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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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[1] G. B. Benedek and E. M. Purcell, J. Chem. Phys. **22**, 2003 (1954).
[2] H. S. Gutowsky and G. Williams, Phys. Rev. **105**, 464 (1965).
[3] R. A. Hultsch and R. G. Barnes, Phys. Rev. **125**, 1832 (1962).
[4] J. J. Billings and A. W. Noble, J. Chem. Phys. **32**, 1072 (1960).
[5] R. Baron, J. Chem. Phys. **38**, 173 (1963).
[6] J. D. Litster and G. B. Benedek, J. Appl. Phys. **34**, 688 (1960).
[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.

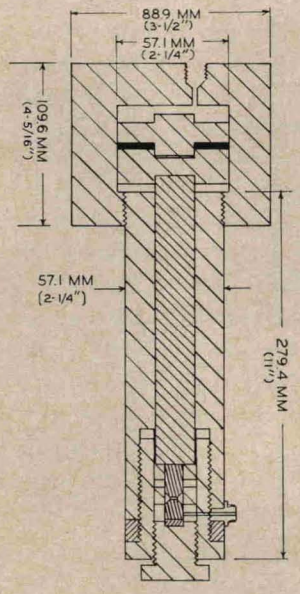

FIG. 1. High pressure NMR system.

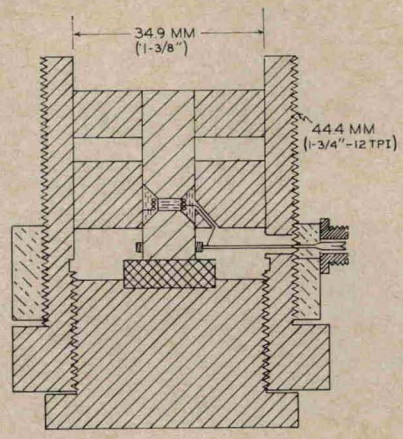

FIG. 2. High pressure NMR cell.

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.)

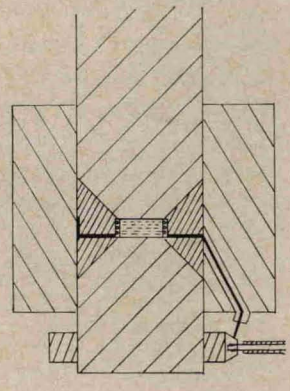

FIG. 3. High pressure ring, pellet, and sample geometry.

hole in the ring and soldered to a brass contact. A length of Teflon spaghetti tubing was used to insulate the lead. To reduce rf losses, the size of the brass contact was minimized and its supporting ring machined out of Bakelite. A length of silver solder, one end of which was soldered to the inner portion of a uhf connector, was screwed into the brass contact. Silver solder was used because it would hold a No. 80 thread and was sufficiently stiff, but not too brittle, to stand up under repeated use. This threaded contact completed the electrical connection between the marginal oscillator and the coil. The hole in the wall of the high pressure cell through which it passed proved to be the weak point in the apparatus.

The first step in the assembly was to place the coil inside the previously machined pellet. A Teflon form proved to be helpful in holding the coil in place until the epoxy resin hardened. Since the resin does not adhere to Teflon the form could later be twisted out of the coil. The grounded lead of the coil was simply bent up against the pellet edge in a shallow groove. Silver-filled epoxy resin was used to insure good electrical contact with the ring wall. Before the pellet was pushed into the ring, notches were filed into its edge. After it was in place in the ring, these notches were filled with epoxy resin. This prevented movement of the pellet, and the consequent shearing of the coil lead, during the rest of the assembly process. The bottom pellet was simply pushed into the ring. To ensure that both pellets fit tightly together in the ring, they were subjected to a slight pressure either in a vise or hydraulic press. The height of the sample chamber was then measured.

In the polyethylene runs, the sample cavity was about 2–2.1 mm (0.080 in.) high. The polyethylene samples were sanded down to a thickness of about 2.1 mm (0.085 in.). For the Teflon studies the over-all length of the sample chamber in the pellet was 3.5 mm (0.140 in.). Pyrophyllite disks, 0.75 mm (0.030 in.) thick, were placed above and below the 2.1 mm (0.085 in.) thick Teflon sample.

