Nuclear magnetic resonance in a diamond anvil cell at very high pressures

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We describe a novel design to study the nuclear magnetic resonance (NMR) properties of materials at high pressure in a diamond anvil cell. A split gasket is used to pressurize the sample and a single turn coil couples the rf field with the sample. Due to the large filling factor, this method has a significantly increased sensitivity compared to previously used techniques and should allow NMR study of materials in a diamond anvil cell into the megabar region. We demonstrate the system with a measurement of the spin-lattice relaxation (T_1) of cyclohexane as a function of pressure at 79 K up to 9.7 GPa. We have also pressurized a sample of hydrogen to 26 GPa. © *1998 American Institute of Physics.* [S0034-6748(98)01402-6]

I. INTRODUCTION

Diamond anvil cells (DACs) can routinely allow for the generation of multimegabar static pressures. Traditionally, investigations of samples have been performed by visual methods or using optical spectroscopy (e.g., IR or Raman). However, these techniques couple to the electron clouds in solids and liquids which can deform substantially at high pressure, complicating the interpretation of results. On the other hand, nuclear spin quantum numbers are in general hardly affected by pressure and remain valid at high density; therefore, nuclear magnetic resonance (NMR) can give straightforward information about the local environments surrounding nuclei in a variety of ways. As the samples in a DAC are typically very small ($\sim 10^{16}$ atoms) and as NMR is an insensitive spectroscopic probe, NMR research using a DAC must deal with the problem of very weak signals. In addition, metallic gaskets used to confine pressurized samples can shield the sample from rf magnetic fields. For example, the skin depth of 223 MHz currents on the surface of rhenium (a commonly used gasket material) is $\sim 15\ \mu$m at room temperature. This results in significantly reduced coupling between the sample and NMR coil as coils are typically mounted outside of the gasket. Previous NMR experiments in a DAC[1–4] used a coil surrounding the gasket to generate rf magnetic fields (H_1) parallel to the gasket surface that only dip into the sample region as shown in Fig. 1. This leads to a small filling factor and low sensitivity for NMR. An additional problem with this geometry is that the resultant H_1 in the sample is inhomogeneous leading to reduced NMR signal. The low sensitivity due to large coil volume and reduced field penetration necessitated large samples which limits the maximum achievable pressure in the DAC. Until now, the highest reported pressure for NMR in a DAC is 8.3 GPa.[3–5] We have more than tripled this range without pushing our technique to its limits.

We have developed a novel technique that significantly reduces the metallic gasket shielding between the sample and coil. Our original idea was to use the gasket itself as the NMR resonator coil, but this has been improved upon as described below. In order to let the rf field penetrate in and out of the sample we use a slotted gasket which has its slit filled with insulating material. The NMR coil is a one-turn inductor that sits on top of the slotted gasket. It is a slotted copper foil that we call the cover inductor, shown in Fig. 2. The resulting sample filling factor is large, determined experimentally to be ~ 0.16,[6] compared to 0.003 obtained by previous researchers.[2] This allows us to work with smaller samples and still have sufficient sensitivity. The split gasket has been easily pressurized to as high as 26 GPa and can go much higher, thereby significantly extending the potential range of pressure study for a variety of materials.

II. EXPERIMENTAL TECHNIQUES

The DAC used in this experiment was the original one described by Silvera and Wijngaarden.[7] It is constructed from thermally hardened nonmagnetic BeCu. Special care has been taken to ensure that most of the parts used in the DAC were nonmagnetic in order to maintain high magnetic field homogeneity over the sample.

The split gasket and cover inductor shown in Fig. 2 comprise the split gasket resonator (SGR). The presence of the slit in the gasket allows high frequency magnetic field lines to penetrate to the sample region with little attenuation. To confine the sample, the slit is filled with an electrically insulating mixture that has two components: diamond powder with particle size comparable to the slit width, and smaller particles of NaCl that will plastically flow around the diamond particles inside the slit due to their much weaker yield strength and will become the sealant to prevent leakage of the pressurized sample. We have tried a variety of nonmagnetic materials as gaskets including copper, phosphor bronze, and rhenium. Rhenium was found to be the best candidate as it has the highest yield strength of the above-mentioned materials and therefore higher pressures can be achieved.

