Cryogen-Free Superconducting Magnet System for Multifrequency EPR up to 12.1 Tesla/340 GHz

***Alex I. Smirnov**, Tatyana I. Smirnova, Andres Ruuge,*
Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204, USA; Alex_Smirnov@ncsu.edu
***Renny Hall**, Stuart Hodgson,*
Cryogenic Limited, Units 29/30, Acton Park Industrial Estate, The Vale, Acton, London W3 7QE, UK; Tel: +44 (0)20 8743 6049;
Fax: +44 (0)20 8749 5315, Sales@cryogenic.co.uk

1. INTRODUCTION

It is now well established that multi-frequency and high field/high frequency (HF) EPR is a natural way to increase the spectral information on paramagnetic systems ranging from organic free radicals to paramagnetic metal ions and spin-coupled pairs. One of the advantages of the multi-frequency EPR approach is in assisting in interpretation of the EPR spectra that are often broaden by interplay of magnetic field dependent and independent terms in the spin Hamiltonian:

$$H=(\beta B\cdot g\cdot S-\beta_n B\cdot g_n\cdot I)+hS\cdot A\cdot I+hI\cdot P\cdot I+hS\cdot D\cdot S+(higher+order+terms)$$

For example, in many catalytically-active and molecular magnet systems paramagnetic metal ions could occur in clusters and therefore be coupled by either dipolar interaction or by an exchange interaction of the type S·J·S. Paramagnetic metal ions can also be coupled to organic free radicals. As a result, electronic spins greater than ½ can be found in some of these systems. With a few exceptions, these spectra typically spread over several thousands of Gauss, have effective g-factors that are very different than ge»2.0023, and could be observed only at cryogenic temperatures because of otherwise fast electronic relaxation. Thus, a superconductive magnet with the main field ramping capabilities and a cryogenic sample insert might be required for such studies.

While half-integer spin systems give rise to EPR signals essentially at any magnetic field, the integer spin systems remain "EPR-silent" if the magnitude of the electron-electron dipolar interaction of the type S·D·S (also called zero-field-splitting or ZFS) exceeds the energy of the microwave quantum. Thus, while some paramagnetic metal ions such as Mn(III) remain EPR-silent at conventional 9.5 GHz EPR frequencies they give rise to EPR signals at frequencies above 100 GHz.

While EPR spectra of some of the spin systems at high magnetic fields could be very broad spreading over a range of several Tesla (such as observed for the effective S=10 spin system of Mn-acetate), other systems, such as, for example, organic free radicals produce spectra just a few Gauss wide. Moreover, spectra of exchange narrowed system and S-state paramagnetic metal ions such as Mn(II) and Gd(III) become even narrower with an increase in the magnetic field. For example, the peak-to-peak EPR line width of Gd-DTPA decreases from ca. 350 G at 9.5 GHz/0.3T to 19.1 G at 95 GHz/3.4 T and then to 7.8 G at 220 GHz/7.9 T. Such narrow EPR lines dictate accurate and precise scans for the magnetic field. It is also important to calibrate these scans so the positions of the resonance lines and, thus, g-factors and other magnetic parameters could be measured with a great accuracy.

Finally, there are other considerations to make such a magnet system convenient in EPR studies. For example, homogeneity of the magnetic field should be sufficient for the line width studied. The magnet should be also designed to accommodate an EPR probe-head and to provide an easy access to the EPR probe and the sample. Finally, but not least, such a magnet should be economical to operate and easy to maintain.

Typically, a magnet system for HF EPR consists of cryogen-cooled superconducting magnets in order to generate magnetic fields above 2-2.5 T. For scanning of magnetic fields two modes of operation are usually employed. For large scans the field is controlled by ramping the current through the main solenoid. During the field ramping, the head load of the magnet increases with the current due to joule heating in the resistive parts. This load adds to the heat transferred through the connected leads and causes extensive liquid Helium boil-off. Fortunately, not all EPR spin systems require large – several Tesla – magnetic field scans. Therefore, a secondary coil (superconducting or a water-cooled) could be employed to generate smaller scans with a greater accuracy and with lesser heat load for the main cryostat.

Here we describe and characterize a versatile magnet system for HF EPR up to 12.1T/340 GHz 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 which does not require any liquid cryogens (liquid Helium or Nitrogen) for operation. The cooling for the magnet is provided by a two-stage Sumitomo RDK-408D cryocooler with the base temperature of the second stage of ca. 3.5 K. Because no cryogens are stored in the cryostat, the whole system is of a rather small size (0.75 m in diameter and ca. 1.22 m in height) for a wide room-temperature bore magnet.

