studying paramagnetic spin systems ranging from organic-free radicals to catalytic paramagnetic metal ion centers in metalloproteins. Typically, HF EPR experiments are carried out at resonant frequencies $\nu = 95-300$ GHz and this requires magnetic fields of 3.4–10.7 T for electronic spins with $g \approx 2.0$. Such fields could be easily achieved with superconducting magnets, but, unlike NMR, these magnets cannot operate in a persistent mode in order to satisfy a wide range of resonant fields required by the experiment. Operating and maintaining conventional passively cooled superconducting magnets in EPR laboratories require frequent transfer of cryogens by trained personnel. Here we describe and characterize a versatile cryogen-free magnet system for HF EPR at magnetic fields up to 12.1 T that is suitable for ramping the magnetic field over the entire range, precision scans around the target field, and/or holding the field at the target value. We also demonstrate that in a nonpersistent mode of operation the magnetic field can be stabilized to better than 0.3 ppm/h over 15 h period by employing a transducer-controlled power supply. Such stability is sufficient for many HF EPR experiments. An important feature of the system is that it is virtually maintenance-free because it is based on a cryogen-free technology and therefore does not require any liquid cryogens (liquid helium or nitrogen) for operation. We believe that actively cooled superconducting magnets are ideally suited for a wide range of HF EPR experiments including studies of spin-labeled nucleic acids and proteins, single-molecule magnets, and metalloproteins.
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I. INTRODUCTION

It is now well established that multifrequency and high field/high frequency (HF) electron paramagnetic resonance (EPR) is a powerful spectroscopy to study paramagnetic spin systems ranging from organic-free radicals to catalytic paramagnetic metal ion centers in metalloproteins.[1] One of the principal advantages of the multifrequency EPR approach is in assisting interpretation of EPR spectra that are often broadened by an interplay of magnetic field dependent and independent terms in the spin Hamiltonian operator $\hat{H}$:

$$\hat{H} = (\beta B \cdot g \cdot \hat{S} - \beta_n B \cdot g_n \cdot \hat{I}) + h\hat{S} \cdot A \cdot \hat{I} + h\hat{I} \cdot P \cdot \hat{I} + h\hat{S} \cdot D \cdot \hat{S} + \cdots . \tag{1}$$

In this equation the two terms in parentheses represent electronic and nuclear Zeeman terms, respectively. Both of these terms are proportional to magnetic field B. $\hat{S}$ is electronic and $\hat{I}$ is nuclear spin operator, β and β_n are the Bohr and nuclear magneton, and g and g_n are electronic and nuclear g matrices, respectively. The rest of the terms in Eq. (1) are magnetic field independent because they are given by scalar products of spin operators $\hat{S}$ and $\hat{I}$ and field-independent hyperfine A, quadrupole P, and zero-field splitting D tensors; h is the Planck constant. Further details on basic EPR theory could be found in Ref. 2.

Because the relative magnitude of contributing magnetic interactions determined by field-independent tensors A, P, and D varies greatly from system to system, the optimum conditions for a particular EPR experiment could only be achieved by varying both the magnetic field and the resonant frequency. Moreover, some integer spin systems are known to remain "EPR silent" if the magnitude of the electron-electron dipolar interaction of the type $\hat{S} \cdot D \cdot \hat{S}$ [also called zero-field splitting (ZFS)] exceeds the energy of the microwave quantum.[3] Depending on the relative magnitude of the ZFS splitting term in the spin Hamiltonian, these electronic spin systems could satisfy the resonance conditions over a wide range of magnetic fields for each particular microwave frequency. Furthermore, for some spin systems field/frequency dependence of EPR signals and associated relaxation times is a source of valuable information. One example is exchange coupled electronic spins. For such spins effective dimensionality of the exchange interaction and the spin diffusion coefficient could be derived from the frequency dependence of the EPR linewidth.[4] Other examples include spin-labeled lipids, proteins, and DNAs. For these molecules

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EPR experiments at multiple resonant frequencies/magnetic fields provide detailed information on various modes of molecular motion.[5] Thus, in order to satisfy the needs of these and other experiments, the magnets for multifrequency HF EPR should operate at various magnetic fields and allow one to sweep the field over the entire range of resonances of interest in a reasonable time (such as 1 h or less). Moreover, narrow (ca. 1–2 G) linewidths of some of the organic radicals dictate the accuracy and precision of the scans of magnetic field around the target values.

