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Design of a High-Power NMR Probe for Low-Temperature Studies

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A low-temperature, high-power NMR probe head design is described which eliminates the problem of electric arc discharge commonly experienced during radiofrequency pulse cycling in a helium environment. A polychlorotrifluoroethylene (Kel-F) coil former, fitted with a solenoid coil, is heat-shrunk onto stainless-steel flanges and spot-welded inside a stainless-steel probe head assembly connected to a hollow coaxial transmission-line probe shaft. By this means, the sample coil and all high-voltage elements can effectively be isolated in a vacuum, while at the same time permitting good thermal contact between the sample and cryogenic gas. This design was used in NMR studies in the 4.6 K $\leq T \leq$ 77 K temperature range for RF pulse durations $\leq$50 ms (and longer for low RF amplitudes) and amplitudes up to $\sim$60 G. © 2000 Academic Press

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Low-temperature NMR spectroscopy (below ~77 K) requires that the sample be exposed to regular and sustained bursts of intense RF radiation while immersed in helium gas. In the presence of high RF voltages, however, the helium is ionized and cascades into a spark spanning the voltage gap. Since the consistency and reproducibility of RF field pulses at all amplitudes and durations lies at the heart of NMR spectroscopy—particularly so for studies in the rotating frame—it is crucial that the probe assembly be impervious to RF breakdown.

Specifically, such a system has to

- insulate all high-voltage components from helium gas;
- permit easy sample interchangeability;
- minimize thermal lag by maintaining good cryogen-sample contact at all times;
- introduce no spurious signals;
- be strong enough to withstand repeated electrical, mechanical, and thermal stresses;
- be sufficiently compact to fit into the tail of a flow-through-style research cryostat.

To better understand these requirements, in their relation both to each other and to the constraints they jointly impose on a low-temperature probe system, we need to look briefly at some of the apparatus typically used in low-temperature NMR. This falls into three basic categories: cryogens to cool the sample; a research dewar to hold the cryogens; and the low-temperature NMR probe system itself. Although there are a variety of other items necessary to this work—vacuum pumps, temperature sensors, vacuum helium-transfer lines, leak detectors, vacuum gauges, etc.—we will confine the discussion to the probe assembly system itself and its function in conjunction with a flow-through-type research dewar.

This is essentially a cryogenic vessel for cooling the sample, with separate reservoirs for liquid helium and liquid nitrogen. The dewar body sits on top of the superconducting magnet-solenoid vessel, with a long tail extending into the solenoid's bore, or in the case of an iron-core electromagnet, between the magnet pole faces, as shown schematically in Fig. 1.

A typical flow-through-type research dewar, with the probe assembly in place, is shown in Fig. 2. It consists of three concentric cylindrical chambers, the central and longest of which acts as the sample chamber into which the probe is inserted. The chamber immediately surrounding this central flow bore is filled with liquid helium, while the outermost chamber is filled with liquid nitrogen to cool the adjacent helium reservoir. The helium chamber communicates with the flow bore via a capillary tube leading to a diffuser plug at its bottom. The rate of helium flow is regulated by a helium-drip valve at the top of the dewar, connected to a needle tip at the entrance of the helium-capillary line. All three chambers of the dewar are isolated from one another by double walls, evacuated prior to the start of an experiment using a vacuum pump.

The probe used with such a system is essentially a coaxial transmission line running from the room temperature top end of the dewar, where it is connected to tuning-circuit elements, to a probe head assembly at the other end, containing the sample coil and temperature sensors/regulators. Typically, the probe is composed of a length of coated copper wire encased in Teflon sleeving, threaded through a stainless-steel tube spanning the entire length of the flow bore.

The probe head itself consists of a cylindrical copper shielding can mounted concentrically with the sample coil. This cylinder is wound with heater wire on its external surface and fitted with temperature sensor holders mounted close to the

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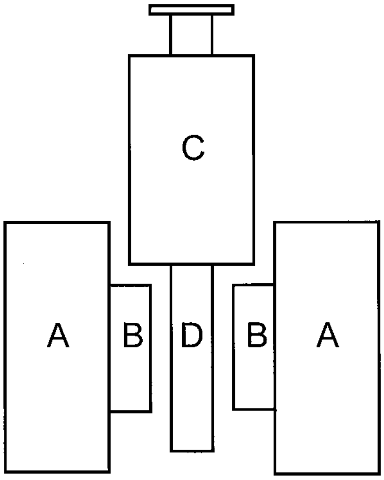

