

# HIGH TEMPERATURE SUPERCONDUCTING RADIO FREQUENCY COILS FOR NMR SPECTROSCOPY AND MAGNETIC RESONANCE IMAGING

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**Abstract.** High-temperature superconductivity has a significant opportunity to improve the performance of nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI) systems. The low rf losses and low operating temperatures of superconducting coils allow them to improve the signal-to-noise ratio in applications where the system noise dominates that of the sample under study. These improvements translate into new capabilities and shorter measurement times for NMR and MRI systems. In this pedagogical paper, we discuss the implementation and impact of high- $T_c$  superconducting thin films in rf coils for NMR and MRI applications.

## 1. Introduction

Nuclear Magnetic Resonance (NMR) has been employed for more than 50 years to study the physics and chemistry of atoms and molecules. It has developed into a highly refined and precise method for characterization and identification of complex molecules, as well as non-invasive imaging. Many generations of scientists have contributed sophisticated methods of using NMR to peer more and more deeply into molecular structure. High Temperature Superconductivity (HTS) comes into this mature field at a relatively late stage in its development. As such, HTS has not introduced any fundamentally new methodology for performing NMR spectroscopy or Magnetic Resonance Imaging (MRI). However, HTS presents the opportunity to significantly enhance existing measurement methods by improving the signal-to-noise ratio of the detection system. This has advantages in

certain applications of NMR spectroscopy or MRI for which the sample noise does not dominate the noise performance of the entire measurement system.

This paper presents a simple pedagogical discussion of the impact of HTS on NMR spectroscopy and MRI. It is written by an outsider; hence, the reader is cautioned to consult the literature for a more complete treatment of the subjects discussed here. A beginning student should consult Slichter's book for the theory of NMR [1], and any one of a number of practical introductions to NMR spectroscopy [2, 3]. There is also an excellent review paper on the use of HTS in NMR spectroscopy [4].

In this paper, we begin by reviewing the fundamentals of NMR, discuss some of the important uses of NMR in spectroscopy, and review the basic methodology of an NMR experiment. We then discuss the requirements for performing good NMR spectroscopy, setting the stage for the impact of HTS rf coils on the measurement process. The conditions under which HTS rf coils reduce system noise will be presented, followed by a discussion of the advantages and disadvantages of using HTS rf coils. We conclude by giving an example in which the HTS coil gives significant improvement in the signal-to-noise ratio in real NMR spectroscopy and MRI applications.

## 2. What is magnetic resonance?

Magnetic resonance occurs under a variety of conditions. First, we require a magnetized object, such as a ferromagnetic domain, or a collection of paramagnetic electron spins, or a set of nuclear spins. The magnetization can be represented by a vector  $\mu$ . Next, a strong dc magnetic field  $\mathbf{B}_0$  is applied to the system. In the classical picture, the magnetic field will exert a torque  $\tau = \mu \times \mathbf{B}_0$  on the magnetization or spins, causing the magnetization vector to precess about the direction of the magnetic field at a rate proportional to the field strength, given by  $\omega_{precession} = \gamma B_0$  where  $\gamma$  is the gyromagnetic ratio. The gyromagnetic ratio depends on the object carrying the magnetic moment. For electron spins it depends on the Landé g-factor, which includes spin and angular momentum degrees of freedom, and for nuclear spins  $\gamma$  depends on the particular nucleus studied. For example for a proton,  $\gamma/2\pi = 42.5$  MHz/T, while for a  $^{13}\text{C}$  nucleus,  $\gamma/2\pi = 10.5$  MHz/T. The precessing spins create an oscillating magnetization in the plane perpendicular to the applied magnetic field. If an rf magnetic field, polarized in that plane, now is introduced, it can be resonantly absorbed if the rf frequency matches the precession frequency of the spins. This resonant absorption is magnetic resonance.