Typically, HF EPR experiments are carried out at resonant frequencies $\nu=95-300$ GHz and this requires magnetic fields of 3.4–10.7 T for electronic spins with $g \approx 2.0$. Such fields could be easily achieved with superconducting magnets, but, unlike NMR, these magnets cannot operate in a persistent mode in order to satisfy various experimental requirements outlined above. In the past, several magnet systems for HF EPR have been described.[6–11] To the best of the authors knowledge all of them are based on cryogen-cooled superconducting magnets (solenoids or split-pair coils). Operating and maintaining these magnets in EPR laboratories require periodic transfer of cryogens by trained personnel. It is worthwhile to note here that conventional EPR spectrometers operating at 9.5 and 35 GHz utilize iron-core electromagnets and therefore many EPR practitioners are unfamiliar with cryogen-cooled superconducting magnets. Moreover, operating superconducting magnets in a nonpersistent (i.e., field sweep) mode is known to be associated with large losses of liquid helium. The first reason for this is that during the field sweep the current leads should be attached to the magnet and this increases the thermal load to the cryostat. For magnets equipped with a persistent mode switch, the heating of the switch would also result in an additional helium boiloff. However, the main losses of liquid helium in these magnet systems occur due to the heat dissipation in the main coil(s) during the sweep due to Joule heating in the resistive parts. Based on previous experience, the authors estimate that for a typical HF EPR magnet each sweep from 0 to 12 T at 0.5 T/min results in a boiloff of at least 1–2 l of liquid helium. Thus, such HF EPR magnets require very frequent (sometimes every 2–3 days) refilling with liquid helium. This necessitates day-to-day maintenance efforts and the cost of cryogens alone could be as high as $10 000–20 000 per year. For sweeping the magnetic field within a narrow range (e.g., ±75 mT) the helium boiloff could be reduced by using a separate superconducting sweep coil. However, even in this case consumption of liquid helium could be substantial. For example, the use of a ±75 mT superconducting sweep coil with a 5 T/116 mm room temperature bore magnet supplied by Cryomagnet Systems, Inc. normally results in a 0.4 l/h helium consumption rate.[7]

Another important consideration is that helium is a nonrenewable resource and is produced from very limited deposits. Many EPR laboratories today are not equipped with helium recovery systems and operating a conventional cryogen-cooled HF EPR magnet in such laboratories would result in large and nonrecoverable helium losses. Thus, the above considerations justified the need for developing a versatile sweepable superconducting magnet system for HF EPR that would not require frequent and expensive cryogen service or preferably no services at all for long periods of continuous operation. Cryogen-free superconducting magnets underwent a significant development over the past decade.[12] However, only very recently such a magnet was first employed for nuclear magnetic resonance (NMR) spectroscopy[13] that requires both highly homogeneous and very stable magnetic fields. Here we describe and characterize a versatile cryogen-free magnet (CFM) system for HF EPR at magnetic fields up to 12.1 T (340 GHz for $g \approx 2$) that is suitable for ramping the magnetic field over the entire range, precision scans around the target field, and/or holding the field at the target value. An important feature of the system is that it is virtually maintenance-free because it is based on a cryogen-free technology and therefore does not require any liquid cryogens (liquid helium or nitrogen) for operating.

II. SYSTEM DESIGN

The cooling for the 12.1 T magnet described here is provided by a single two-stage Gifford-McMahon (GM)-cycle cryocooler supplied by Sumitomo Heavy Industries of Japan (model RDK-408D). The cryocooler is suitable for operating in the stray field of the magnet providing in excess of 10 000 h continuous operation without any service. The base temperature of the first stage of this cryocooler is specified to be about 35 K (33 K is typical) while the second stage is at about 4 K (3.5–3.6 K is typical). Sumitomo compressor unit is water cooled.

Schematics of the magnet with a cryostat and a cryocooler are shown in Fig. 1 and a photograph of the entire HF EPR system is presented in Fig. 2. The outer case of the CFM and the outer top and the bottom plates are manufactured from an aluminum alloy. The room temperature bore is made of nonmagnetic stainless steel. Radiation heat load to the magnet is minimized by means of a high purity aluminum radiation shield and multilayer superinsulation between the room temperature outer wall and the shield. The radiation shield is attached to the first stage of the cryocooler and during operation cools to 46–48 K. Special thermal links constructed from copper connect the second stage of the cryocooler with the 12 T superconducting solenoid (Fig. 1). These thermal links are sufficient to maintain the entire solenoid at temperature below 5 K without immersing the coil into liquid helium. The magnet operates in a vacuum. Because no cryogens are stored in the cryostat, the whole system is rather compact (0.75 m in diameter and ca. 1.22 m in height) for a wide (89 mm diameter) room temperature bore of 12 T magnet. The compact cryostat design and the absence of cryogen service ports (and associated extra ceiling clearance to accommodate a liquid helium transfer line) allowed us to install and operate the magnet in a standard laboratory space with no magnet pit and/or high ceiling required.

The main solenoid coil is made from NbTi and NbSn superconductors with superconducting joints to provide a persistent mode of operation. The system also includes a ±0.12 T superconducting sweep coil to provide accurate scans of the magnetic field in the vicinity of the target value.

