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A Ferromagnetic Shim Insert for NMR Magnets – Towards an Integrated Gyrotron for DNP-NMR Spectroscopy

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Abstract

In recent years high-field Dynamic Nuclear Polarization (DNP) enhanced NMR spectroscopy has gained significant interest. In high-field DNP-NMR experiments (400 MHz ¹H NMR, 9.4 T) often a stand-alone gyrotron is used to generate high microwave/THz power to produce sufficiently high microwave induced B_{1e} fields at the position of the NMR sample. These devices typically require a second, stand-alone superconducting magnet to operate.

Here we present the design and realization of a ferroschim insert, to create two iso-centers inside a commercially available wide-bore NMR magnet. This work is part of a larger project to integrate a gyrotron into NMR magnets, effectively eliminating the need for a second, stand-alone superconducting magnet.

Graphical abstract

Keywords

Dynamic Nuclear Polarization; DNP; Gyrotron; Ferroschims; Two-iso-center Magnet

Introduction

In recent years Dynamic Nuclear Polarization (DNP) enhanced NMR (DNP-NMR) spectroscopy has significantly grown in popularity and the method is of large interest for applications ranging from particle physics, material science and structural biology [1-9]. In a

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DNP experiment the thermal polarization of the electron spin bath is transferred to surrounding nuclei (^1H , ^{13}C , ^{29}Si , etc.) by saturating the corresponding Electron Paramagnetic Resonance (EPR) transition of a paramagnetic polarizing agent. Nitroxide-based bi-radicals such as TOTAPOL, AMUPol or bTbK are preferred in solid-state DNP-enhanced NMR experiments because they enable the highly-efficient cross-effect due to their broad high-field EPR spectra and enhancement factors as high as 515 (80 % of the theoretically possible maximum for protons) have been reported [2, 10-13]. In general DNP-NMR experiments require four additional components besides the traditional NMR hardware [14]:

1. a transmission line,
2. a low-temperature DNP-NMR probe with THz interface,
3. a paramagnetic polarizing agent, and
4. a microwave/THz Source.

The amount of microwave/THz power required to saturate the EPR transition of the polarizing agent strongly depends on the electronic relaxation times T_{1e} and T_{2e} of the unpaired electron and therefore the sample temperature [15, 16]. At cryogenic temperatures ($< 40\text{ K}$, helium cooling), the electron relaxation time (T_{1e}) can be sufficiently long and low-power solid-state sources can be used. However, the available output power for solid-state devices drops rapidly with increasing frequencies. Currently about 263 GHz (400 MHz ^1H NMR, 9.4 T) is the highest frequency for which DNP-NMR experiments with solid-state sources have been reported [17-19]. DNP-NMR experiments under magic-angle-spinning (MAS) conditions are typically performed at temperatures $< 100\text{ K}$ because this temperature can easily be achieved by cooling the sample with cold nitrogen gas [20, 21]. At these temperatures, the T_{1e} relaxation time of TEMPO-based polarizing agents are typically 100 to 500 μs [11] and strong microwave induced B_{1e} fields are required to efficiently saturate the associated EPR transitions and to drive the DNP mechanism [2, 9, 22]. To create sufficiently high B_{1e} fields at the position of the sample, several watts of microwave power are required for high-field MAS-DNP experiments, since typically no microwave resonance structures are used. While there are a number of different devices available to provide sufficient output power at frequencies $< 100\text{ GHz}$ ($< 150\text{ MHz}$, ^1H NMR) [23, 24], the gyrotron is the only demonstrated device capable of reliably generating tens of watts of continuous-wave (cw) power at microwave/THz frequencies ($> 200\text{ GHz}$) [2, 22].

In this article we present a method for converting a standard, wide-bore NMR magnet into a two iso-center magnet using ferromagnetic inserts. This work is part of a larger effort to completely integrate the gyrotron into the NMR magnet and to develop a compact and cost-effective DNP-NMR instrument [25]. An integrated setup avoids the losses due to long transmission lines and may simplify the cryogenic MAS probe. It does not need an additional superconducting magnet and the gyrotron can be operated as an efficient fundamental mode device. This can be especially important for high-field DNP-NMR experiments at frequencies $> 400\text{ MHz}$ or to provide a cost-effective upgrade path for existing NMR system with DNP-NMR capabilities.