We now describe the fabrication method of the SGR for our recent experiment carried out on cyclohexane. The split gasket was cut from a 254 μm thick sheet of rhenium metal. The gasket was preindented to $\sim 110\ \mu$m thickness and a

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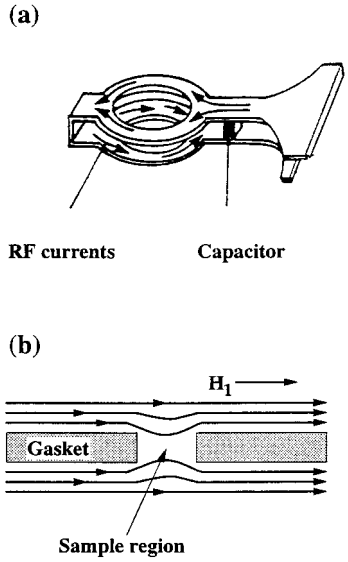

FIG. 1. An existing method to couple magnetic flux with the sample in a DAC, after Ref. 2. (a) Diagram of a typical rf coil. The gasket, which fits inside, is not shown. (b) Magnetic flux lines pass parallel to the gasket and dip into the sample region coupling with the spins.

230 μm through hole was cut by electric discharge machining (EDM) in the center of the 300 μm flat imprints made by the 1/3 carat, 16 faceted, single bevel diamonds. A $\sim$40 μm wide slit was then EDM'd as shown in Fig. 2. After thorough ultrasonic cleaning of the gasket using methylene chloride, hexane, and acetone in that order, the slit was packed with a mixture of 75% diamond powder ($\sim$8–16 μm particle size) and 25% NaCl powder ($\sim$5 μm particle size) by weight. Then, the gasket composite was heated to over 800 °C using a butane small torch to melt the NaCl inside the slit. The NaCl holds the diamond particles together and seals the slit. The gasket was then ready for loading.

On top of the gasket a similar single loop copper coil (150 μm thick, hole diameter 0.9 mm) was constructed and (see Figs. 2 and 3) was soldered to a 270 pF nonmagnetic ceramic chip capacitor (American Technical Ceramics). The

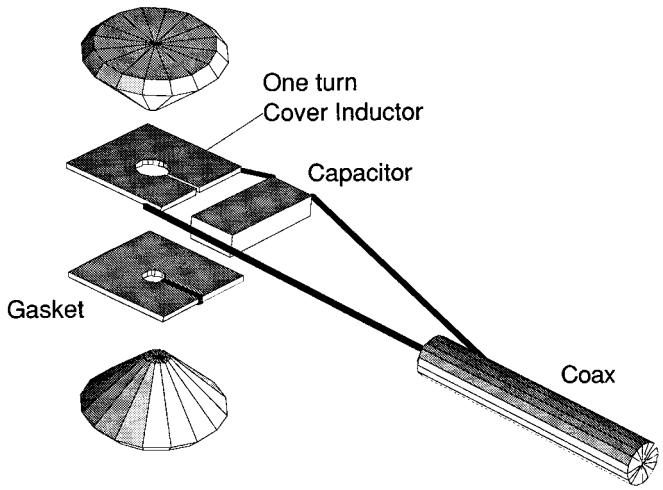

FIG. 2. Schematic depicting how the gasket, NMR resonator, and diamonds fit relative to each other. The components have been offset for clarity.