The quantum-mechanical description of magnetic resonance is as follows. The applied magnetic field gives rise to a Zeeman splitting between

“up” and “down” spin states (i.e., spin aligned along and against the magnetic field direction). This comes about from the interaction of the magnetic moment  $\mu$  with the applied field  $\mathbf{B}_0$ , with an energy  $E = -m_I \gamma \hbar B_0$ , where  $m_I$  is the component of the nuclear spin in the direction of  $\mathbf{B}_0$ , and  $\hbar$  is Planck's constant divided by  $2\pi$ . The Zeeman splitting energy between “up” and “down” states for a spin  $1/2$  is given by  $\Delta E = \gamma \hbar B_0$  (the proton and the  $^{13}\text{C}$  nuclei both have nuclear spin  $I = 1/2$ .) If an rf photon of energy  $\hbar\omega_{rf} = \Delta E = \gamma \hbar B_0$  is present, and the polarization conditions are satisfied, there is resonant absorption. Both the classical and quantum-mechanical descriptions give the same condition for magnetic resonance.

As mentioned above, magnetic resonance occurs in many different systems: nuclear spins (NMR), electron spins (electron spin resonance and electron paramagnetic resonance), ferromagnetism (ferromagnetic resonance), and antiferromagnetism (antiferromagnetic resonance). In this paper we shall focus on NMR.

### 3. What does NMR tell you?

The precession rate of the nuclear spin is a sensitive function of the magnetic field experienced by the nucleus. Although the applied external field can be substantial (1 - 20 T), there are other magnetic fields at the site of the nucleus which can contribute to the precession rate. These fields come from electrons orbiting the nucleus, and their value will depend on the chemical structure of the atom or molecule into which the nucleus is incorporated. As a result, the nuclear spin precession rate will vary slightly depending upon the chemical bonding of the electrons around that nucleus. This variation in the precession rate, and therefore in the NMR frequency, is called the chemical shift [2, 3]. It gives important information about the molecule and can be used as a “fingerprint” of the chemical structure of the molecule, because in general, each nucleus experiences a slightly different chemical shift.

The degree of chemical shift depends on the gyromagnetic ratio of the nucleus involved. For protons, the chemical shift range is on the order of 10 parts per million (ppm). This means that the NMR frequency will vary from the nominal value by about 1 part in  $10^5$  due to chemical effects for a given applied magnetic field. For  $^{13}\text{C}$ , the chemical shift range is about 200 ppm.

Other information which can be obtained from NMR relates to molecular dynamics. For instance, segments of molecules may be free to rotate, and nuclei in these segments give information about their rate of rotation. Other information comes from the way in which polarized nuclear spins become de-polarized through their interactions with the environment. There

are two measurable relaxation time scales,  $T_1$  and  $T_2$ .  $T_1$  is the spin-lattice relaxation time and  $T_2$  is the spin-spin relaxation time. Multi-dimensional NMR spectroscopy also can give information about which nuclei are neighbors in a complicated molecule, simplifying the structural determination and also providing unique information for molecular identification [2, 3]. All of this information contributes to understanding the molecules under study.

#### 4. How is NMR done?

An NMR experiment begins by polarizing the nuclear spins with a strong static magnetic field. In modern NMR spectrometers and MRI systems, the magnetic field is created by a low- $T_c$  superconducting magnet. State-of-the-art NMR spectrometers have static magnetic fields  $B_0$  which are typically 7.1 to 18.8 T (proton precession frequency of 300 to 800 MHz), MRI magnetic fields are 0.5 to 1.5 T (proton precession frequency of 21 to 63 MHz), but low cost systems can be 0.1 T and clinical research systems can be 4.7 T. With this field applied, the nuclear spins are set into precession at a rate given by the field strength and the gyromagnetic ratio of the nucleus of interest,  $\omega = \gamma B_0$ . In NMR spectrometer systems the precession frequency is typically in the range of 100 to 800 MHz. In MRI systems, the precession frequencies are in the range of 10 to 100 MHz. Rf magnetic fields of the correct frequency and polarization now are introduced to manipulate the precessing spin system using rf drive coils. The rf fields are usually pulsed. These pulses are designed to perform basic quantum-mechanical manipulations of the spin system. The details of these pulse sequences can be quite intricate, and the reader is referred to the extensive and detailed literature on the subject [1, 2, 3]. A simple and useful rf pulse is the  $\pi/2$  pulse. This causes the spins to rotate through an angle of  $90^\circ$  away from the applied magnetic field direction, causing the spins to lie in the plane perpendicular to the applied field. This produces a maximum transverse rf signal, which is easily detected by the pickup coils of the NMR spectroscopy or MRI system.