Background

The gyrotron is a “fast-wave” vacuum electronic device (VED) that utilizes a mildly relativistic electron beam immersed in a strong magnetic field to transfer energy between the electron beam and a transverse electric (TE) mode of the gyrotron cavity [26]. Its output (cyclotron) frequency ω_c is given by:

$$\omega_c = s \frac{eB_0}{\Gamma mc} \quad \text{Eq. 1}$$

with s the harmonic number of the operational mode, e the electron charge, B_0 the static magnetic field strength, m the electron mass and c the vacuum speed of light. In eq. 1 Γ represents the Lorentz factor¹ (relativistic mass factor), which is given by

$$\Gamma = \frac{1}{\sqrt{1 - v^2/c^2}} = 1 + \frac{eU}{mc^2} = 1 + \frac{U[kV]}{511}. \quad \text{Eq. 2}$$

In general, the gyrotron requires a magnetic field strength of about 1 T for every 28 GHz of THz radiation such that a total field strength of about 9.4 T is required for a 263 GHz fundamental-mode ($s = 1$) gyrotron. This high magnetic field strength is typically generated in superconducting magnets based on niobium-titanium wire. To achieve magnetic field strengths > 10 T, as required for NMR experiments at > 600 MHz (14.1 T), the superconducting magnet is based on more expensive niobium-tin wire [27, 28]. Because the output frequency of the gyrotron is dictated by the magnetic field strength, a fundamental-mode gyrotron requires a magnetic field strength similar to the corresponding NMR experiment. To avoid costly superconducting magnets, most gyrotrons for DNP-NMR spectroscopy are designed as 2nd harmonic device ($s = 2$), which require only about half of the magnetic field strength of the NMR experiment and even gyrotrons operating at 527 GHz (800 MHz, ¹H) can use superconducting magnets based on less expensive niobium-titanium wire. However, operating the gyrotron as a 2nd harmonic has some major drawback such as:

1. The threshold current for the THz emission is higher for a 2nd harmonic device compared to a fundamental mode device.
2. The overall efficiency is greatly reduced. Therefore, a higher electron beam power is necessary, requiring larger power supplies and large sized collectors to disperse the spent electron beam.
3. 2nd harmonic operation is more susceptible to mode competition, especially from the fundamental mode, limiting the operating parameter space of the gyrotron.

¹In this article we use the uppercase gamma to avoid confusion with the lowercase gamma, which in magnetic resonance spectroscopy is reserved for the gyromagnetic ratio.

Despite these drawbacks, many stand-alone 2nd harmonic gyrotron systems with sufficient output power for DNP-NMR spectroscopy have been demonstrated [1, 8, 14, 29-31]. However, a fundamental-mode gyrotron is preferred when operating it inside the NMR magnet because it requires less beam power and offers a larger tuning range compared to a 2nd harmonic device [31, 32].

Due to the gyrotrons relativistic nature, the magnetic field strength at the position of the gyrotron cavity has to be slightly higher to match the corresponding EPR frequency [26]. For example, at a proton NMR frequency of 400 MHz (9.39 T) the free-electron Larmor frequency is 263.28 GHz. Typical operation parameters for a fundamental mode gyrotron are 3.5 kV/50 mA (175 W total beam power) [32] corresponding to a required field increase of only 0.7 % (see equation 2) or a total field of 9.45 T. In contrast, the beam voltage required for a 2nd harmonic gyrotron operating at 263 GHz, is ~15 kV/200 mA (3 kW total beam power) and, according to equation 2, the magnetic field strengths at the position of the gyrotron cavity has to be about 3 % higher (9.7 T, 413 MHz ¹H) compared to the field strength required for the NMR experiment [1, 31, 33]. While this increase of magnetic field strength is easily generated in a gyrotron that uses an additional stand-alone superconducting magnet, it presents a serious challenge when designing an integrated gyrotron system.