FIG. 1. Schematic diagram of a flow-through-type research dewar (C) located between the coils of an electromagnet (A) with the tail (D) extending between the pole caps (B).

sample coil. The whole probe head assembly is then soldered onto the stainless-steel probe shaft and the sample coil to the central coaxial line, thereby ensuring structural/electrical integrity. Temperature regulation is achieved by means of a feedback loop; gaseous cryogen flows past the probe head, where the sensors relay the ambient temperature to an externally mounted electronic temperature controller. This in turn sends out current to the heater wire, thereby warming the cryogen in the immediate vicinity of the sample to the desired temperature. With this scheme, a steady-state temperature—attained when the cooling rate of flow of the cryogen gas is just balanced by the heater output—can be maintained to within ±0.5 K for a length of time dependent on the target temperature chosen.

The system just described works very well when the cryogen used is nitrogen, but fails with helium due to RF breakdown caused by helium-facilitated arcing. The intuitively obvious solution is to insulate all high-voltage components from coming into contact with helium gas; this, however, proves to be more elusive than expected.

Early attempts in this direction using Teflon-coated wire failed completely, due to the presence of microscopic holes in the Teflon material through which arc-discharge paths readily formed.

The first operational design involved using sulfur as a potting material for the sample coil, in conjunction with a vacuum feed-thru (*1*); molten sulfur was allowed to coat all exposed high-voltage-carrying surfaces in the probe head itself, physically “embedding” the coil in a solid block of sulfur, while the vacuum feed-thru prevented helium gas from entering the probe shaft. Although fairly successful, this system suffered from the need for frequent overhauls; the sulfur potting was prone to cracking following even one low-temperature experimental cycle, due to the difference in thermal expansion coefficients between the potting material and coil.

A more promising approach was to design a system which, while allowing the circulation of helium gas past the sample, kept the whole coil/high-voltage coaxial line system separated from the surrounding environment by a vacuum. Initially, quartz-glass tubes were used as coil formers: the coil would be mounted on a thick quartz tube placed in the probe head, where a stainless-steel enclosure could be made to compress indium metal in a band around the tube, thereby creating an “indium seal” (*2*). Following thermal cycling, however, the glass invariably shattered at points of compression or rarefaction. The problem, therefore, was to find a material that could withstand temperature cycling, maintain a vacuum-tight seal to metal at low temperatures, and at the same time not interfere with RF radiation.

The solution came in the form of polychlorotrifluoroethylene, also known as fluoroethene, or Kel-F. This substance is

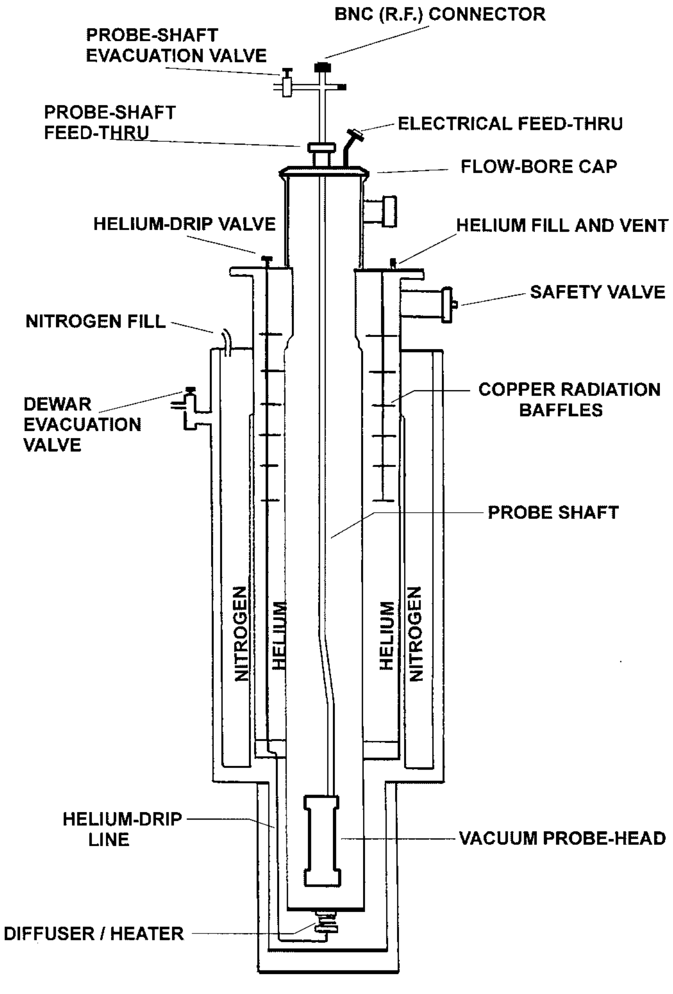

FIG. 2. Schematic diagram of a typical flow-through-type research dewar for low-temperature NMR studies, with vacuum-probe assembly in place.