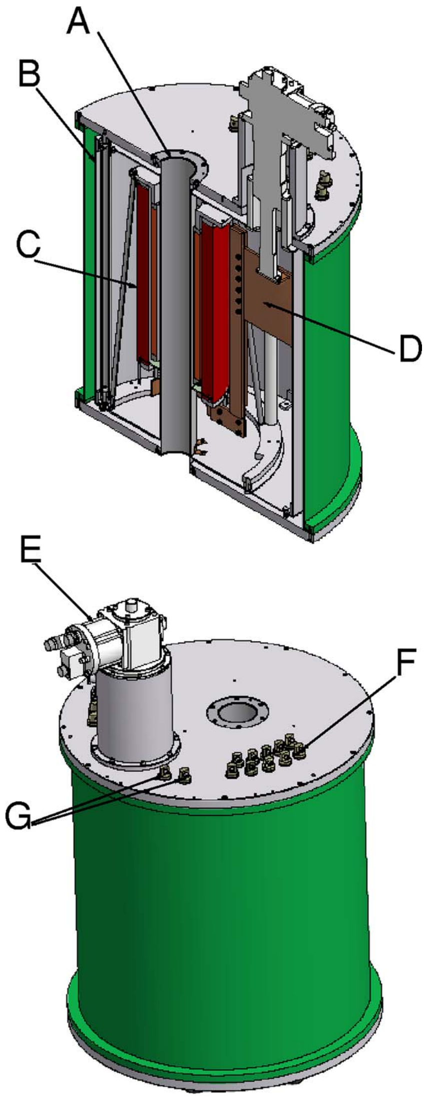

FIG. 1. (Color online) Schematic of the cryogen-free magnet: (A) 89 mm room temperature bore, (B) radiation shield, (C) 12.1 T superconducting solenoid, (D) copper thermal links, (E) cryocooler, (F) protection terminals, and (G) magnet terminals.

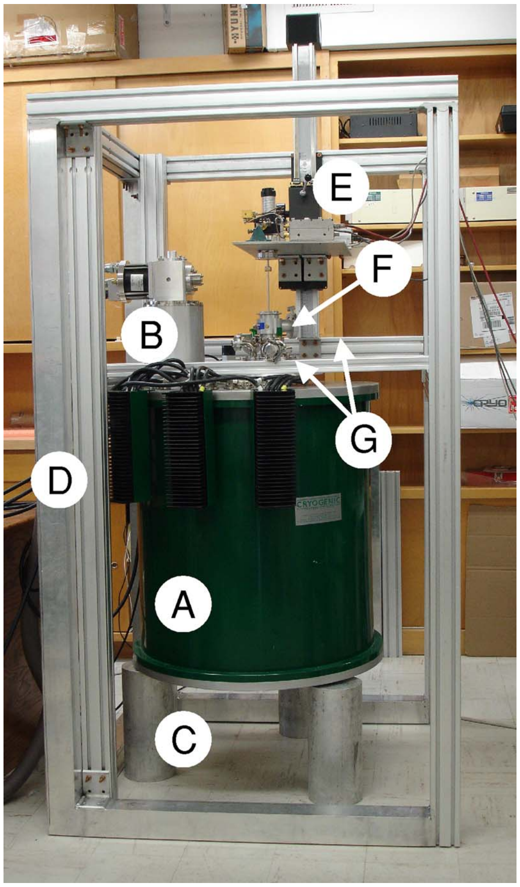

FIG. 2. (Color online) Photograph of the entire HF EPR setup at the NCSU installation site: (A) a 12 T cryogen-free magnet, (B) cryocooler, (C) aluminum support legs with rubberized pads sandwiched between the legs and the magnet, (D) aluminum cage that is mechanically insulated from the magnet (note that the height of the vertical beams is 6 ft), (E) movable platform with a millimeter-wave bridge for EPR experiments, (F) flow cryostat for variable temperature measurements that is supported by the cage and is therefore mechanically insulated from the magnet, and (G) cryostat support beams.

The sweep coil has been designed such that its magnetic coupling to the main coil is minimized. The main coil has a persistent mode switch while the sweep coil does not. The sweep coil is operated using a model 80A Cryogenic, Ltd. (London, UK) power supply while the main coil is operated using a system 8000 (Danfysik A/S, Jyllinge, Denmark) low drift power supply. The system 8000 is a unipolar dc power supply with an output of up to ± 5 V/200 A. At maximum 200 A current and 1 V output short term (30 min) stability was better than ± 1 ppm and long term stability was better than ± 1 ppm. Current stabilization is digital with a 20-bit digital-to-analog converter (DAC). Current setting from the front panel or through RS 232C or IEEE 488 interface has 18 bit resolution. The ramp rates for the main coils can be varied from approximately 10^{-8} to $5 \times 10^{-4}/s$ of the full value. The overall schematic of the magnet and auxiliary systems is shown in Fig. 3.