Towards an Integrated Gyrotron for DNP-NMR Spectroscopy

To date, almost all DNP-NMR instruments for MAS-DNP experiments are gyrotron-based, utilizing a stand-alone superconducting magnet for the gyrotron. Close inspection of state-of-the-art NMR systems reveals ample space in the NMR magnet bore above the NMR probe – a volume which is often only occupied by the sample-eject tube or the cooling stack. In contrast the volume below the magnet iso-center is occupied by the NMR probe and very crowded; including: gas lines for spinning, RF cables, tuning rods etc.

Additionally, the magnetic field above the sample space has a high degree of homogeneity, especially in wide-bore magnets, which are commonly used for (low-temperature) solid-state NMR spectroscopy. Since the gyrotron only requires a field homogeneity of < 0.1 % over the length of the cavity (typically a few millimeters) this region is still suitable to operate the gyrotron and we propose to operate the gyrotron in the space above the NMR probe to eliminate the additional superconducting magnet [25, 34].

The ostensible problem with an integrated THz source (gyrotron) is that the magnetic field strength at the position of the gyrotron cavity has to be slightly higher than that at the position of the sample, due to the relativistic nature of the gyrotron (see above). There are two approaches to solve this problem: 1) *Increase* the magnetic field strength at the position of the gyrotron cavity or 2) *decrease* the magnetic field strength at the position of the NMR sample. In this work we describe a simple, elegant approach of implementing a ferroschim assembly (FSA) to decrease the magnetic field strength at the position of the NMR sample while simultaneously increasing the field homogeneity in the region of the gyrotron cavity – effectively creating an NMR magnet with two isocenters. A similar approach was proposed to generate multiple homogeneous field volumes inside the bore of a superconducting magnet [35, 36].

Ferroshims are commonly used to alternate the magnetic flux lines and increase homogeneity in magnets with large bore sizes, commonly used in Magnetic Resonance Imaging (MRI) experiments [37, 38]. They have also been used to increase the homogeneity of Bitter magnets [39], to create two iso-center magnets for DNP-shuttling experiments [40] or two-field NMR spectroscopy [36], or to create multiple homogenous field volumes inside a superconducting magnet [35]. In comparison to incorporating a high-current electromagnet into the bore of the NMR magnet, ferroshims can provide a relatively simple design and implementation to solve the field offset problem inherent to an integrated gyrotron.

We would like to note that in principal it would be possible to design a ferroshim insert to operate a 2nd harmonic gyrotron at about half the magnetic field strength that is required for the NMR experiment. This would have the advantage that the distance between the position of the gyrotron cavity and the position of the NMR sample would be much larger compared to a fundamental mode gyrotron resulting in fewer space restrictions for the overall system design. However, in this case the gyrotron cavity would be located in a region of large field gradients, which would require an aggressive approach to achieve sufficient field homogeneity [36, 40]. In addition, as noted above, a 2nd harmonic device is often less efficient, and requires higher beam power (kilowatts) to produce a similar output power. This drastically increased beam power, presents a serious challenge for the collector design since the radius of the electron beam is only typically about 1 mm. Furthermore, the magnetic field strength is still increasing in the propagation direction of the electron beam and the beam will further focus. Once the electron beam passed the gyrotron cavity, its energy is dispersed inside the collector and the heat removed is by a water cooling circuit. However, it is crucial to keep the energy density (W/m^2) to a minimum to avoid damaging the collector and a fundamental mode gyrotron, with greatly reduced beam power has a clear advantage over a 2nd harmonic device.

Materials and Methods

All calculations were based on original analytical expressions and numerical optimizations evaluated in Matlab (Mathworks, Natick MA, USA). Finite element calculations were performed in FEMM (David Meeker, Version 4.2, <http://www.femm.info>) interfaced with Matlab to provide additional mechanical force and safety analysis.