If there are several types of nuclei in the sample, then each nuclear spin precesses at a frequency depending on its gyromagnetic ratio and environment. Very often multiple-frequency rf pulses are used to simultaneously stimulate NMR in several different nuclear species. Once all of the spin manipulations have been made, the system is allowed to relax in a process called free induction decay (FID). The system uses pickup coils to collect the FID voltage signal as a function of time. This signal is then Fourier transformed to get the NMR spectrum of the system. The direct FID signal can give the relaxation time scales  $T_1$  and  $T_2$ , while the FID spectrum

gives the chemical shift and other information.

In good spectrometers with high signal-to-noise, the NMR spectrum is remarkably clean [2, 3]. In practice, the NMR spectrum linewidths are on the order of 1 Hz for NMR frequencies on the order of 500 MHz. This means that very small splittings, on the order of 0.01 ppm can be resolved, making NMR spectroscopy extraordinarily information rich.

One can get an idea of what an NMR spectrometer looks like from browsing the web sites of commercial manufacturers of spectrometers [5, 6]. The bulk of the instrument is made up of the low- $T_c$  superconducting magnet and its associated dewar. The dewars are remarkably efficient and may require the addition of liquid nitrogen only once every few weeks, and liquid helium once every few months.

## 5. Requirements for Good NMR Spectroscopy

In NMR spectroscopy one often deals with small samples, sometimes smaller than 1 microgram. Hence, the most important consideration for an NMR spectrometer is maximizing the signal-to-noise ratio (S/N) of the system. The most direct way to maximize the S/N is to use the strongest static magnetic field,  $B_0$ , possible. It is found that the voltage S/N ratio scales as  $S/N \sim \omega_{precession} M / \sqrt{R} \sim B_0^{7/4}$  [7, 8, 9]. One power of  $B_0$  comes from the fact that the magnetization  $M$  of the (paramagnetic) sample increases linearly with  $B_0$ , and a second power of  $B_0$  comes about because the rf voltage inductively picked up by the receive coil scales with  $\omega_{precession}$ , which is directly proportional to  $B_0$ . However, the (normal-metal) probe resistance  $R$  increases as  $B_0^{1/2}$ . In other words, as the precession frequency increases, the skin depth in the metallic coil decreases, enhancing the losses. Hence, the overall gain in S/N is a bit less than a power of 2. Because of this strong scaling of S/N with static magnetic field strength, and the fact that spectral features are more easily distinguished at high fields (greater dispersion), there are efforts to create stronger ( $B_0 \geq 20$  T) superconducting magnets for use in NMR spectrometers. However, the great expense and engineering efforts of creating these more powerful magnets is prohibitive, so NMR spectroscopists are looking for other ways to improve system S/N.

HTS materials present a unique opportunity to improve S/N without great expense or replacement of the superconducting magnet. The low resistance and low operating temperature of HTS pickup coils significantly increase the S/N of the detection system. The fact that the HTS pickup coils are kept under cryogenic conditions also presents the opportunity to introduce other cooled circuit elements such as a preamplifier, matching network and transmit/receive switch. These considerations have made HTS pickup coils very attractive, in lieu of an increase in static magnetic field strength.

The improvement in S/N allows smaller samples to be studied. This in turn could reduce the cost of an NMR spectrometer because a superconducting magnet would not have to create a homogeneous field over a great volume.

