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NMR probe for high pressure and high temperature

M. de Langen and K. O. Prins
Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

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A description is given of a probe which is designed for nuclear magnetic resonance (NMR) experiments at 180 MHz on samples at hydrostatic pressure up to 10 kbar. Temperature control has been designed to allow experiments from room temperature up to 600 K, regulated with an accuracy of 0.1 K. Radio frequency feedthroughs can sustain high-voltage pulses of considerable length. The probe has been used successfully in a proton spin relaxation study at 180 MHz of polyethylene near the melting line. © *1995 American Institute of Physics.*

I. INTRODUCTION

Since the first NMR experiments at high pressure[1] various high-pressure NMR probes have been developed. A wide variety of designs, for wide line and high-resolution NMR, for relatively low pressure and for intermediate pressure up to about 10 kbar, for use at temperatures from a few to about 1000 K have been reviewed by a number of authors in a volume[2] on high-pressure NMR. For extremely high pressure, a number of successful designs based on a diamond anvil cell (DAC), for use up to about 8.5 kbar, have been reported.[3–5]

Until recently, our group has concentrated its efforts mainly on high-pressure NMR studies of motion and phase transitions in systems of simple molecules, in which high-pressure probes[2,6] allowing accurate control of temperature from about 380 K down to about 2 K have been used up to 10 kbar. In connection with these studies we became interested in the dynamics and phase transitions of synthetic polymers at high pressure. In particular, the investigation of the molecular dynamics at the phase transitions[7] of polyethylene required the development of a new probe with the following essential qualifications:

(1) The capability of accurate and stable temperature control (from room temperature up to 600 K) is required, without significant temperature gradients occurring across the probe. (2) The vessel must be able to maintain high pressure (up to 10 kbar) in this temperature interval. (3) The probe must be suitable for ^{1}H NMR at 180 MHz. (4) The rf feedthrough must allow high-voltage rf pulses of considerable length without breakdown. (5) The completely assembled probe must fit inside the 13 cm bore of our 4.2 T superconducting magnet (Oxford Instruments).

In the following we will give a detailed description of all important aspects of the probe. The probe has been used successfully in a proton spin-lattice relaxation and line shape study of polyethylene near the melting line.

II. THE HIGH-PRESSURE PROBE

A. Vessel

NMR probes for intermediate pressure values essentially are pressure vessels out of a nonmagnetic alloy of high tensile strength. Beryllium–copper (Berylco 25) is frequently used because of its low magnetic susceptibility and high thermal conductivity. However, it loses its high tensile strength (about 1300 MPa at room temperature) at temperatures above about 400 K. At higher temperatures titanium alloys have been applied successful in the construction of high-pressure probes.[8–10]

The high-pressure NMR probe we developed is shown in Fig. 1. The central part is the high-pressure vessel. It consists of a large cylinder (1) made out of a titanium alloy.[11] This low-susceptibility material is chosen because it maintains a high tensile strength at high temperatures (about 900 MPa at 600 K) and it has only a small effect on magnetic field homogeneity. The outer diameter of the vessel is 82 mm, the inner diameter is 14 mm, and the total length is 88 mm. The vessel is closed by a bottom plug (2) which is held by a backing nut (3). The latter parts are made out of the same titanium alloy. The sealing of this closure is achieved by a D-shaped ring (4), made out of a softer kind of titanium (grade 2 unalloyed titanium) to avoid damage to the 45° faces (a) of the vessel and of the plug and in order to secure the sealing.

Pressure is applied using a gas medium (usually nitrogen or helium) which is led into the vessel through a stainless-steel capillary (5) that can be connected to our pressure generating equipment.

B. Radio frequency parts

A serious obstacle in building a high-temperature, high-pressure probe is the construction of a reliable low-capacitance, high-voltage radio frequency feedthrough. In fact, the limits of temperature and pressure of the probe are almost entirely determined by the limitations of the feedthrough and not by the dimensions of the vessel, which can just be made larger if required. The design of a feedthrough is always a compromise between wanting a large layer of insulation to avoid high-voltage breakdown and reduce capacitance, and wanting minimum size in order to withstand high pressure at high temperature.

The problem of designing a suitable feedthrough has been addressed before by a number of authors.[12–15] We have thoroughly tested some of these feedthroughs and further developed the most promising type in order to create a feedthrough that would satisfy all our requirements. The design of the feedthrough for this probe is based on an earlier