The presented ferroshim assembly (FSA) was fabricated from commercially available steel (grade 1018, Yarde Metal, Pelham, NH, USA) and the two spacer rings were fabricated from aluminum (grade 6061, McMaster-Carr, Princeton, NJ, USA). The FSA was built per design specifications without further optimization steps. All parts were manufactured on a tool making lathe to tolerances of $\pm 0.001''$ ($\pm 25.4 \mu\text{m}$). Special attention was paid to not scratch or otherwise deform any parts of the FSA to not compromise the magnetic field homogeneity. The iron rings were coated with a single layer of spray paint to avoid degradation through rusting. Once installed inside the magnet bore, the FSA is held in place using two PVC tubes located above and below the FSA, which allowed for small longitudinal adjustments ($\pm 5 \text{ mm}$) along the magnet bore.

Mapping of the on-axis magnetic field strength was performed using a Gaussmeter (Lake Shore Cryotronics Inc., Westerville, OH, USA, model 425) and an axial Hall probe (Lake Shore, model HMMA-2504-WL, accuracy +/- 1%). The probe was held inside the magnet using a home-built support structure that allowed moving the hall sensor along the magnet bore using a lead screw driven by a (NEMA-17) stepper motor. The stepper motor is controlled by an Arduino Uno R3 microcontroller (www.arduino.cc) running the LINX firmware for Arduino (LabVIEW MakerHub, www.labviewmakerhub.com) and an EasyDriver stepper motor driver (Sparkfun, Niwot, CO, USA). Data acquisition was performed using LabVIEW (National Instruments, Austin, TX, USA).

All experiments were performed in a standard, actively shielded, wide-bore (89 mm) 9.4 T superconducting magnet (Agilent, 400/89/ASP). The magnetic field was charged and discharged using a bipolar power supply for superconducting magnets (Cryomagnetics, Inc. Model 4G-100/SHIM). The NMR spectrometer is equipped with a two-channel Agilent VNMRs NMR console. Solid-state NMR spectra of Adamantane were recorded using a 3.2 mm triple-channel magic-angle spinning probe (PhoenixNMR, Fort Collins, CO, USA). Prior to all experiments the magic angle was set using a sample of KBr. The probe is oriented with the rotor axis coinciding with the x-axis of the magnet. A 4 mm Agilent MAS probe was used to monitor field fluctuations using a sample of H₂O/D₂O (5/95, v/v, non spinning).

Results and Discussion

Adding a FSA to a superconducting magnet is a simple approach to generate a multi-center magnet which satisfies the operating parameters of an integrated THz source such as a gyrotron. For our specific application, the design constraints are as follows:

1. Reduce the magnetic field strength *at the position of the NMR sample* by 55 mT (corresponding to a gyrotron operation voltage of 3 kV and a background field of 9.4 T) with respect to the magnetic field strength *at the position of the gyrotron cavity*.
2. Provide about 70 mm separation between the location of the NMR sample and the center of the gyrotron cavity.
3. Preserve the magnetic field homogeneity at the position of the NMR sample.
4. Create a second iso-center with a field variation of < +/- 500 ppm over a length of 28 mm (the length of the gyrotron cavity).
5. Restrict the outer diameter of the FSA to < 88 mm to fit a standard wide-bore NMR magnet, and the inner diameter to > 72 mm to fit a standard wide-bore NMR and probe.

In Figure 1 the native, on-axis field profile of our wide-bore NMR magnet is shown in blue (bottom, dashed line). The magnet has a large homogeneous region spanning > 60 mm with an overall field variation of less than +/- 0.5 ppm. This high homogeneity at the center of the magnet, which is typically found in wide-bore magnets, is a large advantage when designing FSA inserts to create two iso-centers.

Ferroshim Design

Based on the design constraints given above we used an analytical model to determine the preliminary physical dimensions of the ferroshim assembly. The axial magnetic field of a magnetized cylinder in an axial external field can be derived using Maxwell's equations at the surface. The field is shown to be equivalent to that produced by a current sheet at the cylindrical surface. In the high field limit, where the magnetization is uniform and aligned along the axis, the surface current density is constant. The expressions for the magnetic field produced by a thin cylindrical current sheet are given by classical electromagnetism. The extension to a hollow cylinder can be derived from the superposition principle, and adds an identical surface current density of opposite sign at the inner side of the cylinder [37-41]. The axial field produced by the hollow cylinder can then be expressed as:

$$B_z(z) = \frac{B_i}{2} \left\{ \frac{z_2}{\sqrt{(z_2^2 + r_o^2)}} - \frac{z_1}{\sqrt{(z_1^2 + r_o^2)}} - \frac{z_2}{\sqrt{(z_2^2 + r_i^2)}} + \frac{z_1}{\sqrt{(z_1^2 + r_i^2)}} \right\} \quad \text{Eq. 3}$$

With B_i the saturation magnetic field ($\mu_0 M_s$) of the ferromagnetic material, $z_1 = z - l/2$, $z_2 = z + l/2$, l is the height of the cylinder, r_o is the outer radius and r_i is the inner radius of the cylinder.