An adequate signal was obtained from cesium metal with a sample cavity approximately 1 mm (0.040 in.) high. The cesium metal which was dispersed in paraffin was loaded in the sample cavity with an eyedropper. Pressure runs with cesium have so far been limited by extrusion.

For pressure calibration the following transition points were used, bismuth I-II at 25.4 kbar and thallium I-III at 36.7 kbar. On one calibration run with 0.9 mm (0.037 in.) thick center we encountered a distinct drop in resistance of bismuth at 1400 kg/cm² (20 000 psi) applied pressure. This appears to be the 87 kbar transition in bismuth. These transitions were observed by measurement of the electrical resistance of the sample. A diagram of the sample and ring arrangement used for the electrical resistance calibration is shown in Fig. 4. Chrome carbide pistons were used since they are electrically conducting. The lower piston was insulated from the rest of the press

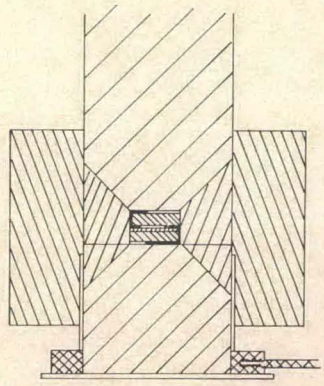

FIG. 4. Geometry of ring, pellets, and leads for calibration using electrical resistance.

by means of a mica sleeve set into the ring and held in place by the bottom pellet and by a mica disk placed beneath the piston between it and the chrome carbide supporting disk. Electrical contact with the lower piston was made by means of a brass disk into which a length of silver solder was threaded.

The sample, approximately 0.012 mm (0.0005 in.) thick, was placed between Bakelite or other plastic disks and in contact with amalgamated copper electrodes. The change in resistance was determined by measuring the potential drop across the sample with a Leeds & Northrup potentiometer. The calibration data are summarized in Fig. 5. The applied pressure is limited to about 1600 kg/cm² (23 000 psi) by splitting of the plug. The rest of the runs were restricted to lower applied pressure, but the system seems operable to 1400 kg/cm² (20 000 psi) for NMR measurements over indefinite periods.

The spectrometer used was a McClure oscillator, a type of marginal oscillator, which has been described elsewhere.[8] Master 10M series 6AK5 tubes were used in the spectrometer. These appeared to give a higher signal-to-noise ratio than ordinary commercial tubes. The oscillator frequency was measured by means of a Collins communications receiver which had been calibrated against WWV. Frequency could be determined to ±100 cps. Because of the small amount of energy in the sample coil, it was necessary to employ an Ameco Nuvistor cascade preamplifier to amplify the rf signal before it was fed into the Collins receiver.

A phase sensitive detector was used to amplify and detect the signal from the spectrometer. The phase sensitive detector used was similar to one that has been described previously.[8] The magnetic field was modulated at about 32 cps by means of an audio-oscillator connected to a pair of coils placed around the pole caps of the magnet. The magnetic field was swept by means of a second pair of coils also placed around the pole caps. The sweep current was produced by a system which regulated the 220 V dc supply

[8] H. S. Gutowsky, L. H. Meyer, and R. E. McClure, Rev. Sci. Instr. 24, 644 (1953).

via three 6528 tubes. The voltage to the grids of the 6528's and, therefore, the current passed, was controlled by a 15 turn precision Helipot. The Helipot was driven, through an Insco speed reductor and precision gear train, by a synchronous motor. The rate of sweeping of the magnetic field could be varied by changing the gear reduction ratio of the speed reductor and by setting the upper and lower sweeplimit potentiometers.

One difficulty encountered in working with the McClure oscillator was frequency drift. To eliminate this, a frequency stabilization system was developed in this Laboratory. The rf signal from the spectrometer was picked up by a second Collins receiver, where the signal was beat against its crystal controlled frequency. The resultant audio-output was fed into a Tektronix 162 waveform generator and then into a Tektronix 163 pulse generator. The square wave output was then rectified and filtered to a dc signal, which was applied to a voltage variable silicon capacitor in the tank circuit of the spectrometer. This system held frequency drifts to approximately 100 cps, sufficiently long for the linewidth to be determined.