High temperature superconductor (HTS) current leads are thermally linked to the first and the second stages of the cryocooler but remain electrically isolated from the cryocooler components and the shield. Electrically resistive current leads extend from the room temperature to the HTS leads at the first cryocooler stage.

A total of six temperature sensors is installed to monitor various internal components during the cool down and subsequent operation of the magnet. Standard rhodium iron (RhFe) sensors were employed for monitoring temperature in positions of the system exposed to moderate or relatively low magnetic fields such as at the first (1) and second (2) stages of the cryocooler, the 50 K shield (3), the outer (4) portions of the coil, and the persistent mode switch (5). For the inner coil, where a thermometer may be subjected to appreciable magnetic fields, a Cernox sensor (6) was used as it exhibits low magnetoresistance. Data from the thermometers are collected with a switching digital voltmeter (model 2000, Keithley Instruments, Inc., Cleveland, OH) and transferred to a personal computer (PC) through a general purpose interface bus (GPIB) for converting to kelvin, logging, and further displaying and archiving.

The magnet also has special quench protection circuitry. This circuitry includes protection diodes installed inside the cryostat and aluminum heat dissipation radiators that are housed outside the magnet (Fig. 3).

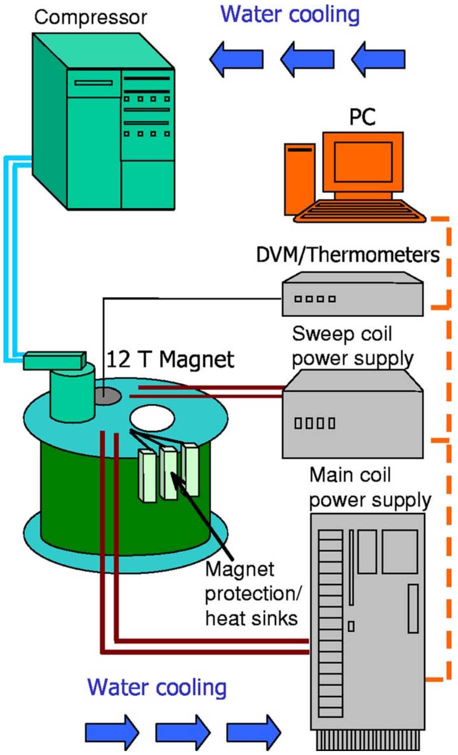

FIG. 3. (Color online) Overall schematic of the cryogen-free magnet and auxiliary systems.

III. MEASUREMENTS AND TESTS

Compared with conventional superconducting magnets, the cryogen-free magnet described here requires very little preparation and labor for the initial cool down and operation. Specifically, after the magnet cryostat inner space has been evacuated below 10^{-6} bar and some other simple operational checks such as proper electrical connections of various system components (as shown in Fig. 3) have been completed, the cool down can commence. The cooling of the magnet is simply a matter of turning on the cryocooler compressor. After that, neither operator presence nor labor is required for the entire process. The system operation and temperature of various magnet components are monitored via a software suite and logged automatically. Figure 4 shows experimental temperatures recorded at different points of the system during a typical cool down. Prior to the cooling cycle, the magnet was at room temperature for about a month.

When fitted with a persistent mode switch, current can only be introduced into a superconducting magnet with the persistent mode switch heater on. The CFM system described here makes it convenient to monitor the switch temperature with a dedicated thermometer. Ramping the magnet causes heat dissipation in the switch that is proportional to the square of the voltage across the switch. In addition to that, a considerable heat is generated by flux flow in the superconductor and eddy currents. In conventional cryomagnets this heat is removed by boiling liquid helium stored in a cryostat. In the CFM system this excess heat is removed by the cryocooler.

Figure 5 shows a typical temperature log file for testing the magnet by sweeping the field from 1 to 7 T up to the rate maximally specified (i.e., up to $5\times10^{-4}/s$ of the full value).

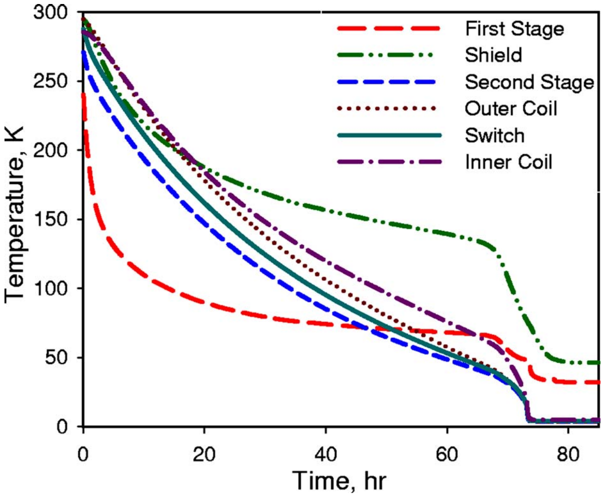

FIG. 4. (Color online) Temperatures of different parts of the cryogen-free magnet system during a typical cool down after storing the system at room temperature.