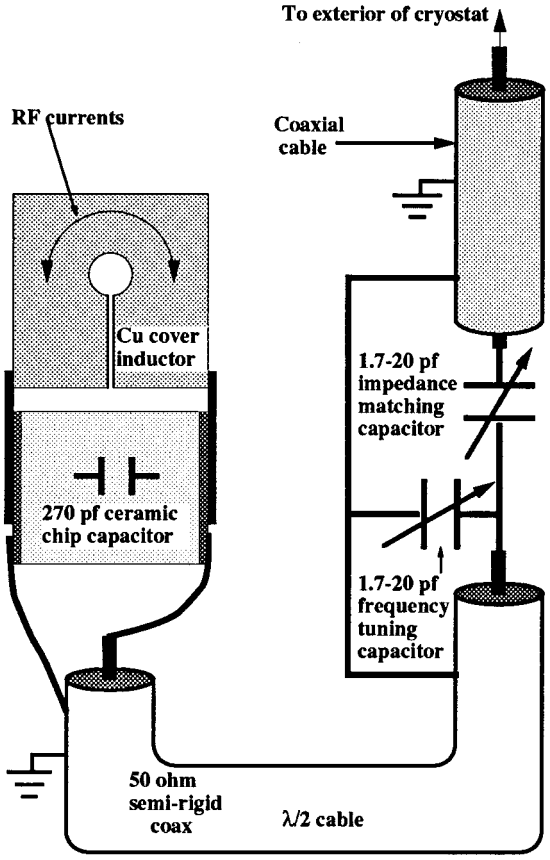

FIG. 3. NMR circuit which includes the NMR resonator (cover inductor plus ceramic capacitor), $\lambda/2$ coaxial cable, and the tuning capacitors all depicted in the figure. The coil generates magnetic field lines perpendicular to the plane of the figure.

cover inductor was in electrical contact with the gasket and the slits were aligned. The inductance of the cover inductor was $\sim$1.8 nH. The oscillating magnetic field lines penetrate normal to the plane of the copper cover inductor and the conducting boundary conditions of the gasket force them through the gasket and slit. The NMR resonator (cover inductor and ceramic chip capacitor) was then soldered to a length of semirigid 50 Ω minicoax (copper outer and inner conductors). The part of the assembly encompassing the NMR resonator and some of the coax adjacent to the NMR circuit was then thoroughly cleaned in an ultrasonic bath, first of hexane and then optical quality acetone to remove any solder flux or other impurities which contain protons. This $\sim$0.45 m long rigid coax is 1/2 of a wavelength of 223 MHz (our chosen NMR frequency) electromagnetic waves traveling in a 50 Ω coaxial cable and is called a lambda/2 cable. The phase of the NMR signal changes by 180° when it passes through the lambda/2 cable but otherwise the impedance characteristics of the NMR resonator remain unchanged (see Refs. 8 and 9, p. 412). This allows us to tune and match the NMR resonator a distance of lambda/2 away from the circuit so that the two variable air dielectric capacitors (1.7–20 pF) can be situated outside of the DAC where more space is available. One variable capacitor is used to tune the resonance frequency of the circuit to 223 MHz whereas the

other is used to match the impedance of the NMR circuit at resonance to 50 Ω (see Fig. 3). In our setup, both variable capacitors are tuned *in situ* by using G10 epoxy tubing that pass out of the cryostat. Furthermore, the lambda/2 cable was not matched to the SGR which had an impedance ($Q\omega L$) of $\sim 149\ \Omega$ on resonance so that there was a calculated loss of a factor of 2 in the signal input to the receiver.

Ruby crystals used for pressure measurement (5–20 μm in size) were placed on both diamond flats and then the entire area near the diamonds was filled with cyclohexane (C_6H_{12}). We chose cyclohexane because (1) it had a low evaporation rate (liquid would remain in the gasket region for several minutes—long enough to load a sample), (2) it would not dissolve any of the slit materials, (3) it had a high concentration of protons, and (4) being a constituent of crude oil, it would be interesting to study under pressure. The diamonds were brought into contact with the gasket and load (measured with a strain gauge) was applied to the DAC, pressurizing the sample. Applying load on the slit causes it to pinch inward where it enters the sample hole and spread apart on the periphery. The diamond particles in the slit prevent contact and are large enough so that they do not extrude out. We visually observed an apparent phase transformation of the sample at a pressure somewhere below 1.3 GPa, when the opacity of the sample changed which was an initial indication that a sample was pressurized. The pressure was later measured by the conventional ruby fluorescence measuring technique.[10] After a sample was confirmed to be pressurized, it was monitored over some hours to ensure that the pressure was stable. Our sample was $\sim 160\ \mu$m in diameter and $\sim 60\ \mu$m thick after loading. Then, fiber optic assemblies were attached to the DAC as shown in Fig. 4, to allow us to measure the sample pressure when the DAC is in the NMR cryostat. The NMR cryostat (Precision Cryogenics) allows for continuous operation of a superconducting solenoid magnet,[8] operated at 5.24 T and at 4.2 K in persistent current mode. The DAC and sample temperatures can be varied between 1.2–300 K by using an ''anti-Dewar'' of our design and construction that isolates the region containing the DAC from the magnet region (see Fig. 5). The low temperature circuit is connected to the outside of the cryostat via 50 Ω low temperature coax (Yotem).