Other considerations for good NMR spectroscopy include the need for good sensitivity in field and frequency to distinguish closely-spaced peaks in the FID spectrum, such as splitting coming from dipole-dipole interactions. Good sensitivity also requires extremely good magnetic field homogeneity. Each nucleus in the sample must see the same external magnetic field if the small ( $\sim 10$  ppb) chemical shifts are not to be smeared. This means that a  $1:10^9$  homogeneity of  $B_0$  must be maintained over the volume of the sample (typically a cylinder about 5 mm in diameter and 15 mm tall). The magnetic field homogeneity is created by a series of shim coils (typically 28 or so) which excite magnetic fields with the symmetries of the spherical harmonics. One also needs good S/N and high dynamic range to see both large and small peaks in the NMR spectrum. Finally, an improved S/N also cuts down measurement time, a key consideration for MRI and for sophisticated multi-dimensional NMR spectroscopy techniques.

## 5.1. OVERVIEW OF AN NMR SPECTROSCOPY SYSTEM

There are three parts of an NMR spectroscopy system of interest to us. The first is the sample which contains the polarized spins producing free induction decay. The second is the probe, which is a tuned resonant rf coil probe for detecting the FID from the sample. The probe is a simple inductor-capacitor (LC) resonator circuit which is tuned to the NMR signals from specific nuclei, such as  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , etc. This is the part of the system which can be made with a large-area HTS thin film. Finally, we have the receiver system which mixes the detected FID signal down to lower frequencies. This part of the system can be improved with a cryogenic preamplifier and matching network.

The probe coil has a quality factor  $Q$ , and frequency selectivity given by  $Q = \omega L/R$ , where  $\omega$  is the angular frequency of the NMR signal,  $L$  is the self inductance of the coil, and  $R$  is the equivalent resistance of the coil. Since  $Q = \omega/\delta\omega$  is inversely proportional to the 3-dB bandwidth of the resonator,  $\delta\omega$ , it is a measure of the frequency selectivity of the coil. HTS coils have the advantage of a significantly smaller resistance  $R$  than their normal-metal counterparts with the same inductance. Hence, the quality factor of the receive coils is significantly higher for HTS coils, making them attractive for certain applications, as we shall see later.

## 5.2. NOISE IN NMR SYSTEMS

There are three sources of noise in the NMR spectrometer detection system of interest to us here. The first is thermal noise from conducting samples. One can think of the sample as a resistor at finite temperature (usually room temperature). For instance, biological samples are often in conducting fluids. There are thermally-induced fluctuation currents in this resistor which produce noise, called Johnson noise. Very little can be done about this source of noise if one wants to characterize the sample (or organism) at room temperature and in its natural state. A second source of noise is thermal noise from resistance of the FID voltage pickup coil. Again Johnson noise in the coil will add noise to any detected signal. A third source of noise is noise in the receiver system, including the preamplifier, the mixer and detector.

HTS is of benefit only when the second and/or third noise sources dominate the system noise.[8] In other words there is no benefit to using HTS pickup coils in NMR or MRI systems where the sample noise dominates the system noise.

## 5.3. HOW DOES HTS IMPROVE THINGS?

In the case where the probe and receiver dominate the noise of the NMR system, one has the following approximate scaling relation for the signal-to-noise ratio (S/N) of the system as the coil properties are varied [4]:  $S/N \sim \sqrt{\frac{\eta Q}{T_p + T_A}}$ , where  $\eta$  is the filling factor of the coil system (i.e. fraction of the rf energy created by the coil which is stored in the sample volume),  $T_p$  is the effective probe temperature and  $T_A$  is the receiver noise temperature. HTS rf pickup coils have higher  $Q$  (because of their lower surface resistance) [10], and they have a lower probe temperature  $T_p$ . These improvements are offset by a reduced filling factor  $\eta$  for the HTS coils. The reduced filling factor comes about because existing HTS coils are made on flat, rigid substrates, whereas optimized normal-metal coils are made on curved substrates which wrap around the sample. Table 1 summarizes the current state-of-the-art for the S/N improvement of HTS pickup coils [4].

In this table, the filling factor is normalized to that of the normal-metal probe. The filling factor is about a factor of 5 worse for the HTS coil because of present-day geometrical constraints in the deposition of the films. However, recent progress in ion-beam-assisted deposition of HTS thin films has created the opportunity to make HTS coils on flexible substrates. Thus improvements in the filling factor of HTS coils should soon be possible.