Note that during these tests the only significant heating was observed for the switch while the temperature of all other components of the system was raised by not more than 1 K.

We have also investigated the operation of the cryogen-free superconducting magnet in nonpersistent mode in which the heater kept the switch at a temperature of 7–8 K and the current was maintained by the Danfysik power supply. The first observation is that the operation of the magnet in a nonpersistent mode with the heater switch "on" and with ca. 60 A current through the leads has little or no effect on the temperature of the inner and the outer coils as well as other parts of the system (Fig. 6). This should not be surprising because compared with traditional copper/brass leads, the use of superconducting high-T_c current leads results in a great reduction of the Joule heat for the nonpersistent mode of operation.

The second observation was that the magnetic field could be effectively stabilized by an ultralow drift power supply such as Danfysik system 8000. This power supply utilizes Danfysik Utrastab current transducer technology that

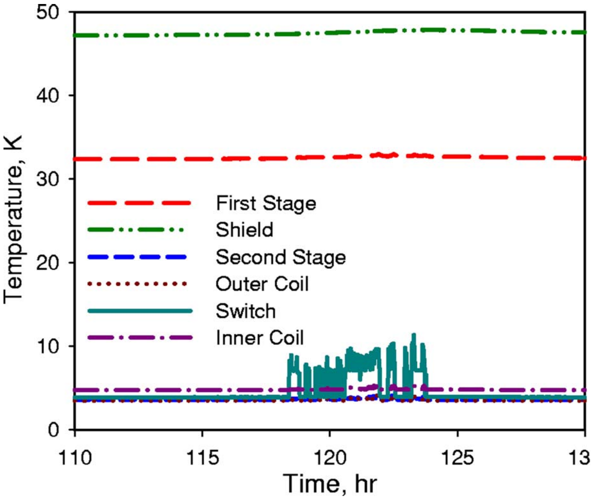

FIG. 5. (Color online) Temperatures of different parts of the cryogen-free magnet system during ramping the main coil from 1 to 7 T in magnetic field up to the maximally specified rate of 5×10^{-4}/ps of the full value.

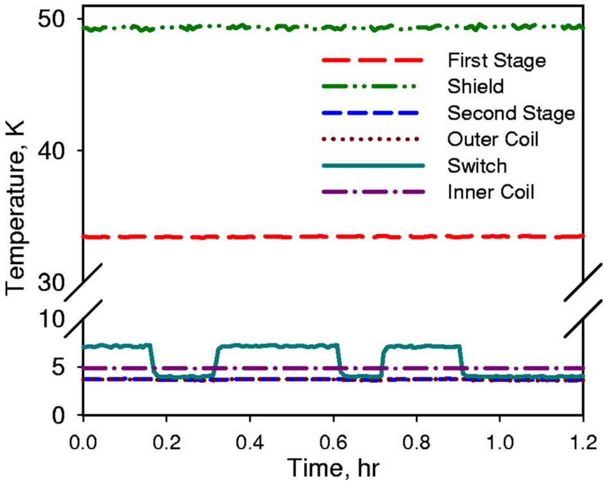

FIG. 6. (Color online) Temperatures of different parts of the cryogen-free magnet system during operating the magnet in persistent and nonpersistent modes at magnetic field of 5.166 T and with 60 A current in the leads. The current was stabilized by a Danfysik power supply. A nonpersistent state was achieved by maintaining the switch at 7–8 K with a heater.

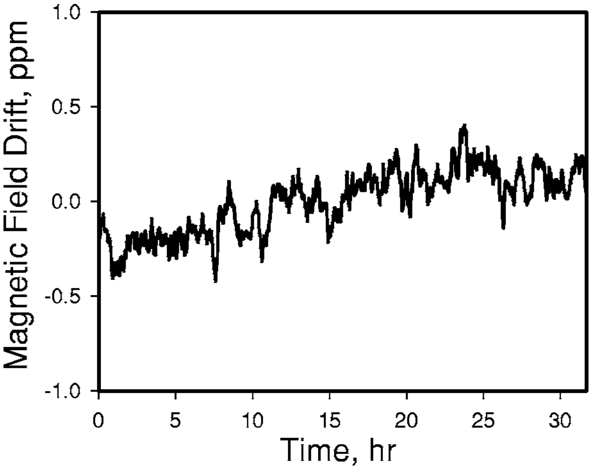

FIG. 7. Long-term (31 h) stabilization of the magnetic field of the main coil in a nonpersistent state by the Danfysik power supply. Note that relative accuracy of the Metrolab PT 2025/00/4 gaussmeter employed for magnetic field measurements is approximately ±0.1 ppm.