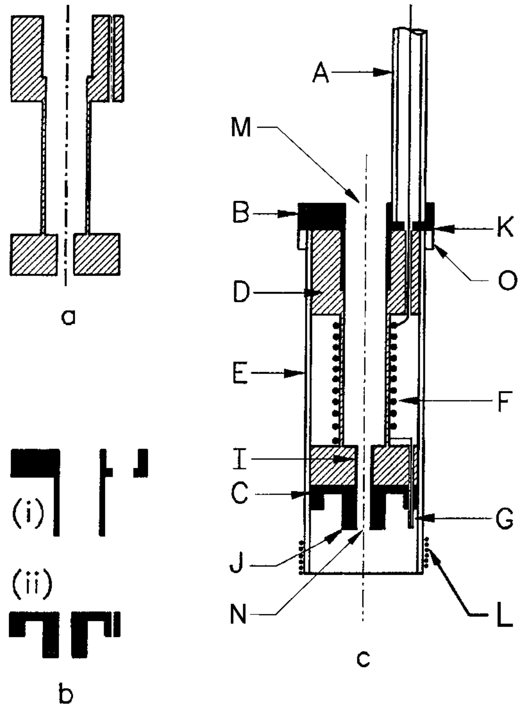

FIG. 3. Vacuum probe head assembly. (a) KEL-F coil former. (b(i)) Top-end stainless-steel snout; (b(ii)) bottom-end stainless-steel plug. (c) Assembled probe head showing the stainless-steel vacuum probe shaft (A); the stainless-steel snout (B) over which the KEL-F coil former (D) is fitted; the stainless-steel bottom-end plug (C); the copper can (E) enclosing the whole assembly; the RF coil (F) with the ground end (G) exiting through the hole in the bottom stainless-steel plug (C) to which it is soldered; the stainless-steel tube (I) heat-shrink-sealed into the bottom of the Kel-F coil former and spot-welded at (J) to the bottom stainless-steel plug (C) previously silver-soldered to the copper can (E); the stainless-steel ring (O) silver-soldered to the top of the outside of the can is spot-welded at (K) to the stainless-steel snout (B) thereby rendering the whole system vacuum tight. The temperature of the helium gas flowing up past the probe is detected by sensors mounted in the probe head bottom plug (C). It is then warmed to the target temperature by the heater-wire (L); the warmed gas passes into the sample area (M) through the inlet (N), flowing past the sample and out through the top of the sample enclosure. The unshaded areas immediately adjacent to the RF coil (between the copper can (E) and the walls of the Kel-F coil former (shaded)), the probe shaft (A) and the connecting hole through the Kel-F between them (through which the RF line passes) are all under vacuum.

rigid, easily machined to any desired specifications, essentially proton-free, and most importantly, can be heat-shrunk onto metal, forming a strong vacuum-tight seal that is able to withstand thermal shock at low temperatures. Making use of these properties, we designed a vacuum-probe system to be used in conjunction with a flow-through-type research dewar.

The heart of our system lies in the Kel-F coil former, a scheme first proposed by Sullivan *et al.* (*3*). In our prototype, a cylinder of Kel-F was machined into a tube having an I-shaped longitudinal cross-section with the specifications shown in Fig. 3a. The inner bore diameter was made ~1 mm larger than the 8-mm sample tubes used in the experiments. In order to create a vacuum seal, the diameter of the upper flange of the cylindrical sample space was machined to be $(2.5 \pm 0.5) \times 10^{-2}$ mm smaller than the corresponding stainless steel snout in Fig. 3b(i). The upper flange was then heated to ~80°C and, with the help of a fluorosilicated lubricant, forced onto the upper metal snout of Fig. 3b(i) (previously welded to the stainless steel probe shaft (A) in Fig. 3c). Subsequently, the bottom flange was treated similarly, but in this case fitted over a short stainless-steel tube (I in Fig. 3c). The thermal contraction of the Kel-F assured a vacuum-tight seal at both Kel-F–metal interfaces.