For the ferroshim design we will constrain ourselves to a superposition of various uniaxial cylindrical tubes. The outer radius of the ferroshim is given by the available bore size of the magnet and the other dimensions and displacements from the field center are determined by numerical optimization (Matlab). The optimization algorithm tries to achieve our design objectives, such as the field offset between the position of the gyrotron cavity and the NMR sample, with optimum field homogeneity at both positions, starting from the experimental field profile of the magnet without the FSA. The analytical expressions based on eq. 3 allow for a very fast optimization (seconds) and high accuracy, in contrast to finite element calculations and provides the solution for the length and thickness of the ferromagnetic shell that has a zero Z2 field gradient in the center. Note that as the field produced by the ferroshim assembly can be represented by a superposition of symmetrical cylindrical current sheets, the field near the magnet center can be expanded in the form of Legendre polynomials and the homogeneity in the radial direction is directly related to the homogeneity in the axial direction. An optimization of the field along the magnet axis automatically ensures a correlated homogeneity also along the radial dimension.

The full analytical expressions for the FSA field profile can then be easily used for a fast numerical optimization based on the design constraints. It is assumed that the ferromagnetic shim tube is made of pure iron with a homogeneous saturation field of 2.15 T [42] and the magnetization is assumed collinear with the applied external field. In this optimization, the outer diameter of the FSA was fixed at 88 mm and the inner diameter was constrained to be larger or equal to 72 mm, to fit the 89 mm room temperature bore of a wide-bore NMR magnet and allow using a standard solid-state NMR probe. All other dimensions are freely optimized. The optimization goal was based on a combination of optimum NMR field homogeneity and gyrotron field homogeneity at the design field offset and weighted by

appropriate factors. To allow for easy manufacturing, all elements are constrained to cylindrical shapes.

To achieve sufficient magnetic field homogeneity at the region of the position of the gyrotron cavity, two smaller rings are added symmetrically on each side of the center ferroshim tube. In principal only one additional ring is required to achieve the desired field homogeneity, however, the second iron ring is introduced to keep the ferroshim assembly symmetrically so that there are no net forces on the assembly. Two aluminum spacer rings are placed between each iron ring and the center tube to keep the iron rings in place. A third small ring near the center is introduced to obtain a better homogeneity at the NMR center. During the optimization a larger weighting factor was given to the central magnetic field homogeneity (at the position of the NMR sample) to reflect the more stringent demands with respect to the field homogeneity at the position of the NMR sample as compared to the field homogeneity required to operate the gyrotron.

The resulting on-axis magnetic field profile with the ferroshim assembly inside the NMR magnet is shown in Figure 1 (bottom, green) together with a rendering of the 3D mechanical model of the FSA (Figure 1, top).

As a consequence of the force-free design, the described ferroshim assembly effectively creates three different regions along the z-axis of the magnet with different magnetic field strengths – the center region used for NMR experiments and two regions with slightly higher magnetic field values of which one will be used to operate the gyrotron cavity.

In Figure 1 the region in which the gyrotron cavity will be operating is highlighted in green and is about 25 mm long. The center of the gyrotron cavity will coincide with the center of the small ring of the ferroshim assembly.

The location of the NMR sample is highlighted in orange in the same figure and this region is about 30 mm long. The sample is still located in the iso-center of the magnet, however, due to the high magnetic field homogeneity of the native magnetic field, the position of the sample can be varied over a wide range as indicated in Figure 1.