To perform NMR we have constructed a phase coherent pulsed NMR spectrometer with two channels in quadrature operating at 223 MHz (see Fig. 6). A continuous rf signal from a signal generator (Hewlett Packard 8640B) is gated to form pulses which are amplified by a pulse amplifier (ENI 300L). The NMR signal from the resonator is first amplified with a low noise preamplifier (Amplifier Research P220VDG) in the NMR receiver and later mixed with the 223 MHz reference signal. The mixed output is then filtered and displayed on a high speed digitizing oscilloscope (Tektronix TDS 520) where signal averages are performed. The results are transferred to a computer for storage, or measurements are made directly on the scope. For the T_1 measurements, we used the standard 90°-t-90° repetitive sequence to measure T_1 (see Ref. 9, p. 172). The repetition rate and length of the pulses were controlled by a Stanford Research systems pulse generator (DG535). Pressure was measured by

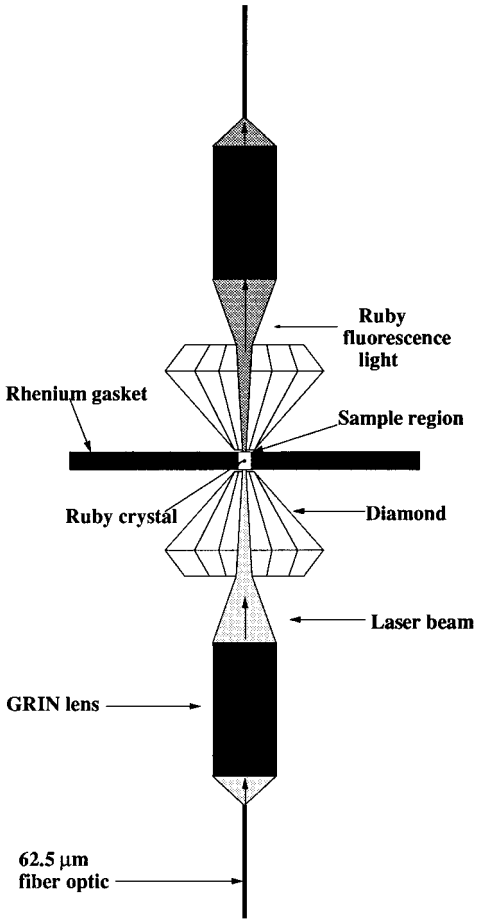

FIG. 4. The fiber optic setup used for pressure measurement. Laser light is focused by a GRIN lens onto ruby crystals in the sample region. A fraction of the isotropic fluorescence light is collected by another GRIN lens and focused onto a 62.5 μm multimode fiber optic cable.

ruby fluorescence excited by a Spectraphysics argon ion laser, using a Spex Triplemate monochromator with a diode array detector. Temperature of the sample was measured with a silicon diode.