The joints were then cooled to liquid nitrogen temperature and tested for leaks using a ^{4}He "sniffer" connected to a helium leak detector. Further tests involving repeated rapid thermal-shock cycles (liquid nitrogen to room temperature and back) failed to induce leaks.

The narrow (middle) portion of the coil former—machined to a wall thickness ~1 mm—was then wound with 13 turns of 14-gauge tinned copper wire into a solenoid coil (F) (~12 mm inner diameter and ~4 cm long for use in the ~30-MHz range) and soldered to the coaxial central line threaded down the shaft of the probe, as shown in Fig. 3c. A Faraday-shield copper can (E), fitted with a stainless-steel ring mounted over its top end (O) and a stainless-steel plug inside its bottom end (C and Fig. 3b(ii)) (both silver soldered to the copper) was then slid over the Kel-F/coil assembly so as to allow both the short stainless-steel tube (I) sealed in the Kel-F and one end of the coil wire (G) to protrude through corresponding mating holes in the plug (C).

To complete the vacuum seal, the stainless-steel ring (O) and plug (C) on the copper can were spot-welded at (K) and (J) to the corresponding stainless-steel snout (B) and tube (I) on the probe assembly and the exposed coil wire was soldered at (G), as illustrated in the assembled probe head shown in Fig. 3c. The rationale behind the use of mating stainless-steel joints now becomes clear: directly soldering copper would overheat the heat-shrunk Kel-F-to-metal seals, whereas spot-welding stainless-steel produced only localized heating, leaving the seals intact.

Metal sensor holders previously mounted in the bottom plug (C) were then fitted with temperature sensors and resistive heater wire was wound at (L) on the copper section of the can extending below this plug. Since during operation the probe head is under vacuum—and thus a very poor thermal conductor—the aim was to establish the desired temperature in the helium gas entering the bottom of the probe head, prior to its flow through inlet (N) past the sample in the sample chamber (M). Because the surrounding assembly acts as an insulator, the temperature of the gas flowing into the sample area was essentially the same as that established at the bottom of the probe, resulting in good temperature uniformity and stability. A small mesh plug fitted into the bottom of the sample chamber