is based on the zero-flux principle. The transducer enables current measurements and regulation without an ohmic correction due to the inherent temperature stabilization problem at high currents. Previously, transducer technology has been applied to improve stability and linearity of a bipolar power supply constructed at the University of Illinois EPR Research Center to drive a water-cooled solenoid sweep coil for 95 GHz (*W* band) EPR.[8] Here we have tested this technology for stabilizing the magnetic field of a superconductive magnet in a nonpersistent mode.

The system 8000 is a 3 ppm power supply with a dc output of up to ±5 V/200 A. Current is stabilized digitally by a microprocessor that receives current reading from a transducer and regulates the current through 20-bit DAC. The current transducer Danfysik 860R-600 is specified to have a resolution of 0.05 ppm and dc accuracies of <1 ppm/°C and <1 ppm/month with output noise from dc to 10 Hz less than 0.1 ppm. This power supply is water cooled and major control components have internal temperature stabilization. However, we have found that the best stability is achieved when the temperature and the flow rate of the cooling water are maintained constant, for example, by a close-loop recirculation system.

Figure 7 demonstrates stabilization of the magnetic field of the main coil by the Danfysik power supply when the magnet was in a nonpersistent state. Magnetic field was measured at the NCSU installation site with a MetroLab PT 2025/00/4 bench unit digital NMR teslameter equipped with a D_2O model 1062-7 probe, ranging from 3.0 to 6.8 T (all supplied by GMW Associates, San Carlos, CA). Absolute accuracy of this gaussmeter is ±5 ppm while relative accuracy is approximately ±0.1 ppm. The latter parameter is the most important for magnetic field stability tests. The temperature stability of the internal frequency counter is better than ±1 ppm within the entire range of operating temperature from −10 to 70 °C. Magnetic field readings from the gaussmeter were automatically logged to a PC through an IEEE 488 interface with a LABVIEW program (National Instruments Corporation, Austin, TX). Because of the limited range of the MetroLab probe available at NCSU, the magnetic field was set at ca. 6.76 T, stabilized over a few hours, and then was monitored over ca. 30 h (Fig. 7). During this period all the measured field values were within ±0.4 ppm and more than 68% of the measurements were within ±0.2 ppm of the average field value. Note that this is comparable with the relative accuracy of the Metrolab gaussmeter that is ±0.1 ppm. Note that 0.4 ppm of 6.76 T is $\approx 3\times10^{-6}$ T and typical EPR linewidths exceed 1×10^{-4} T. Thus, the demonstrated stability of magnetic field in a nonpersistent mode of operation for our crygen-free superconducting magnet appears to be sufficient for EPR experiments.

One could ask the question of why the stability of the magnetic field we observed in our magnetic field measurements exceeds specifications of the Danfysik power supply (3 ppm). It should be noted here that the test of this power supply with a resistive load demonstrated a stability better than ±1 ppm. This is expected for a 20-bit DAC employed. The feedback circuit of this power supply is based on a transducer sensor with a 0.05 ppm resolution and a microprocessor unit that updates DAC every 70 μs. When the power supply is connected to a high inductance solenoid, such as 58.4 H in our case, any current ripples including those caused by digital-to-analog conversion updates are effectively averaged out over the main coil response time (greater than several seconds). Then the field stability is mainly determined by the noise of the current transducer sensor that is less than 0.1 ppm.

We have also monitored the temperature of the magnet components upon a spontaneous transition of the magnet wire to the resistive state (quench). Quenching sometimes occurs upon initial energization of superconducting magnets when small disturbances (mechanical or thermal) can cause a spontaneous loss of superconductivity. While NMR magnets are typically energized only a few times during their lifetime, the HF EPR magnets are reenergized rather frequently. Depending on the experimental needs, these magnets could be operated in a nonpersistent mode even continuously. For

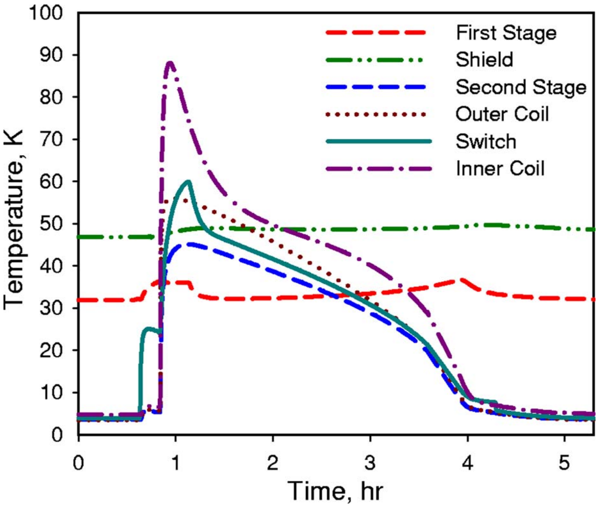

FIG. 8. (Color online) Temperatures of different parts of the cryogen-free magnet system during quenching the main coil upon testing the magnet for the maximum attainable energization rate. Note that just after 3 h and 15 min after the quench the CFM system was ready again for operation.