In Table 1 the quality factor,  $Q$ , of HTS coils is conservatively estimated to be about 10,000, versus about 250 for their normal-metal counterparts.

TABLE 1. Signal-to-noise comparison of normal-metal and HTS rf probes

Factor	Normal Probe	HTS Probe
$\eta$	1	0.2
Q	250	10,000
$T_p$	300	75
$T_A$	80	80
S/N	1	4.5

Higher quality factors in HTS coils have been demonstrated (e.g.,  $Q = 70,000$  at 7 T) [8, 11], and the  $Q$  appears to be limited by flux motion [8]. However, there are upper limits on the  $Q$  of the coil imposed by the NMR measurement process itself - see below.

The probe temperature comparison in this table is a bit unfair. The normal-metal probe is taken to be at room temperature, while the HTS coil is, of course, cooled below the HTS transition temperature. A more fair comparison would be between HTS coils and cooled normal-metal coils, as has been done for the case of MRI coils [8]. However, the amplifier noise temperature is taken to be the same for each system. Overall, an improvement of 4.5 in the S/N is expected simply by substituting an HTS pickup coil for a normal-metal coil. Such an improvement in S/N has been demonstrated in a commercial cryogenic product made by Conductus and marketed by Varian [4, 6, 12]. Similar improvements have been made with the commercial cryogenic probes made by Bruker [5].

## 6. HTS and MRI

The use of HTS pickup coils in magnetic resonance imaging (MRI) also is quite promising. The most familiar example of MRI, that of whole-body imaging, does not benefit from the introduction of HTS coils because the noise of the sample dominates the system noise. However, low-field MRI, with magnetic fields  $B_0 \sim 0.1$  T and NMR frequencies on the scale of 5 - 20 MHz, can benefit from the use of HTS rf pickup coils. These systems are designed to look at small body parts or other small samples [13, 14, 15, 16]. They also are much less expensive than full-body MRI systems, and may find their way into other applications. However, in order to recover the small signals generated in low-field MRI, the S/N of the receiver system must be enhanced. HTS rf coils are a clear solution to this challenge. Here, HTS has an additional advantage because the rf coils are used only for receiving the



FID signal; hence, issues of nonlinearity in the material are less pressing.

In addition to standard MR imaging, there is the application of NMR microscopy, where MRI is performed over a small volume with high resolution [8, 10, 17]. In this case the sample (and therefore the signal) of interest is small. System noise can have a significant contribution from the receiver, and introduction of an HTS coil is clearly beneficial. A simple estimate shows that the coil  $S/N \sim \sqrt{Q/T_p}$ , where  $Q$  is the quality factor and  $T_p$  is the probe temperature [8]. One group has demonstrated a signal-to-noise improvement of a factor of 60 in an HTS coil at 10 K versus a Cu coil at room temperature [8]. This dramatically improves the capability of the NMR microscope.

Once again the main benefit of HTS is to improve the  $S/N$ . Improved  $S/N$  leads to shorter acquisition time for the image because the image acquisition time scales as  $(S/N)^{-2}$  [8].

## 7. Constraints on HTS RF Coils

Although the above discussion makes it appear that HTS pickup coils should be clearly superior to their normal-metal counterparts, there are serious challenges to their introduction into NMR and MRI applications. Here, we discuss three significant constraints imposed on HTS coils in NMR spectrometer systems.

### 7.1. MAGNETIC FIELD PERTURBATION

First, the HTS coil must be introduced in such a way as to minimize the perturbation of the static magnetic field  $B_0$  [4, 18]. As noted above, the nuclei in the sample must all experience the same external magnetic field to at least 1 part in  $10^9$ . This is required to maintain NMR spectral line widths on the order of 1 Hz, or less, for high-quality spectroscopy. However, the introduction of a superconductor into this magnetic field is likely to alter its distribution since the superconductor will enter the critical state and create an inhomogeneous distribution of magnetic flux within itself. This in turn could ruin the homogeneity of the magnetic field in the sample.