The symmetry of the FSA reduces the net forces on the assembly to (near) zero. From the simulations it is estimated that the outer rings of the FSA will experience a small force of about 20 N towards the center of the magnet, which is counteracted by the aluminum spacers. If the FSA is displaced along the z-axis, a non-zero force is generated that will drive the FSA back to its center position where the net force in the z-direction is zero. Due to its radial symmetry, the net forces in the radial direction are zero. If the FSA is displaced, the radial force will become non-zero towards the direction of the displacement.

Installation of the Ferroshim Assembly

Installation of the FSA requires a complete discharge of the superconducting magnet. Once the FSA is installed, the magnet is brought back up to its maximum field strength according to the manufacturer's instructions. Positioning the FSA is critical to achieve the desired magnetic field-profile and the required homogeneity. The FSA is sandwiched between two PVC pipes which can be moved along the magnet bore (z-axis) by ± 5 mm for fine

adjustment of the shape of the field profile. During the process of ramping the current up to its desired value, audible clicking sounds were observed with the FSA present, which were attributed to the relief of mechanical stresses in the magnet. After the magnet was brought up to full field the cryo-shims were changed according to the values recommended by the manufacturer. No further adjustments to the values of the cryo-shims were performed to optimize field homogeneity.

On-Axis Field Profile

In Figure 2 (top) the on-axis field profile as measured using a Hall probe and the simulated field profile are shown. The experimental and theoretical field profiles are in excellent agreement, with noticeable differences (>1 mT) occurring at regions several centimeters removed from either the location of the gyrotron cavity or the NMR sample. However, these differences are well within the field resolution of the Hall sensor and are negligible for operating a gyrotron.

In this particular configuration, we observed a field offset of 54 mT between the location of the NMR sample and the location of the gyrotron cavity, which is in very close agreement to the theoretically predicted offset of 55 mT. The small discrepancy between the experimental and theoretical value can be compensated by a small solenoid (± 40 mT), located at the gyrotron cavity, allowing for fine tuning of the magnetic field strength and frequency tuning of the gyrotron. Note that the gyrotron output frequency is a function of the static magnetic field (including the field generated by the solenoid) and the beam voltage. More detailed views of the NMR sample and cavity region are shown in the inserts below (see Figure 2, bottom). Within the resolution of the Hall probe (10 mT) the simulated and experimental field profiles match very well.

As described above, the gyrotron requires a homogenous field of ± 500 ppm over a range of 28 mm. In Figure 2, bottom (right) these limits are indicated by the dashed red lines and it is evident that the presented ferroshim design easily fulfills the required design specifications.

The physical dimensions of the FSA strongly depend on the actual saturation constant of the steel. However, without measuring the saturation constant of the exact material that is used to fabricate the ferroshim inserts, we must rely on values published in the literature. We found that published data for generic steel grades were sufficiently accurate for the design of the FSA [42] and no further iterations were necessary to match the actual field offset created by the ferroshims to the desired field offset. All experimental data shown in Figure 2 are from the first fabricated set of steel tubes.

The overall experimental field profile presented in Figure 2 shows some asymmetry between the two regions of maximum magnetic field strength. This asymmetry can be a result of the specified machining tolerances or a small offset from the magnet center along the vertical axis. However, in this particular application, only one region has to fulfill the requirements for the operation of the gyrotron, since the second region of maximum field strength is only present to create a symmetric force-free design of the FSA.

Magnetic Field Homogeneity

In Figure 3 ^{13}C MAS-NMR spectra of adamantane are shown with (top, green) and without (bottom, blue) the FSA installed. Without the FSA present we observed a ^{13}C linewidth (FWHM) for adamantane of 1.6 Hz and 2.1 Hz for the methylene and methine carbons, respectively.

The quality of the linewidth can be assessed by observing the natural abundance ^{13}C satellites with a splitting of ~ 32 Hz [43], indicated by arrows in Figure 3 (insert). Without the FSA present, the satellites are clearly visible, while they only appear as a shoulder in the adamantane spectrum with the FSA present. The linewidth at the signal intensity of the ^{13}C satellites is 16 Hz without the FSA present and about 31 Hz with the FSA present. This superior line width is achieved by only optimizing the longitudinal position of the probe without the use of room-temperature shims. A linewidth well below 5 Hz (FWHM) for the methylene carbon is achieved within a few seconds of optimizing the probe position, while linewidths well below 2 Hz (FWHM) require more careful adjustments but still can be achieved very quickly (tens of seconds). Furthermore, we found that the linewidth is highly reproducible once the optimum probe position is known inside the magnet.