such magnets, a quench could occur when the energizing rate is higher than the magnet was designed for. To protect the cryogen-free magnet from overheating and damage due to a rapid Joule heat release during the quench, a special protection system has been implemented. In this system the heat load is directed to a diode bank and heat sinks located outside of the cryostat.

We have observed a quenching of the CFM system upon testing the magnet for the maximum attainable energization rate. Figure 8 shows the temperature log of such a test. The energizing of the magnet started 38 min after the beginning of the log. Initially, the temperature of the switch quickly reached 25.15 K and then started to decrease. The temperature of the inner NbSn coil also increased from 4.73 to 6.77 K but after 12 min decreased to 6.48 K. At this moment, when the magnet was at approximately 6 T magnetic field, we have observed a quench which resulted in a rapid rise in temperature for all of the system components (Fig. 8). The highest temperature of 88.2 K was recorded by the inner coil temperature sensor in 6 min after the quench. It should be noted here that quenching of a conventional cryogen-cooled superconducting magnet typically results in a large loss of cryogens and flooding the installation site with gases unsuitable for breathing. Since the CFM system does not store any cryogens, this hazard does not exist upon quenching such a magnet.

Quenching of a superconducting magnet with conventional liquid cryogen cooling typically necessitates repeating the entire initial cool down procedure that could easily take several days. In contrast, after just 3 h and 15 min following the quench the CFM system was ready again for operation (Fig. 8). It should also be noted that during the entire quench test the shield temperature remained below 50 K and, thus, a high vacuum insulation was maintained. The temperature of the cryocooler first stage was also raised but rather insignificantly. This demonstrates that CFM systems could be operated again in a relatively short time after quenching.

One of the challenges of utilizing actively cooled superconducting magnets for HF EPR experiments is uncoupling mechanical vibrations generated by a cryocooler from an EPR probehead and a millimeter-wave bridge. Both types of currently available cryocoolers—either based on Gifford-McMahon (GM) cycle or on pulse tube (PT) design—generate some mechanical vibrations. Currently available GM-cycle cryocoolers have higher cooling power and are less expensive than those based on PT design. Generally, the magnitude of vibrations generated by the room temperature parts of GM-type cryocoolers is higher than that of PT because the former cryocooler operates by periodic movement of a regenerator-displacer.[14] Although PT cryocoolers do not have any cold moving parts, the oscillating helium gas in the second stage generates vibrations of approximately the same level as in the second stage of a GM cryocooler.[14] In our design the second stage is mechanically connected to the magnet by specially constructed thermal links made out of copper. Thus, with either cryocooler type, mechanical vibrations of similar magnitudes would propagate throughout the system. Although the frequency of the cryocooler cycle is only a few hertz, even minimal (micron scale) displacements of millimeter-wave components and especially sample vibrations in high quality factor resonators employed in HF EPR could result in significant increase in noise level.

To decouple the millimeter-wave components of the HF EPR spectrometer from the cryogen-free magnet we employed simple but efficient design in which the entire microwave bridge and the probehead are suspended independently from an outside aluminum cage that has no mechanical contact with the magnet cryostat (see Fig. 2). The magnet itself rests on rubberized pads that are fixed on top of aluminum legs (Fig. 2). To investigate the effectiveness of this design, we have carried out control experiments that are the most demanding in terms of sensitivity and accurate positioning of a sample in an EPR resonator. This is usually the case for liquid aqueous solutions of spin-labeled biomolecules. At 95–300 GHz the microwave losses are exceptionally high and optimal sample configuration is rather difficult to attain. Typically, in order to achieve the best sensitivity such aqueous samples are sandwiched between quartz cover slips that are spaced by only 0.017–0.020 mm (Ref. 15) or drawn into quartz capillary of only 0.1–0.2 mm in diameter.[16]

For our tests we have chosen an aqueous solution of a stable nitroxide radical Tempone (perdeuterated 2, 2′, 6, 6′-tetramethyl-4-piperidone-1-nitroxide, purchased from Cambridge Isotope Laboratories, Andover, MA) at a low concentration of only 10 μM. The test was carried out using a single-channel continuous wave of 95 GHz (*W* band) bridge similar to the one described earlier.[8] Aqueous solution was drawn into a 0.15 mm i.d. quartz capillary (VitroCom, Mountain Lakes, NJ) and carefully positioned exactly at the center of a cylindrical TE_{012}-type resonator. When loaded with this sample, the quality factor of this resonator remained exceptionally high [$Q \approx 3800$, estimated by measuring the width of the cavity resonance with an EIP (San Jose, CA) model 548B frequency counter]. It should be noted here that any vibrations of an aqueous sample in this high Q resonator would be easily noted from a large noise increase in EPR spectra.