2. ESSENTIAL SPECIFICATIONS

a) Cryostat

Vertical room temperature bore diameter	89 mm
Cryostat height (exc. Cryocooler)	817 mm
Cryostat height (inc. Cryocooler)	1220 mm
Cryostat diameter	750 mm

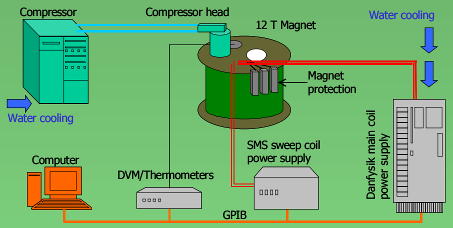
b) 12 T Magnet

Time to cool from room temperature to 4 K	ca.70 hrs
Measured magnet homogeneity	8.6 ppm in 10 mm DSV
Maximum tested field	12.1 T
Recommended ramp time from 0 to 12.1 T	67 min

c) Supeconducting sweep coil

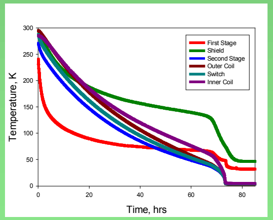
Maximum range tested	+/-1200 G
Measured magnet homogeneity with magnet at 12 T and coil at +/-600 G	9.8 ppm in 10 mm DSV

3. SYSTEM SCHEMATIC



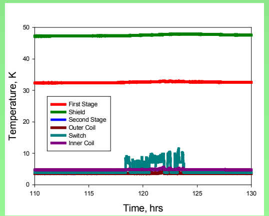
4. SYSTEM COOLDOWN

No prior knowledge of cryogenics is required to cool down and operate the system. When HF EPR experiments are planned, the cryocooler can be switched on and after three days of maintenance-free cooling the magnet is ready for operation. The graph below shows experimental temperatures recorded at different points of the system during the cool down started on July 2, 2004. Prior to cooling down, the magnet was at room temperature for about a month.



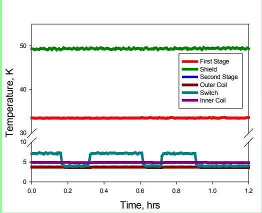
5. FAST FIELD RAMPING

When the magnetic field is charged both on sweeping the field up and down, considerable heat is generated by flux flow in the superconductor. This heat must be removed. For fast ramps the heat load can exceed the cooling power of the cryogenerator. The patented thermal reservoir is used to extract this heat from the magnet. The graph below shows a typical temperature log file for testing the magnet from 1 to 7 T.



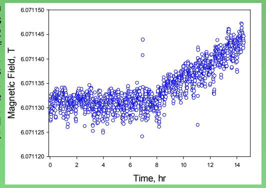
6. HEAT LOAD IN NON-PERSISTENT MODE

It is worthwhile noting here that operation of the magnet in a non-persistent mode with the heater switch "on" has little effect on the temperature of the inner and the outer coils as well as other parts of the system (see the Graph on right). Thus, in non-persistent mode an increase in the magnet heat load due to the switch heater is rather insignificant.



7. OPERATING THE SYSTEM WITH A DANFYSIK POWER SUPPLY

To ensure high precision of the magnetic field ramps or high stability of the magnetic field during the experiment we employ a Danfysik System 8000 power supply. This power supply utilizes a Danfysik Utrastab current transducer technology that is based on the zero-flux principle and enables current measurements and regulation without an ohmic correction due to the inherent temperature stabilization problem at high currents. The System 8000 is a 3 ppm power supply with DC output of up to ±5 V / 200 A. Current setting is digital with 18 bit resolution. The Figure below demonstrates stabilization of the magnetic field of the main coil by the Danfysik power supply when the magnet was in non-persistent mode. During this test, for the first 8 hrs the magnetic field drift measured by a Metrolab NMR Gausmeter was less than –4.4×10^{-8} T/hr (or -0.0072 ppm/hr) with standard deviation of ±2.5×10^{-7} T or ±0.037 ppm. During the next 5 hrs the drift was +1.8×10^{-6} T/hr (or +0.3 ppm/hr). The overall drift over 15 hrs of the experiment was less than 150 mG. This demonstrates exceptional magnetic field stability for an EPR experiment.