The field was calibrated during each sweep by means of a Perkin-Elmer gaussmeter. Since the commercial gaussmeter probes would not fit in the pole gap of the magnet with the high pressure press in place, a special probe was used which consisted of an aqueous solution of cupric sulfate and lithium chloride in a melting point capillary tube. This probe was taped to the pole cap, adjacent to the press, at the center of the field. All runs were made with a Varian V-4012-B magnet equipped with tapered pole caps and having a 63.5 mm ($2\frac{1}{2}$ in.) pole gap. The diameter of the

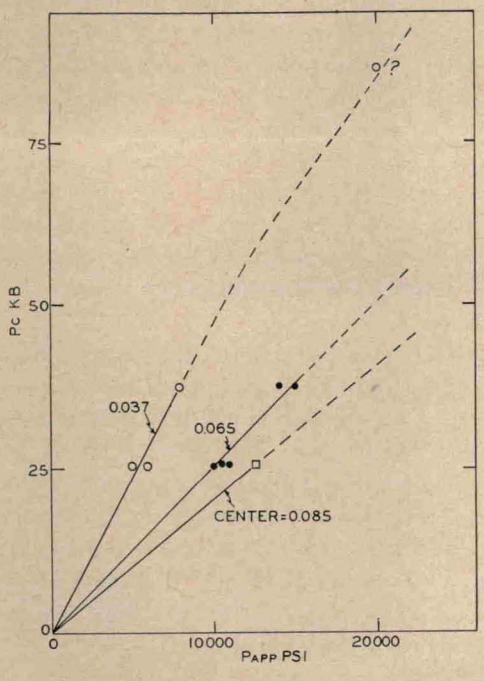

FIG. 5. Pressure calibration.

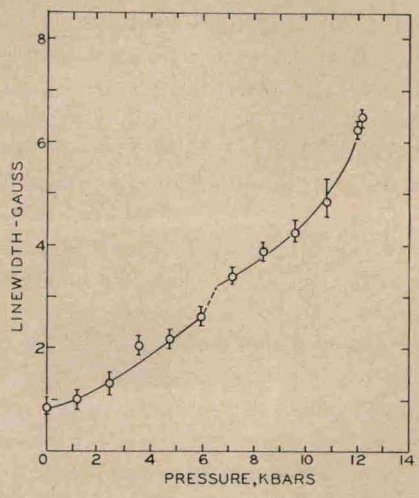

FIG. 6. ^{19}F linewidth vs pressure for Teflon.

flat portion of the pole caps was 215.9 mm ($8\frac{1}{2}$ in.). In runs on polymers the field was set at approximately 7000 G; for cesium, the field was approximately 11 600 G.

The linewidth vs pressure data for the ^{19}F resonance of Teflon are plotted on Fig. 6. These linewidth values were corrected for modulation broadening. The linewidths increase with pressure, until at 10 kbar, a break in the linewidth curve occurs. A further, almost linear, increase takes place to 11 kbar, at which point a rapid increase occurs.

Teflon is an unusual polymer in that it has several temperature and pressure induced phase transitions. Below 20°C, the structure of the Teflon molecule consists of a helix, twisted 180° every 13 chain atoms.[9] Transitions occur at atmospheric pressure at 20 and 30°C. These transitions have been studied by a number of investigators[9–13] and appear to involve either an untwisting of the molecular helix or even a reversal of the twist of some of the helices from a left handed to a right handed orientation. Teflon also undergoes a phase transition at a pressure of 6.5 kbar. This is the Teflon II-III transition. It was discovered independently by Bridgman[14] and Weir.[15]

The transition is associated with a volume change of 2.25%. Beecroft and Swenson have investigated this transition and delineated the phase diagram for Teflon.[16] They also report indications of a second incomplete transition at approximately 11 kbar. None of the transitions are sharp and all exhibit considerable hysteresis. Brown[10] has suggested, on the basis of his high pressure infrared study of Teflon, that the 6.5 kbar transition involves the assump-

[9] C. W. Bunn and E. R. Howells, Nature **174**, 549 (1954).
[10] R. G. Brown, J. Chem. Phys. **40**, 2900 (1064).
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[15] C. E. Wier, J. Res. Natl. Bur. of Std. **46**, 207 (1951).
[16] R. J. Beecroft and C. A. Swenson, J. Appl. Phys. **30**, 1793 (1959).