Once the FSA is installed, we observed a minimum ^{13}C linewidth for the methylene and methine carbon of 3.4 Hz and 3.2 Hz, respectively. Again, the linewidth was optimized by only moving the NMR probe vertically along the magnet bore (z-axis). Installing the FSA shortens the homogeneous region of the magnetic field considerably (see Figure 1). However, we found that we were able to move the probe from the iso-center to a position about 20 mm below the iso-center and still acquire linewidth well below 5 Hz. Changes of the Larmor frequency are easily corrected by adjusting the carrier offset of the NMR channels and line shape distortions can be corrected using the Z1 cryo-shim.

Having this large range of probe positions is very advantageous when designing an integrated gyrotron. In this FSA design the distance between the position of the NMR sample and the center of the gyrotron cavity is 80 mm (see Figure 2). In the current mechanical design of the integrated DNP-NMR system the distance between the center of the gyrotron cavity and the end of the collector is about 35 mm, and the distance between the center of the solid-state rotor and the top of the NMR probe is about 40 mm. This leaves about 5 mm between the bottom of the collector and the top of the NMR probe for optimizing the axial position of the gyrotron. For an integrated gyrotron system it is crucial to keep the distance between the center of the cavity and the bottom of the collector as short as possible. Therefore, we chose to extract the microwave power on the same side at which the electron beam enters [25, 26]. This is different to the more common design in which the electron beam first enters the cavity, passes through the internal mode converter, before being absorbed by the collector [26]. However, extracting the microwave power at the same side at which the electron beam enters results in a considerably more compact gyrotron design. The overall length of the transmission line connecting the gyrotron to the NMR probe is only about 70 mm long, which is significantly shorter than transmission lines used to connect a stand-alone gyrotron to the DNP-NMR probe. Inside the bore of the NMR magnet, the space above the sample is almost completely occupied by the collector of the gyrotron and having this extra space due to the large homogenous field region of a wide-

bore NMR magnet removes some of the very strenuous constraints in the mechanical design of an integrated gyrotron for DNP-NMR spectroscopy. Additional details of the overall system design and the gyrotron will be given in a forthcoming publication.

In its current implementation, the room-temperature shims are removed for simplicity. However, small, zonal room-temperature shim coils can be integrated into either the aluminum spacers or directly integrated into the NMR probe to allow compensating for any field gradients.

Field Drift due to Temperature Drifts

In NMR experiments, especially solution-state NMR experiments, the static magnetic field must be extremely stable and modern NMR magnets are engineered to minimize the drift rate to values well below 10 Hz/hr. To further stabilize the magnetic field, it is common in solution-state NMR experiments to use a separate lock channel in combination with a Z0 room-temperature coil to compensate the magnetic field drift to achieve high resolution spectra. For solid-state NMR experiments, particularly DNP-enhanced solid-state NMR experiments, these drift requirements can often be somehow relaxed because the intrinsic linewidth of the samples under study are often larger compared to solution-state NMR experiments and slightly higher drift rates can be tolerated.

While ferromagnetic inserts are a simple way to modify the magnetic flux lines inside a superconducting magnet to achieve a desired field profile, they also introduce further complications with respect to the field stability. Because the saturation field of the steel not only depends on the carbon content of the steel but also on the ambient temperature, we have observed significant shifts of the resonance frequency during characterization of the FSA – far beyond the 10 Hz/hr native drift rate of the magnet – due to changes of the ambient temperature. Independent measurements of the ambient temperature showed a direct correlation between the resonance shift and the room temperature and without any further regulation the proton frequency can change at a rate of about 600 Hz/K. During initial characterization of the FSA we found that restricting the airflow throughout the magnet bore can reduce the temperature induced drift significantly. In addition, having a constant, temperature controlled flow of air through the magnet bore and tight regulations on the ambient temperature greatly minimize the temperature induced field drift.