The solution to this problem starts with use of thin-film superconductors for the rf coils. The thickness of these films is typically less than  $1 \mu\text{m}$ . Next, an external field  $B_0$  is applied in the plane of the film, leading to minimal disruption of the magnetic flux by the superconductor. In addition, the superconducting coils also must be kept relatively far away from the sample to minimize the inhomogeneity of the field at the sample. Unfortunately, this has the effect of decreasing the filling factor  $\eta$  of the coil, although this reduction is dictated to some extent by the cryogenic constraints as

well. Finally, there also is the significant engineering challenge of keeping the superconducting rf coils aligned with respect to the direction of the field  $B_0$  as the coils are cooled from room temperature [19]. If the coils tilt too much from the ideal orientation, the magnetic field homogeneity at the sample position would be lost. In addition, the HTS rf coils must not move during the pulsing of gradient coils used in spectroscopy, when significant forces can act on the currents flowing in the coil [19]. These pulses last for milliseconds, and can excite mechanical resonances of the coil assembly.

## 7.2. HIGH TRANSMITTER CURRENTS

The rf coils in NMR spectrometers often are used for both transmitting and receiving rf pulses. This is a challenge because it requires that the coils operate over a wide dynamic range, from high power during transmission to low-level signal recovery during receive mode. In transmit mode, a high-power pulse is sent to the sample. For instance, a  $\pi/2$  rf pulse of  $H_{rf} = 1$  mT for a duration of 10  $\mu$ sec at a frequency of 400 MHz requires about 10 A of current to flow through the coil [4]. Superconductors have a limit to how much current they can support before dissipation sets in. This is defined by the critical current density,  $J_c$ . For this rf pulse, the film must have a critical current density  $J_c \geq 10^6$  A/cm<sup>2</sup> [4]. Achieving such a large critical current density in a strong magnetic field ( $B_0 \sim 20$  T) is not possible with conventional low- $T_c$  superconductors. Only superconducting materials with high critical temperatures and high upper critical fields can operate in the environment of an NMR spectrometer. Hence, HTS thin-film superconductors are required. In addition, the critical-current constraint means that the films must be cooled significantly below their transition temperature to achieve  $J_c \sim 1$  MA/cm<sup>2</sup>. In practice this means that a superconductor such as  $YBa_2Cu_3O_7$  with a  $T_c$  of about 90 K must be cooled below 77 K to operate under these conditions.

The HTS film should remain superconducting after transmitting such a pulse. In addition, its rf properties should remain linear [10]. This means that the  $Q$  and probe temperature  $T_p$  should remain constant during and after rf transmit pulses. This imposes another constraint on the HTS films. These constraints can be met through the use of epitaxial HTS thin films.

## 7.3. THE Q SHOULDN'T BE TOO HIGH!

In principle, the resistance of a superconductor at rf frequencies can be made arbitrarily small at low temperatures if it has an isotropic non-zero energy gap. This means that the  $Q$  of an rf coil made up of this superconductor can be made arbitrarily large, since  $Q = \omega L/R$ . However, larger  $Q$  is not necessarily good for an NMR spectrometer [10]. For an rf coil with

a  $Q = 10,000$ , the probe has a bandwidth of 100 ppm at 400 MHz, limited by its 3-dB bandwidth. Recall that typical chemical shifts of  $^{13}\text{C}$  are on the order of 200 ppm. Thus, a probe with a higher  $Q$  would not be able to measure all of the chemical shifts in a  $^{13}\text{C}$  NMR spectrum. However, a larger  $Q$  may be of benefit for proton NMR, where the chemical shifts are on the order of 10 ppm.

Another problem with a high coil  $Q$  is the long ring-down time of the rf energy stored in the coil. The characteristic decay time for the circulating power in the coil is given by  $\tau = Q/\omega_0$ . For an NMR resonance at 400 MHz with a coil  $Q$  of 10,000, the decay time  $\tau = 4 \mu\text{sec}$ . This means that the coil will not be able to measure the free induction decay signal from the sample for some time after the drive pulse sequence is ended. Higher coil  $Q$  factors would increase this "dead time" further. In principle, after the pulse sequence ends, one can actively decrease the  $Q$  of the coil to dissipate the stored energy. However, another danger is that a high  $Q$  can decrease the characteristic time for energy transfer between the spin system and the pickup coil. This spin damping time scale  $\tau_{\text{damping}} \sim 1/Q$ , may become too short for accurate measurement of chemical shifts or of the relaxation time scales  $T_1$  and  $T_2$  [10].