III. RESULTS

After loading, the cyclohexane was cooled to near 77 K by introducing liquid nitrogen into the inner chamber of the NMR cryostat. We verified that the NMR free induction decay (FID) was from ringing spins by observing 90°_x-t-90°_y solid echoes (see Ref. 9, p. 251). For our system, a 90° pulse was $\sim 2.5\ \mu$s in length. We also observed the difference between the spectrometer ringdown with field tuned near resonance at 223 MHz, and with the field detuned, shown in Fig. 7. T_1 values were obtained by measuring the amplitude of the FID as a function of repetition rate of 90° pulses. Each point required a few thousand averages to obtain a satisfactory signal-to-noise ratio. The equation used to fit the data was of the form $M_0(1-e^{-t/T_1})+A$, where M_0 (static sample magnetization), A (dc offsets from the spectrometer and/or oscilloscope), and T_1 are constants. We present a plot of T_1 as a function of pressure in Fig. 8. The error bars shown were obtained from the fitting program.

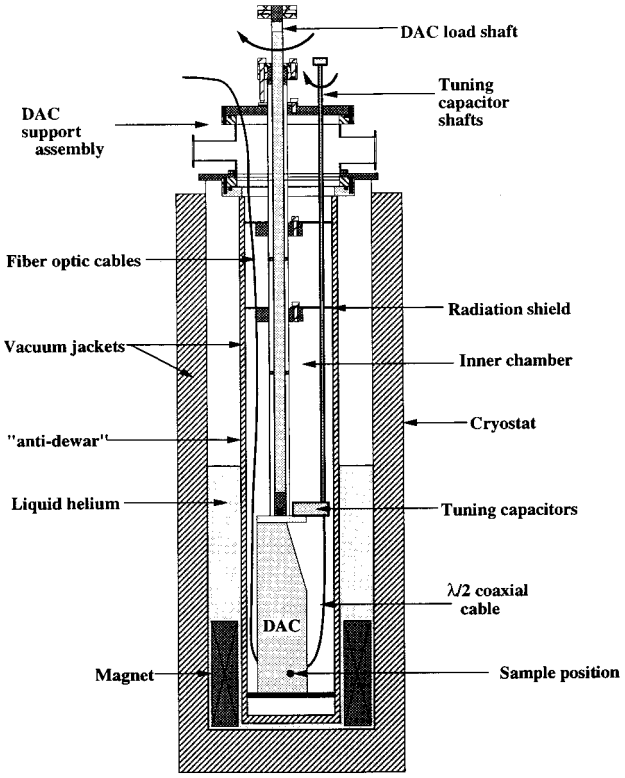

FIG. 5. Schematic of the NMR cryostat. The anti-dewar allows operation of the superconducting solenoid at 4.2 K and the inner vacuum chamber containing the DAC at any temperature from 1.2 up to 300 K.

As we performed our measurements at low temperature, T_2 was of lesser importance and we observed little change in the length of the FID, T_2^*, similar to NMR measurements of methanol/ethanol under pressure.[1] T_2^* was found to be $\sim 9\ \mu$s throughout the experiment and was obtained by fitting the FID to the product of an oscillatory and a Gaussian function.

Pressure was generally measured with the magnetic field off as its presence splits and broadens the ruby R_1 and R_2 lines. The error in each pressure determination is ~ 0.15 GPa. The highest pressure we studied (9.7 GPa) was by no means the ultimate achievable pressure but we decided to be conservative in this demonstration experiment.

IV. SENSITIVITY CONSIDERATIONS

In this section we discuss the filling factor and the dependence of the sensitivity on geometry for the SGR. The voltage induced in the coil is

$$V = -\frac{300}{c}\,\eta Q\,\frac{d}{dt}\,\phi, \tag{1}$$

where η is the filling factor and Q is the circuit quality factor, we use the traditional Systeme International units[11] of V in volts and other quantities in cgs units. The rate of change of flux is

