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

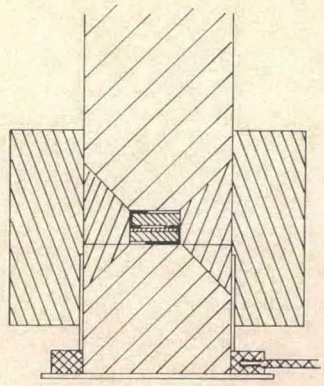

FIG. 4. Geometry of ring, pellets, and leads for calibration using electrical resistance.

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

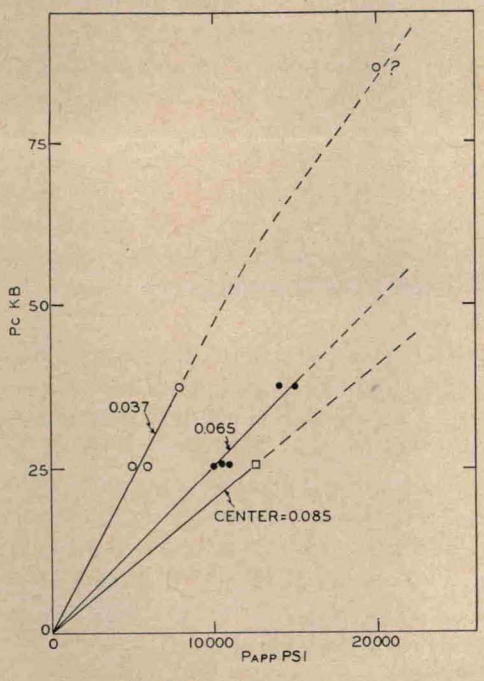

FIG. 5. Pressure calibration.

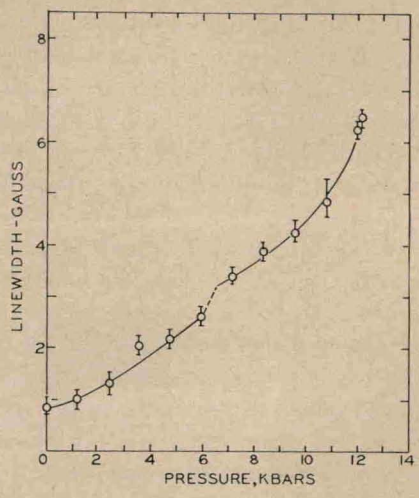

FIG. 6. ^{19}F linewidth vs pressure for Teflon.

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-

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