In fact, the HTS materials do not have an isotropic energy gap. Hence they have intrinsic losses which cannot be eliminated, limiting the ultimate  $Q$  attainable from an HTS rf pickup coil [20]. Nevertheless, it is believed that higher  $Q$  factors can still be achieved at rf frequencies [8]. To summarize, if the NMR measurements requires significant bandwidth, the  $Q$  of the rf receive coils must be limited. Fortunately, a high- $Q$  rf pickup coil can always have its  $Q$  reduced in a controlled manner, so that a variety of bandwidths can be achieved [10, 11].

## 8. HTS Probes for NMR Spectroscopy

We now are in a position to go into more detail about how HTS films are used in an NMR spectrometer.

### 8.1. BASIC PROBE CONFIGURATION

A basic NMR spectrometer consists of a room-temperature sample tube surrounded by rf coils, all of which are contained in the bore of a superconducting magnet. There are one or more self-resonant rf coils made of HTS films. Each coil is a simple lumped-element loop-gap LC resonator. The loop acts as the inductance and the gap acts as a capacitor. The geometry of the loop and the gap are adjusted lithographically to bring the resonant frequency,  $\omega_0 = 1/\sqrt{LC}$ , equal to the NMR frequency of interest for a given magnetic field  $B_0$ . A translating paddle can be used to fine tune

the resonant frequency of the rf coil after it is installed in the probe [18, 21]. The NMR frequency depends on the nucleus of interest (e.g.,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , etc.) and the applied static magnetic field,  $B_0$ . Hence, probes are designed specifically with one or two nuclei and a certain magnetic field in mind [22]. Often the probes are used to excite simultaneously one nucleus of interest, in addition to deuterium. The deuterium signal (from a deuterated solvent) is used in a feed back circuit to control the magnetic field  $B_0$ . The intricacies of rf probe design for high-field and low-field applications are discussed in a number of papers [11, 16, 23, 24, 25, 26].

The films are typically grown on either sapphire, MgO or  $\text{LaAlO}_3$  single-crystal substrates, which have low rf losses. In addition, the substrates must have good thermal conductivity because in use they may be cooled only along one edge [21]. These coils typically show quality factors  $Q \sim 10,000$ , even in a field of 9.4 T, as compared to normal metal coils which have  $Q$  on the order of several hundred to a few thousand.

## 8.2. CRYOGENICS AND PACKAGING

The HTS coils must be cooled to temperatures significantly below  $T_c$  to establish a large critical current density. This must be done with a cryogenic system which is independent of the neighboring superconducting magnet. Closed-cycle refrigerators, such as a Gifford-McMahon cryocooler, have been employed [4, 5, 11, 21]. There are several constraints on these cryocoolers. First, vibrations of the cold head must be minimized to maintain magnetic field homogeneity in the sample. This requires careful vibration isolation of the compressor from the cold head. Second, mK-level temperature control must be maintained because the rf properties and resonant frequency of the coil are temperature dependent. Third, the cryostat must be non-inductive, so that the rf pulses can pass through the cryostat walls without distortion. Finally, the cryostat also must accommodate a temperature-controlled sample holder which is kept near room temperature. Bruker has sold probes under the name CryoProbe<sup>TM</sup> which uses coils held at 15 to 30 K and a preamplifier and transmit/receive switch at 60 to 90 K [5, 9].

## 8.3. PREAMPLIFIER

Once the signal is received by the HTS rf coils, it must be demodulated and detected. The first step is to preamplify the signal with a low-noise amplifier. Having cooled coils presents the opportunity to reduce the noise temperature of the preamplifier by cooling it as well [27, 28]. This will decrease the equivalent amplifier temperature  $T_A$ , and increase the system S/N. A GaAs field-effect transistor amplifier operating at 77 K has a noise

temperature of just 20 K [4, 8]. The use of an all-77-K preamplifier and cables is expected to improve the system sensitivity by 75% [4]. The rf matching network also can be cooled, or even made superconducting [11]. Finally, the transmit/receive switch also can be kept at cryogenic temperature to minimize noise and losses [9].