$$\frac{d}{dt}\,\phi = \omega_0 B a, \tag{2}$$

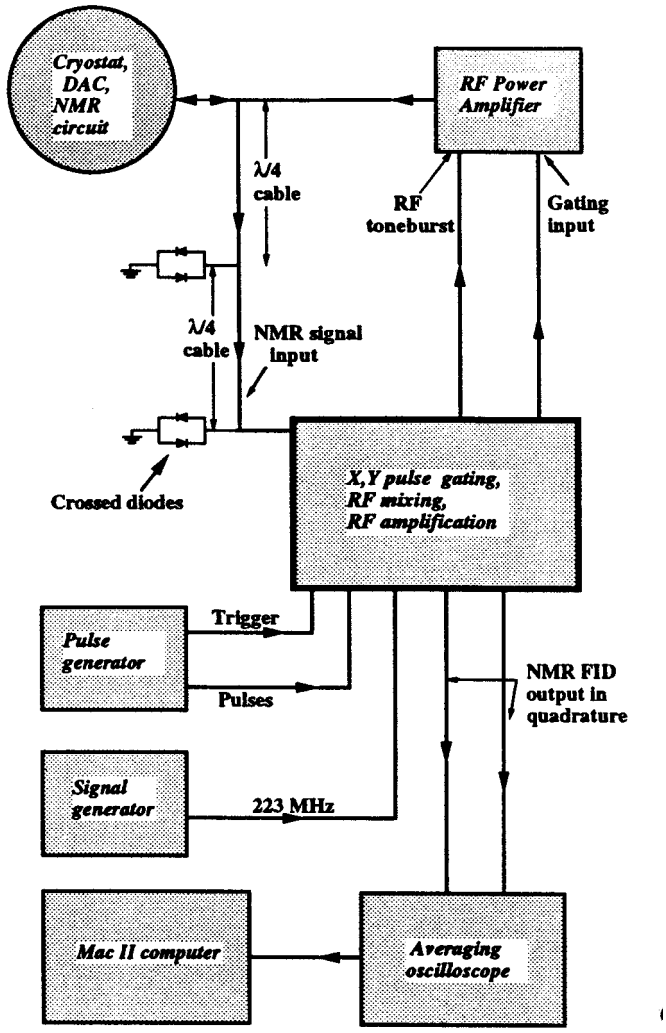

FIG. 6. Block diagram of the NMR spectrometer (see the text).

where ω_0 is the resonant frequency and B is the field of the magnetized sample of area a, varying sinusoidally in time. The magnetization of the sample is $M = \chi H_0$ where (for spin 1/2) the nuclear susceptibility is $\chi = N\mu^2/kT$ for nuclear magnetic moment μ at temperature T and N spins per unit volume in applied field H_0. The field B due to the magnetized sample is $2\pi z M/r$, so we find

$$V = -2\pi^2 10^{-8}\,\eta Q \chi H_0 r z, \tag{3}$$

where r and z are the sample radius and thickness, respectively. We see that the signal increases with the gasket radius and thickness (rather than $\pi r^2 z$). In this analysis we have implicitly treated the problem as if the gasket and the cover inductor were one; equivalently we assumed that the hole in the cover inductor and the gasket hole are of the same diameter, and all of the flux from the cover inductor goes through the gasket hole, and that the slit is of infinitesimal width. The filling factor was determined empirically by measuring the Q, the FID voltage, and other parameters in the above equation. At liquid nitrogen temperature the value of the Q was 59.

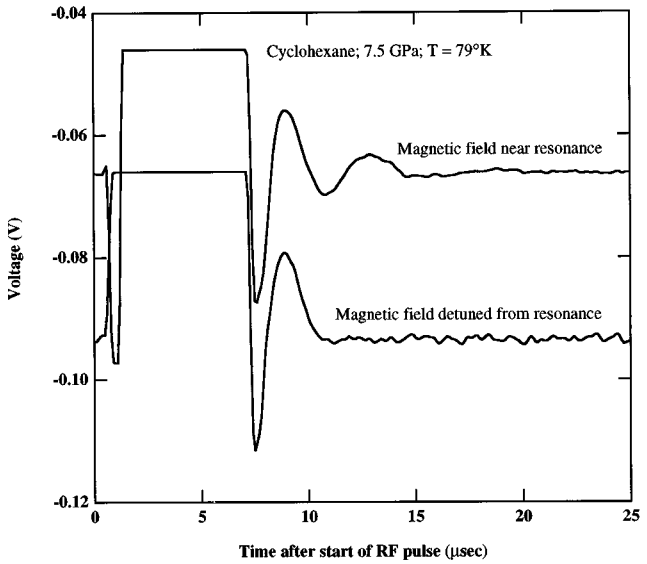

FIG. 7. A characteristic FID at 7.2 GPa after the application of a 2.5 μs rf pulse (upper curve). Spectrometer ringdown with the magnetic field detuned is shown in the lower curve. Approximately 1500 acquisitions were averaged for each curve. The curves have been vertically offset from each other for clarity.