This field drift can be further minimized by actively controlling the temperature of the FSA either by integrating a water jacket into the FSA design or immersing the FSA into a stream of temperature regulated air. In combination with Z0 room temperature shim coil, which can either be integrated into the aluminum spacer of the FSA (see Figure 1) or the MAS probe, we anticipate the temperature induced field drift to be negligible. These options are currently under consideration and will be integrated into future designs.

Changes in the ambient temperature will cause an expansion/contraction of the FSA center tube and the aluminum spacer (Figure 1). Given a length of the center tube of about 119 mm and a thickness of the aluminum spacers of about 19 mm, we estimated an axial displacement of the center of the magnetic field at the position of the gyrotron of 1.1 $\mu\text{m/K}$ using the published thermal expansion coefficients for aluminum and steel [42]. We

concluded that this small axial displacement will have no effect on the gyrotron performance, given the very modest field homogeneity requirements (0.1 %) over the length of the cavity.

Conclusion

In summary, we are presenting a simple and elegant approach to create a two-isocenter magnet required to operate an integrated gyrotron inside a superconducting NMR magnet. The modeling procedure allows for very fast optimization of the FSA geometry and the presented design is easily adapted to other types of wide-bore NMR magnet. The only requirement is a sufficiently specified axial field profile of the superconducting magnet. The simulated and experimental field profiles are in excellent agreement and we demonstrate that it is possible to generate a section with a homogeneity of ± 500 ppm with the correct field offset for the gyrotron. In addition, we have shown that using a ferromagnetic insert to produce the desired field profile has only minimal effects on the field homogeneity and therefore minimal impact on the observed line width in a NMR experiment.

We believe the described approach is especially interesting for high-frequency (> 500 MHz, 11.7 T), (solid-state) DNP-NMR experiments at liquid nitrogen temperatures. At this temperature solid-state microwave/THz source currently don't produce sufficient output power and gyrotrons remain the only demonstrated device to reliably deliver sufficient microwave/THz power to effectively drive the DNP process. However, since static magnetic field strength required to operate a fundamental mode gyrotron is similar to the magnetic field strength required for NMR experiments, the presented FSA offers an attractive way to incorporate the gyrotron into the NMR magnet without altering an existing magnet design.

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Highlights

- A ferroschim design to create a two iso-center magnet is presented
- The proposed ferroschim design allows for integrating a high-power microwave source such as a gyrotron into a superconducting NMR magnet
- The magnetic field homogeneity for high-resolution, high-field solid-state NMR spectroscopy is conserved

Figure 1.

(Top) 3D rendering of the mechanical design CAD model showing the steel rings and tubes (dark) and the aluminum spacers (light). (Bottom) Native on-axis magnetic field profile (dashed, blue) and simulated field profile with FAS present (green). The position of the gyrotron cavity is indicated by the dark green area and the position of the NMR sample is indicated in light orange. The dashed orange lines indicate the location of the steel ring and tubes. The field is scaled to a maximum of 9.4 T of the native magnetic field.

Figure 2.

Top: Experimental on-axis magnetic field profile with FSA installed (solid green line) and simulated field profile (dashed orange line). The positions of the gyrotron cavity and the NMR sample are indicated by a green and an orange square, respectively. The positions of the ferroschim tubes are indicated at the top of the figure, dark areas indicate sections made of steel, light areas indicate parts made from aluminum. (Bottom) Detailed view of the NMR sample region (left) and the cavity region (right). The ± 500 ppm limit for the field homogeneity at the location of the gyrotron cavity are indicated by horizontal red, dashed lines.

Figure 3.

Room temperature ^{13}C (Bloch decay) MAS-NMR spectra of adamantane with (top) and without (bottom) FSA installed. Both spectra were recorded under identical conditions. A total of 16 transients were recorded at 5 kHz spinning frequency and 10 KHz ^1H decoupling during an acquisition time of 600 ms. No line broadening was applied during data processing. The insert shows a detailed view of the methylene carbon region. The arrows indicate the natural abundance ^{13}C satellites. Spectra are referenced to the methylene carbon at 38.48 ppm [44].