## 9. Results with HTS Coils

### 9.1. NMR SPECTROSCOPY

There are several very convincing demonstrations that HTS provides significant S/N improvements in NMR spectroscopy and MRI applications. Bruker Instruments has demonstrated a factor of 4 improvement in S/N in their 500-MHz and 600-MHz  $^1\text{H}$  and  $^{19}\text{F}$  cryogenic probes, as well as  $^{13}\text{C}$  probes [5]. These improvements are along the lines of those estimated above. This translates to the ability to measure samples with one fourth the mass, or to measure in one sixteenth the time required with a conventional NMR probe. The measured NMR linewidths are almost as good as those measured by the conventional probe. These cryogenic probes are commercially available.

NMR spectroscopists use many sophisticated techniques to learn about the interactions of nuclear spins in complex molecules. One of these techniques is called Total Correlation Spectroscopy (TOCSY). This is basically a way of examining how spin polarization diffuses through a molecule due to nucleus-nucleus interactions. Hill has demonstrated that a Conductus HTS probe can significantly increase the S/N of a TOCSY spectrum - see Fig. 5 in Hill's paper [4].

Another spectroscopy method, called Heteronuclear Multiple Quantum Coherence (HMQC), excites two different nuclei simultaneously (e.g.,  $^1\text{H}$  and  $^{13}\text{C}$ , this is an example of two-dimensional NMR) and establishes which of these nuclei are directly bonded to each other. This kind of information can be used as a fingerprint to uniquely identify a complex molecule. However, since the  $^{13}\text{C}$  isotope is so rare (1.1% natural abundance), it takes considerable time (on the order of 12 hours) to acquire enough data to establish the HMQC spectrum. This is a situation for which HTS rf coils provide a clear advantage. With the improved S/N brought by HTS, and good long-term stability, the HMQC spectrum can be acquired in much less time. Bruker has a very clear dramatic demonstration of this improvement on their Web site for the cases of HSQC and HMBC two-dimensional NMR [5].

With the significant improvements in S/N brought by HTS coils, it may be possible to develop altogether new types of multi-dimensional NMR spectroscopy which would be impractical using conventional rf coils. Other

companies thought to be investigating cryogenic and/or HTS rf coils for NMR spectroscopy include Dupont, IGC and Nalorac.

## 9.2. MRI

The improved signal-to-noise ratio of HTS pickup coils can significantly decrease image acquisition time in MRI systems. Penn, *et al.* have demonstrated a factor of 3 improvement in S/N using an HTS coil versus a silver coil, for both at 77 K in a 0.15-T low-field MRI system [29]. A factor of 10 improvement in S/N was demonstrated by Black, Early and Johnson in an HTS pickup coil versus a room-temperature copper coil in an NMR microscope with 30  $\mu\text{m}$  resolution [10]. A factor of 5 improvement of S/N in MR imaging of a rat spine was found by Wosik, *et al.* [30]

MRI of sodium has been useful for examining cell integrity and has advantages over proton MRI for detecting certain kinds of brain disorders. However, sodium MRI suffers from lower S/N, making HTS pickup coils attractive for this application [24]. A very interesting market analysis of the impact of HTS on MRI has recently been published [31].

## 10. Conclusions

We have given a simple pedagogical overview of the impact of HTS on NMR spectroscopy and magnetic resonance imaging. Although HTS does not introduce any radically new measurement process to this field, it does make significant improvements to the signal-to-noise of the pickup system. This comes at a time when other improvements to signal-to-noise are becoming prohibitively expensive to pursue. Commercial products which employ cryogenic technology in the rf pickup coils are now available and have clearly established their superiority over normal-metal rf probes. Further improvements can be made to the HTS coils, most notably with films grown on flexible substrates for improved sample filling factor.

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