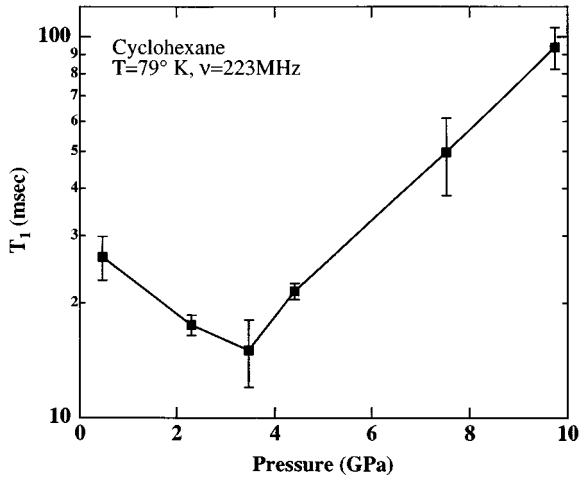

FIG. 8. Plot of T_1 vs pressure for cyclohexane at $T=79$ K and $\nu=223$ MHz.

V. DISCUSSION

Initially, the split gasket played both the role of confining the sample and the single loop coil. However, the best materials for confining the sample (e.g., rhenium) were generally poor electrical conductors and low resonator Qs resulted from their use. Materials with high electrical conductivity (namely high purity copper and aluminum) are very soft (low yield strengths) and therefore would not allow large pressurization of the sample. We electro-deposited copper onto a rhenium gasket in the interest of boosting the NMR resonator's Q but found that using a separate cover inductor and split gasket was the best solution. As a test of the sensitivity we first filled the cover inductor with paraffin and measured the NMR signal. We then cleaned the paraffin out and loaded a split gasket with paraffin. The resulting signal was 9 times smaller, even though the volume of the paraffin in the gasket was 26 times smaller. Thus, using the (empty) cover inductor with a sample filled split gasket, the signal/spin was larger; however, we did not pursue this interesting enhancement. The signal we measured can be further increased by matching the lambda/2 cable to the on-resonance impedance of the SGR.

The insulating material used to fill the slit was originally a mixture (by weight) of 75% alumina powder (particle size comparable in dimensions to the slit width) and 25% NaCl powder. We had no problems pressurizing gaskets with slits filled with this material. However, a critical problem did manifest itself later. In an earlier experiment, we loaded a sample of hydrogen and pressurized it up to 26 GPa. Unfortunately, we were plagued by NMR signals from impurities which resulted in a complicated spectrum and the experiment was eventually terminated. Subsequent study revealed a strong NMR signal originating from the 2850FT epoxy (Stycast) that fixed the diamond bases to the nonmagnetic tungsten carbide seats[12] which are located ~ 2.3 mm above and below the cover inductor. We then developed a technique to fix the diamonds in the DAC mechanically, without epoxy. Further investigation revealed that adsorbed water on the alumina that filled the gasket slit also contributed to the impurity signal. We found no NMR signature from the NaCl powder. In the subsequent efforts to find a suitable nonproton containing material for the slit, we found that zirconia (ZrO_2) and diamond powder had no discernible NMR signature to the level of our highest sensitivity.

We performed empty cell runs both before loading cyclohexane and after releasing the sample to verify that the NMR signals investigated were solely from the sample.

VI. DISCUSSION

We have successfully demonstrated a new NMR system to study materials under very high pressures that has dramatically improved sensitivity due to an increase in the filling factor of order 50, compared to earlier used geometries. Already in these preliminary experiments, we have more than tripled the range of pressures for NMR in a DAC. The split gasket resonator should allow NMR investigations into the megabar pressure regime.

ACKNOWLEDGMENTS

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