8. SWEEP COIL OPERATION

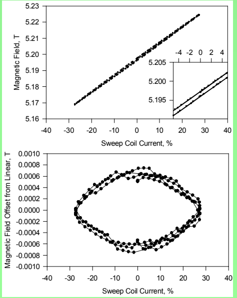
In general, in order to obtain high-resolution scans of magnetic field to record precise line shape of sharp EPR lines, a secondary coil is employed. One reason for using such a coil is to decrease the heat load to the magnet– this we have mentioned earlier. Also, it is difficult to change the current in the main solenoid quickly because of its rather high inductance. Finally, a greater precision of magnetic field ramps can be achieved this way. Indeed, if the accuracy/re-setability of a power supply is , say, 100 ppm, this would limit the resolution to about 10 G if this supply is used to ramp the field of a 10 T magnet. However, if the magnet is put in persistent mode and the same power supply is employed to ramp the current through a small inductance auxiliary solenoid, the resolution will be significantly improved. For example, for a 0.05 T coil, the steps will be as small as 50 mG and this is sufficient for many experiments.

In practice, however, the mutual inductance affects the linearity of such scans and decreases the magnitude of achievable scans because of the coupling effects of the main coil which is in persistent mode. The mutual inductance is especially a problem for a superconducting sweep coil because of the close proximity to the main solenoid. In the 12 T system Cryogenic Ltd. employs a proprietary design which minimizes the mutual inductance effect.

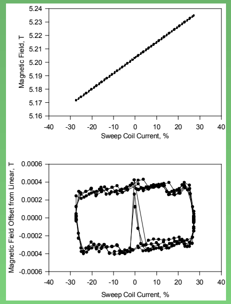
We have carried extensive tests of our magnet system in order to characterize the behavior of the sweep coil. The Figure below shows the results of such a test when the magnet was put into persistent mode at 5.2 T and the sweep current was ramped repetitively from +10 A to –10 A at the rate 0.0308 A/s. The maximum tested current through the sweep coil was 55 A with the rate up to 0.142 A/s so the entire range could be scanned within 13 min. In the tests we utilize smaller maximum currents and rates to allow for an automatic field tracking by the Metrolab Gaussmeter.

For ±10 A the sweep width was 555 G. It was also noticed that for the same current values the field readings were slightly different depending on the direction of the ramp. These deviations are easier to characterize when we plot the deviation from the linear scan.

This hysteresis-like behavior has been noticed previously for a water-cooled sweep coil developed at the Univ. of Illinois for the W-band spectrometer. While the exact physical origin of this effect is unknown, it is attributable to the magnetization of the super-conductor wire. The hysteresis loops are repeatable, and, in principle, the scans can be corrected for such a non-linearity. Some scatter in the data is caused by the limited tracking ability of the Metrolab Gaussmeter.



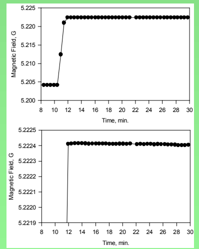
We have also investigated the behavior of the sweep coil when the magnet was maintained in a non-persistent mode at a constant current by a Danfysik System 8000 power supply, All other conditions were identical. The graph on right shows the sweep range of such a coil increased from 555 G to 633 G (i.e., by 14%). The shape of the hysteresis curve was also affected: basically, with exception of a few % of the scan near the turn points, the slopes of the up and down scans were essentially identical but with about a 6 G offset. This observation gives the possibility of highly linear scans and data averaging with just a minimal correction if both up and down scans are acquired.



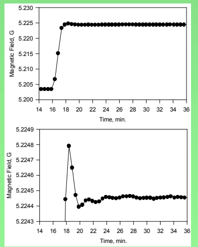
9. FIELD STABILIZATION TIME

This hysteresis behavior should not be surprising because stabilization of the magnetic field current in the main coil is much longer than for the sweep coil. To demonstrate this we have collected magnetic field data upon stepping the current through the sweep coil from 0 to 10 A at the maximum tested rate of 0.142 A/s when the magnet was in persistent and non-persistent mode. The Figures below demonstrate that while for the magnet in persistent mode the field was stabilized in less than 0.5 min (this was the time interval between the data points), oscillations of the magnetic field in non-persistent mode occur at least for a 12 min. period.

PERSISTENT MODE



NON-PERSISTENT MODE



10. ACKNOWLEDGMENTS

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