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Apparatus for NMR Studies at High Pressure*

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An apparatus has been developed which permits NMR measurements at somewhat higher pressures than was previously possible. It makes use of supported taper pistons of chrome oxide with pyrophyllite or boron nitride as the supporting material. With a sample 2 mm thick, pressures of 40 kbar are obtainable; with a sample 0.9–1.0 mm thick, pressures as high as 80–90 kbar may be possible. Data of line width vs pressure are presented for Teflon and polyethylene, and the effect of pressure on the structure of these materials is briefly discussed.

THIS paper describes a high pressure NMR apparatus which has been operated to 27 kbar and calibrated to perhaps 90 kbar. Under favorable circumstances it should be operable for NMR measurements in this range.

The first high pressure NMR experiments were those of Benedek and Purcell[1] wherein self-diffusion studies were made in liquids to 10 kbar. Since that time Benedek and his co-workers have done a variety of experiments on solids to 10 kbar. Gutowksy and Williams[2] measured the pressure dependence of the quadrupole splitting in $NaClO_3$ to 3 kbar. There has been a variety of other high pressure NMR work in this range including studies by Hultsch and Barnes,[3] Billings and Noble,[4] and Baron.[5]

The only experiments at higher pressure have been the zero field nuclear resonance study of Litster and Benedek[6] of ^{57}Fe to 65 kbar, and a similar experiment by Anderson[7] on cobalt.

A diagram of the high pressure system, including the press, cell, and ring, is shown in Fig. 1. The press, cell, and ring were all machined from Berylco 25, a beryllium copper alloy. After machining, the parts of the apparatus were heat treated to 320°C for three hours and then quenched in oil. Pressure was generated by means of a hand operated hydraulic pump and transmitted via steel high pressure tubing to the press head. The press head piston was 57.1 mm ($2\frac{1}{4}$ in.) in diameter. Since the press head was too large to fit into the pole gap of the magnet, it was necessary to place it out of the gap. Pressure was therefore transmitted from the press head to the cell by means of a 31.7

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[5] R. Baron, J. Chem. Phys. **38**, 173 (1963).
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[7] D. Anderson (private communication).

mm ($1\frac{1}{4}$ in.) diam beryllium copper rod, 209.5 mm ($8\frac{1}{4}$ in.) long.

Pistons were made of chrome oxide or chrome carbide. Both types were 15.9 mm ($\frac{5}{8}$ in.) in diameter and were ground with a 45° taper. The flat portions of the pistons were 6.3 mm ($\frac{1}{4}$ in.) in diameter. Neither type was damaged during the high pressure experiments. Pistons made of chrome oxide are much superior for NMR work. Chrome oxide is an insulator while chrome carbide is a conductor. Pistons made of the latter caused such high rf losses when brought near the small sample coil that the operation of the marginal oscillator was completely disrupted. For calibration of the high pressure system by measurement of electrical resistance, however, chrome carbide pistons are very convenient since electrical contact with the sample can be made via the pistons.

The high pressure cell is shown in Fig. 2. The ring, pellet, and sample geometry are shown in Fig. 3. This geometry was also used to obtain signals from cesium metal at atmospheric pressure. Since in much of the research the proton magnetic resonance was being studied, it was necessary to design a system which did not involve the use of proton containing materials near the coil, as these would produce an absorption signal. The general features of this design, however, are applicable to the study of other nuclei, as well as protons.

Pyrophyllite has been widely used for high pressure work, but is not always suitable for NMR experiments because it contains protons. Pellets were therefore machined from boron nitride. Its greater compressibility which results in higher pressures on the sample, make it perhaps even better than pyrophyllite as a material for pellets, as long as pressures are below 100 kbar where boron nitride undergoes a first order phase change.

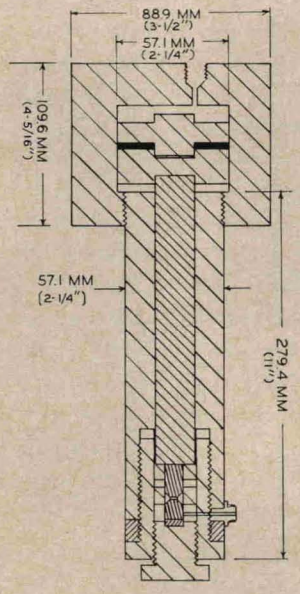

FIG. 1. High pressure NMR system.

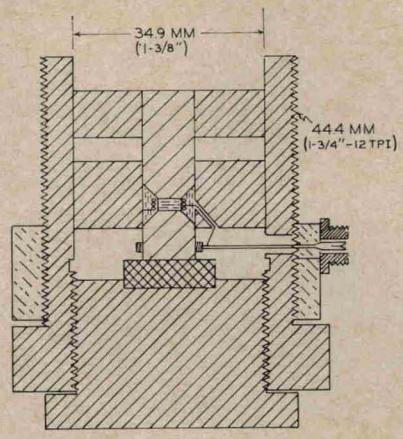

FIG. 2. High pressure NMR cell.

It was also necessary to minimize the use of epoxy resin in the sample cavity. For all nonproton work, epoxy resin is convenient to use both for cementing the coil in the pellet and for filling spaces between the turns of wire. Here, however, resin was used only to cement the leads of the coil. The problem of a filler was essentially avoided by making the coil of the largest possible gauge of copper wire that would fit into the space allotted for the coil.

The measurements of the ^{19}F resonance in Teflon were performed before chrome oxide pistons were available. To keep the chrome carbide pistons away from the small sample coil, it was necessary to use 0.75 mm (0.030 in.) thick pyrophyllite disks above and below the sample. Here as in most nonproton resonance work, pyrophyllite and epoxy resin may be freely used. Beryllium copper jackets were pressed around the top pistons to prevent chipping and to serve as a guide. The bottom piston rested on a 19 mm ($\frac{3}{4}$ in.) chrome carbide disk which was set into the bottom plug of the cell.

For the polyethylene and Teflon studies, which were performed at frequencies of approximately 30 Mc, $4\frac{1}{2}$ turns of wire were required in order to obtain the proper inductance. Cesium metal, which was run at a frequency of about 6.5 Mc, required the use of a two layer, 20 turn coil. One lead of the coil was grounded to the ring. The other was passed through a slanting 0.4 mm (1/64 in.)

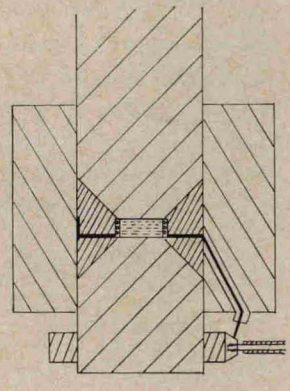

FIG. 3. High pressure ring, pellet, and sample geometry.