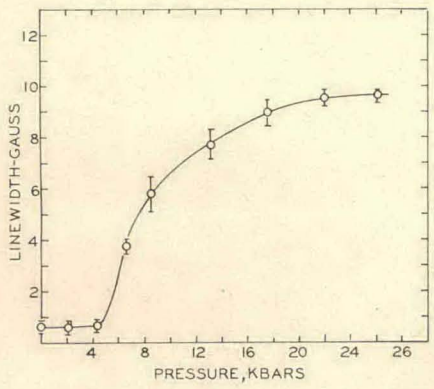

FIG. 7. ^{1}H linewidth vs pressure for polyethylene.

tion by the carbon skeleton of the polymer of a planar configuration.

The NMR linewidths vs pressure curve obtained in this study shows a discontinuity at 6-7 kbar which is probably the Teflon II-III transition. If the Teflon molecule does assume a planar structure this would be expected to restrict the motion of the chain and lead to an increase in the NMR linewidth. The rapid increase in linewidth which occurs at 11 kbar may be the higher incomplete transition reported by Beecroft and Swenson.[16] To obtain an idea of the molecular structure at this point by broadline technique, accurate second moment values would be required. These would then be compared with values calculated from a model. Since the experiments were not conducted at a temperature sufficiently low to freeze out molecular motion, approximate corrections for this would have to be made. An estimate would also have to be made of the reduction in interatomic distances and the theoretical second moment corrected for this as well. Thus, while the exact nature of the molecular reorientation cannot be determined, the NMR results show that the transformation does involve a more severe restriction of chain mobility than the 6.5 kbar transition.

The Teflon linewidth obtained at atmospheric pressure at the conclusion of the high pressure run agreed with the values obtained before the run. This indicates that the pressure induced changes are reversible; in agreement with the results obtained in other studies.

Linewidth vs pressure data for polyethylene are shown in Fig. 7. There is no measurable change in linewidth until a pressure of 5 kbar is reached. A rapid increase occurs above this pressure which finally levels off near 22 kbar. Lineshapes obtained at pressures of 1 atm and 26.4 kbar are shown in Figs. 8 and 9.

The polyethylene molecule is planar. It is not helical and there are no known phase transitions. Polyethylene and Teflon crystallize from the melt in the form of lamella or platelets.[17] The polyethylene chains are folded back and forth perpendicular to the plane of the platelet. Bridgman's measurements on the compression of polyethylene[10] do not reveal any phase transitions. The compression vs pressure curve does show a rounding off at the higher pressures similar to that exhibited by the NMR linewidth vs pressure curve. It appears then that while a phase transition may not occur at 5 kbar, the motion of the polyethylene chains is being severely restricted; this restriction may occur primarily in the amorphous region of the polymer. The pressure induced changes in polyethylene, like those in Teflon, appear to be reversible.

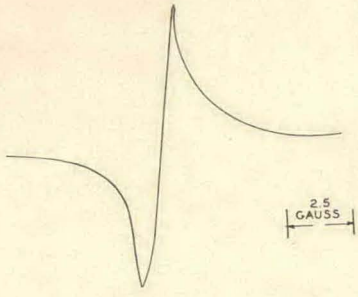

FIG. 8. NMR lineshape of polyethylene at 1 bar.

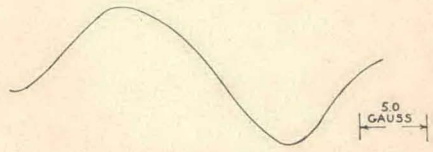

FIG. 9. NMR lineshape of polyethylene at 26.4 kbar.

The high pressure system developed in this research is suited to spin echo, as well as broadline NMR measurements of T_1, T_2 and coefficient of self-diffusion in solids.

The commercial availability of superconducting magnets opens up other possibilities. For example, if a 40 kG superconducting magnet were used instead of a 10 kG electromagnet, the magnetic resonance frequency for studying ^{133}Cs would be about 22.4 Mc instead of 5.6 Mc. The coil required would consist of 5 turns of wire instead of 20. Perhaps more important, the signal-to-noise ratio in a 40 kG field would be increased approximately eight times.

ACKNOWLEDGMENT

The helpful suggestions and interest of H. S. Gutowsky are gratefully acknowledged.

[17] P. H. Lindenmeyer, J. Polymer Sci. **31**, 539 (1963).