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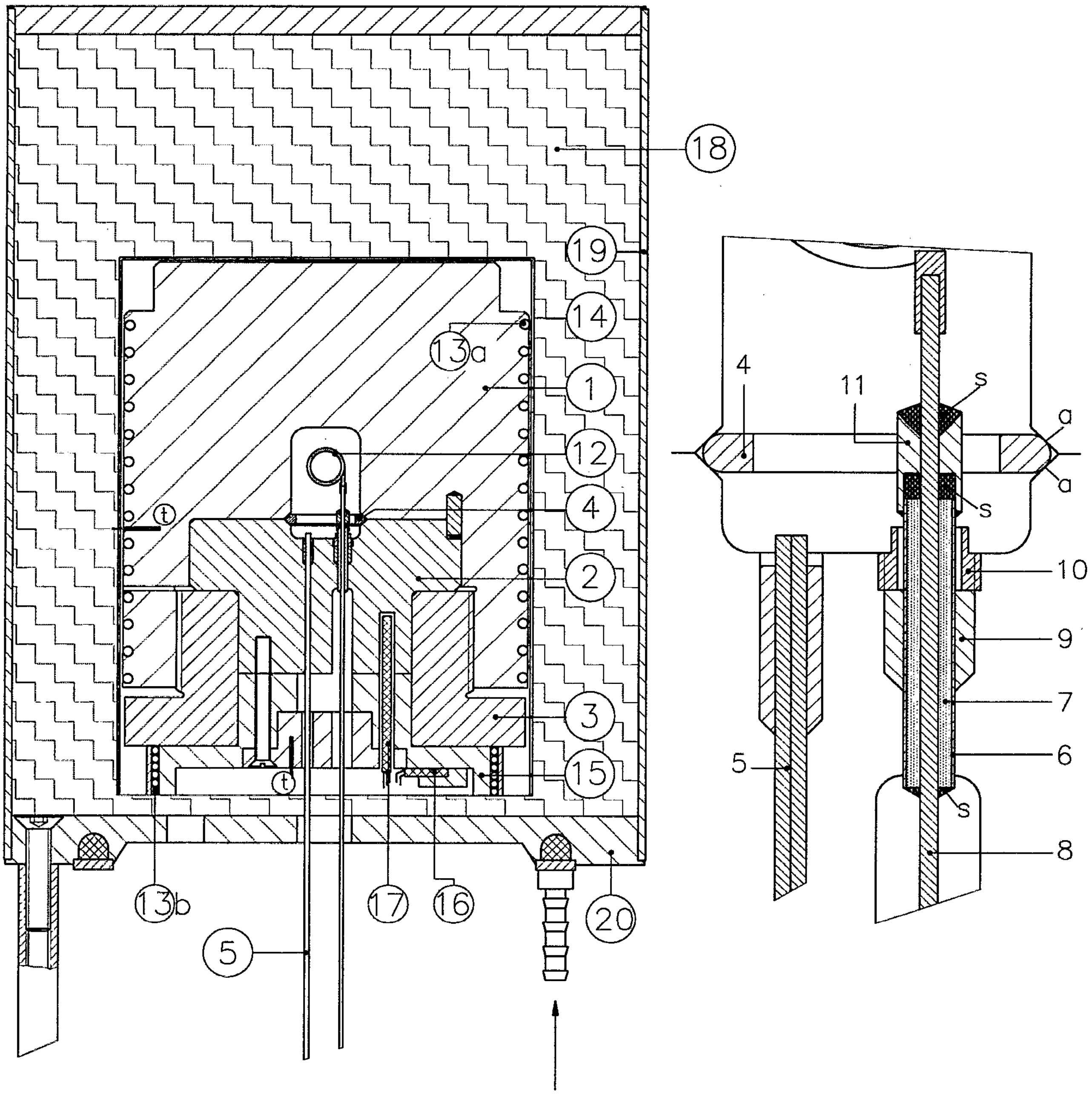

FIG. 1. Schematic drawing of the completely assembled NMR probe. The inset shows a magnification of the sample chamber with the feedthrough, the capillary, and the D ring. See text for key to figure.

design by Huber *et al.*. We modified it to make it suitable for use at high temperature, and with high rf frequency.

The feedthrough is shown in detail on the right-hand side of Fig. 1. It consists of a 13-mm-long piece of coaxial heating wire called Thermocoax[16] with a 2 mm diameter. The type we used consists of an Inconel sheath (6), an insulating layer (7) of magnesium oxide, and an inner conductor (8) of NiCr wire through which current can be supplied to the rf coil. High-pressure sealing is achieved by a 4.5 mm Inconel sealing cone (9), silver soldered onto the sheath of the feedthrough. A titanium gland nut (10) is used to prestress the feedthrough. On top of the feedthrough a Vespel[17] cap (11) is glued with Stycast[18] (s) in order to keep the inner conductor from being pushed out when high pressure is applied. Stycast is also used for sealing both ends of the Thermocoax in order to prevent moisture from getting into the insulating layer.

In order to allow tuning of the electric circuit to the desired frequency (180 MHz) while still maintaining a reasonable Q factor, it is essential to reduce the capacitance of the feedthrough as much as possible. The minimum capacitance we have achieved so far by choosing optimal dimensions of the coaxial part, without making significant concessions to the mechanical properties of the feedthrough, is 7 pF.

The rf coil (12) (solenoid type with a length of 8 mm and a diameter of 4 mm) is made of silver-coated copper wire. It is connected to the feedthrough using a silver sleeve that is clamped onto the ends of the coil and the inner conductor of the feedthrough. This has been done because soldering to NiCr wire is very difficult, especially at such a short distance from the feedthrough cap. Furthermore, the clamping sleeve technique allows easy assembly and disassembly combined with excellent electric contact, even after many cycles of temperature and pressure. The ground contact of the rf coil is made by a solid titanium pin, mounted in plug (2). This pin has the same shape and dimensions as the feedthrough because in the near future we intend to modify the probe head into a double-tuned $^1H-^{13}C$ probe head by replacing the pin with a second rf feedthrough. For our present experiments on ^1H, however, we avoid the extra capacitance of such a configuration by using a solid pin.