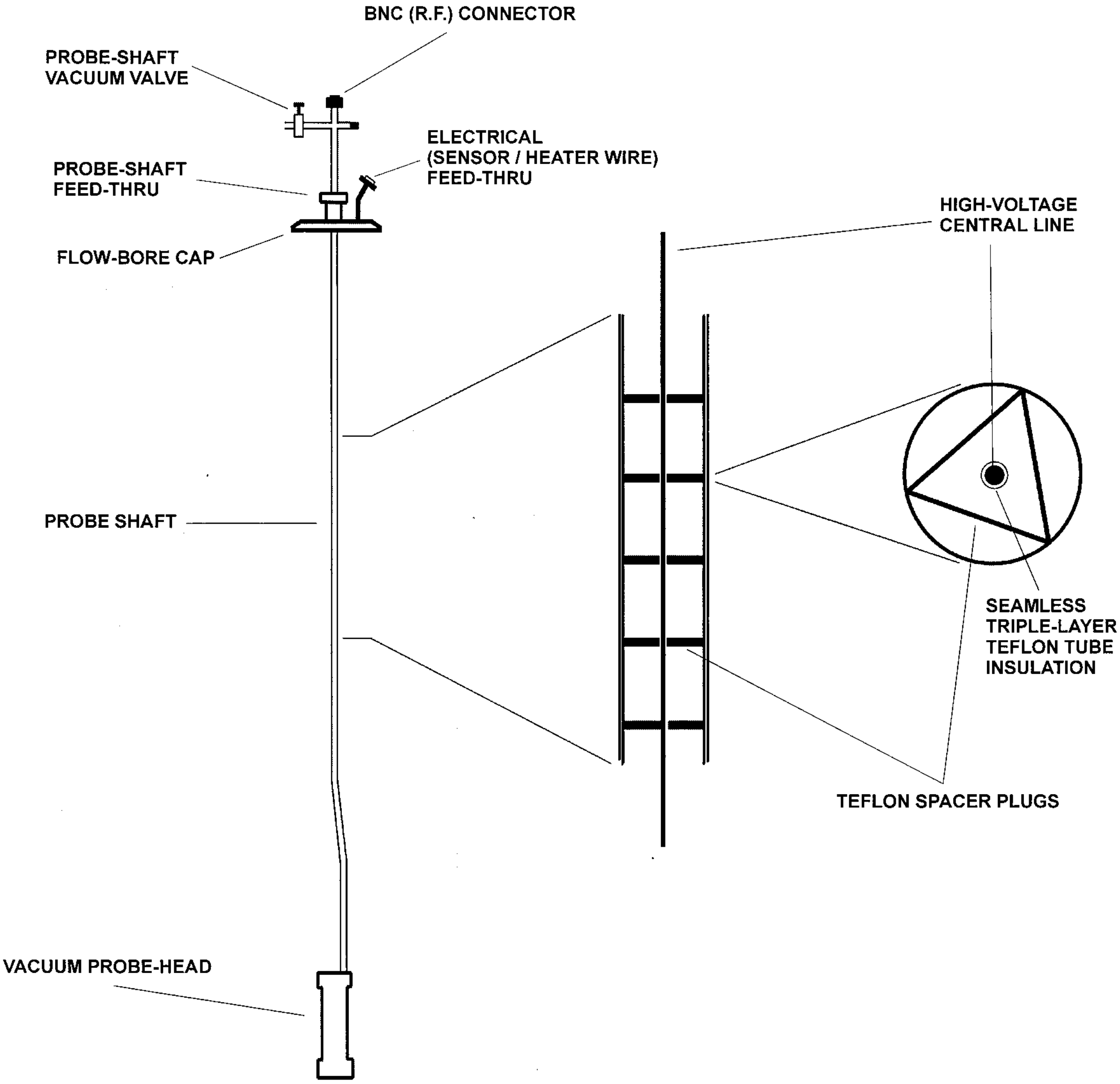

FIG. 4. Vacuum probe shaft assembly. The expansion and inset show the geometry and disposition of the Teflon spacers used to support the insulated high-voltage line. The triangular form of the plugs, threaded over the entire length of the central line and fitted into the probe shaft, was found to be optimal for positioning, support, and further isolation of the high-voltage line, while presenting a minimal obstacle to probe head/shaft evacuation prior to vacuum operation.

(M) prevented the sample from obstructing the helium flowing from (N) through the short stainless-steel connecting tube (I).

The coaxial shaft construction consisted of a triple-layer Teflon-tube-insulated high-voltage line, centered by triangular Teflon plugs threaded 7 cm apart along the length of the steel shaft, as shown in the expansion and inset of Fig. 4. This configuration was found to be optimal in terms of positioning, support, and providing further isolation for the high-voltage line, while presenting a minimal obstacle to probe head/shaft evacuation prior to vacuum operation.

The shaft of the probe was passed through the flow-bore cap using a standard screw-down “O”-ring feed-thru assembly; this allowed the probe head to be adjusted up or down or rotated in order to optimize sample positioning within the magnetic field, while preventing helium escape into the outside air. Electrical wiring from the sensors and heater passed to a connector welded to the flow-bore cap, through a second O-ring feed-thru. The cap was sealed to the top of the flow-bore using an O-ring/spring-loaded clamp device that permitted rapid removal and reinsertion of the probe, resulting in minimal probe head warming during sample exchange. A vacuum valve mounted at the top of the probe allowed the whole apparatus to be evacuated. To prevent leakage at the top of the probe, a special pressure-mounted Teflon feed-thru was used in conjunction with a high-voltage BNC connector. Once assembled, the probe head and shaft were evacuated using a rotary vacuum pump and again tested for leaks following rapid thermal cycling (295 to 77 K and back); no leaks were ever detected.

In order to estimate the thermal gradients in the system, two carbon–glass (Lakeshore) sensors were mounted in the probe head: one embedded in powder inside a sample tube placed in the coil (simulating a sample under normal operating conditions) and the other inside one of the sensor mounts in the bottom of the probe head. Upon slow cooling (starting at ~100 K), agreement between the two sensors was maintained to within ±1° down to ~5 K. Rapid plummeting to the target temperature, on the other hand, produced thermal gradients which lasted ~15 min, after which agreement between the two sensors was again maintained to within ±1°. This meant that, if needed, samples could be exchanged and the target temperature reestablished during the course of a low-temperature run, with a minimum of delay for thermal equilibration.

Using this device we have performed numerous experiments in the 4- to 50-K temperature range, where the maximum RF field amplitude was ~60 G, for pulse durations exceeding 50 ms without any sign of RF breakdown. Indeed, it was the heating effect of long RF pulses that became the limiting factor determining pulse amplitude and duration.

ACKNOWLEDGMENT

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