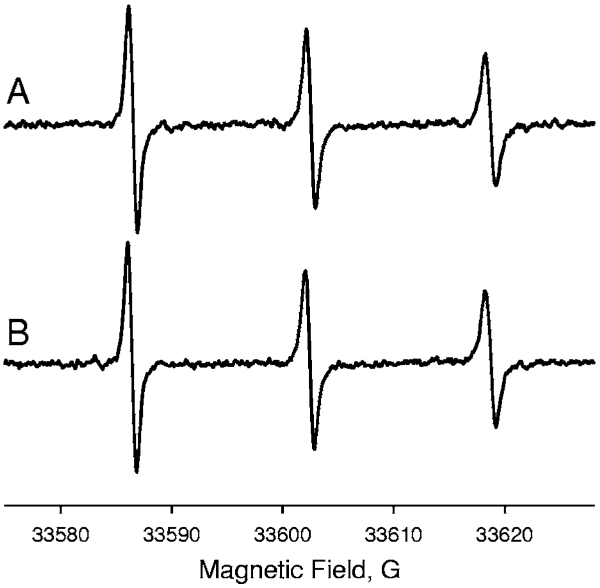

FIG. 9. Experimental 95 GHz (*W* band) EPR spectra from 10 μM nitroxide radical Tempone (perdeuterated 2,2′,6,6′-tetramethyl-4-piperidone-1-nitroxide); single scans with 0.1 s time constant and 0.5 G magnetic field modulation amplitude. (A) A spectrum with the magnet actively cooled by a GM-cycle cryocooler and (B) A spectrum taken without active cooling and, thus, in the absence of any vibrations from the cryocooler.

Figure 9 shows two single-scan *W*-band EPR spectra taken from such a sample at 298 K with a time constant of 0.1 s and 0.5 G magnetic field modulation amplitude. Spectrum A was taken with the GM cryocooler fully operational. Because the thermal capacity of the system was sufficient to keep the magnet in its superconducting state for at least 5–10 min without any active cooling, we were able to record another spectrum B when the cryocooler was switched off and no vibrations were present. Figure 9 demonstrates that these two spectra are nearly identical in both the resolution and noise level, indicating effective isolation from vibrations generated by the cryocooler.

Recently, the Oxford superconductivity group described a NMR 9.4 T (400 MHz proton resonance) magnet that was actively cooled by a PT cryocooler.[13] While the Oxford utilizes a "dry" 50 K shield (i.e., no nitrogen vessel), the magnet is still bathed in liquid helium that is recondensed by the second cryocooler stage located above the cryostat. In order to decrease vibrations, the liquid helium is then transported to the main reservoir in the form of droplets. While these precautions against vibrations seem to be the necessity for high resolution solution NMR, many solid-state NMR and high field EPR experiments could be carried out with less homogeneity of magnetic fields. For example, magnetic field homogeneity of a typical HF EPR magnet is about 10 ppm in 1 cm sphere.

Here we demonstrated the exceptional performance of a versatile sweepable superconducting magnet system for HF EPR that is actively cooled and is free of any stored cryogens. In contrast to the Oxford design, our system, while offering higher magnetic field (12.1 vs 9.4 T), is significantly smaller because there is no liquid helium storage reservoir in the cryostat. Also, we demonstrate that the operation of our system including initial cool down, temporary shutdown, or even restarting the system after an accidental quenching is greatly simplified. Finally but not lastly, we have demonstrated that in a nonpersistent mode of operation the magnetic field can be stabilized to better than ±0.4 ppm over 30 h period by employing a transducer-controlled power supply. Such stability is sufficient for many HF EPR experiments.

The cryogen-free HF EPR magnet system described here equips researchers for both stabilization and rapid scanning of magnetic fields. Conventional superconductive magnets that are currently employed for such measurements require much more frequent (typically weekly) cryogen service than NMR systems of comparable field that are operated only in a persistent mode. The HF EPR magnet system described here eliminates the need for these frequent and labor-intensive cryogen refills. Thus we believe that actively cooled superconducting magnets are ideally suitable for a wide range of HF EPR experiments including spin-labeled nucleic acids and proteins, single-molecule magnets, and metalloproteins.

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