Tuning and impedance matching of the probe are achieved with two variable capacitors which are mounted just below the bottom plate (20) of the probe. In this configuration a Q factor of about 90 has been achieved.

C. Temperature control and measurement

Because the heat conductivity of titanium is quite poor, it was necessary to pay special attention to the construction of an accurate and stable way of controlling temperature without the occurrence of gradients across the high-pressure vessel.

The vessel is heated by a Thermocoax heating wire, wound into a groove (13a), machined on the outside of the pressure vessel. The heater is kept in place by an aluminum cylinder (14). A second heating wire (13b) is wound onto an aluminum block (15) which is attached to the bottom of the vessel. This second wire is needed to compensate for the larger heat losses at the bottom of the probe (due to thin isolation and heat conduction through all the wires), which may cause unwanted temperature gradients across the titanium pressure vessel. Both heating wires are controlled by separate PI-regulating devices. The temperature of the bottom of the vessel is regulated at the desired temperature by comparing a platinum resistor (16) attached to the aluminum block to a standard resistor by using a Thomson resistance bridge. A differential thermocouple (t) (copper-constantan) between the bottom and the center of the probe is used to control the power applied to the vessel heater (13a) in order to maintain the top part of the vessel at the same temperature. In this way a possible temperature gradient across the pressure vessel, caused by the low heat conductivity of titanium, is kept to a minimum. Accurate temperature measurement is performed using a four-lead platinum resistance thermometer placed in a small hole (17) close to the sample space inside the pressure vessel.

The complete system is placed inside a cylinder made out of stacked rings (18) of compressed Kaowool[19] insulating material. The outside of the completely assembled probe is formed by a copper cylinder (19) with a 129 mm diameter and a wall thickness of 1 mm. The cylinder makes good heat contact with the copper bottom (20), which is water-cooled in order to prevent the probe from transferring too much heat to the bore tube of the superconducting magnet.

The probe is supported by four copper rods, extending to a platform (not shown in Fig. 1), which is connected to the bottom flange of the magnet.

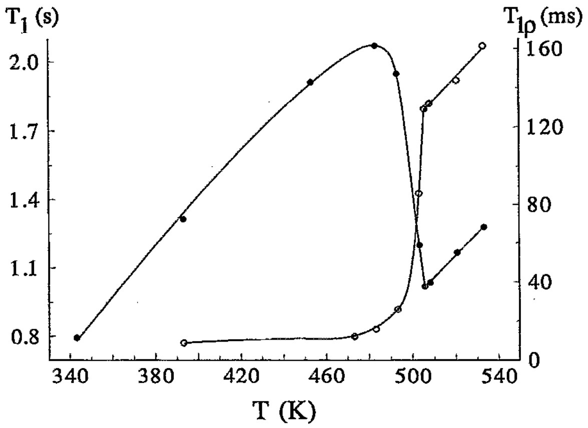

FIG. 2. Values of T_1(solid circles) and $T_{1\rho}$(open circles) in ultrahigh molecular weight Polyethylene at 5500 kbar as a function of temperature.

III. CONTROL AND MEASUREMENT OF PRESSURE

Solid samples can be studied by using an inert gas, for instance nitrogen or helium, as the pressurizing medium. The solid material, contained in an open thin-walled glass tube, is placed in the rf coil. The pressurizing gas is introduced through the high-pressure capillary. Gas pressure is generated by a two-stage gas compressor.[20] The pressure is measured using a manganine resistance cell calibrated up to 10 kbar against a Harwood dead-weight gauge. The inaccuracy in the measured pressure is within 0.2%.

IV. TESTING, OPERATION, AND PERFORMANCE

After the construction of the probe, all properties have been tested thoroughly. Test runs consisting of taking the bare vessel to high pressure and high temperatures showed no significant leakage up to 600 K at a pressure of 10 kbar. Tests of the fully mounted probe indicate that temperature can be regulated within 0.1 K and pressure can be controlled within 5 bar.

The performance of the electronic circuit including the feedthrough can be specified as follows. rf $\pi/2$ pulses on protons have a duration of 1 μs at a power of 500 W. The feedthrough sustains this power level in spin-lock pulses of a duration up to at least 0.2 s.

So far the probe has been used in a proton spin-lattice relaxation study of polyethylene near the melting line. A complete report on this work will be published shortly. As an example Fig. 2 shows some experimental data on the proton spin-lattice relaxation time T_1 and of the rotating frame relaxation time $T_{1\rho}$ (with $B_1 = 2.9$ mT) in ultrahigh molecular weight polyethylene, showing a phase transition from low to high molecular mobility at a pressure of 5500 bar and a temperature of about 500 K.

The probe will be modified into a double-tuned probe for future work on $^1H-^{13}C$ double resonance in polymer solids.

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