

of ( $T_2'$ ) at constant temperature.

### III. EXPERIMENTAL DETAILS

#### A. NMR Equipment

A block diagram of the spin-echo apparatus is shown in Fig. 1. The system was constructed according to previously published designs.<sup>24,25</sup> A crystal-controlled oscillator operating at 5.25 MHz supplies the radio frequency to the rf gate and to the reference. The phase shifter in the reference allows the phase difference between the reference and the nuclear signal to be varied by  $360^\circ$ .

The transmitter develops pulses of 1600 V without a load. When coupled to the sample circuitry and pressure vessel, the pulse voltage at the transmitter output decreases to approximately 400-V peak to peak. Pulse widths of 10–15  $\mu\text{sec}$  are sufficient to produce a  $90^\circ$  pulse with respect to aluminum. This corresponds to a rotating magnetic field  $H_1$  of 25 Oe. With a higher  $Q$  tank circuit, such as a high-temperature probe or simply a coax pipe and sample coil connected in the sample circuitry, pulses as short as 2  $\mu\text{sec}$  yield a  $90^\circ$  pulse for protons at 10.5 MHz. This corresponds to  $H_1 = 60$  Oe.

The recovery time of the receiver was originally estimated to be near its nominal value of 20  $\mu\text{sec}$ , as it took this long after the end of a rf pulse for the detected receiver output to fall from its saturated value to near zero. Attempts to reduce this with switching circuits and balancing networks did not noticeably improve the recovery time.

Later it was found that the true recovery time can only be seen in the presence of a signal, such as the steady reference signal which is normally used to bias the crystal detector. The recovery of normal gain is really the condition of interest. This can most easily be seen by looking at a steady signal at the rf output of the receiver. It was found that after a pulse had been applied to the sample circuitry, the receiver was saturated for 20  $\mu\text{sec}$  following the pulse and then returned to nearly the amplitude determined by the reference signal but did not fully return to normal amplification until 75  $\mu\text{sec}$  after the pulse. Accurate amplitude measurements are restricted to echoes which occur 75  $\mu\text{sec}$  or more after the second pulse, or more than 150  $\mu\text{sec}$  after the first pulse. This limitation is important if the relaxation time  $T_2$  is about this short. A rf output was added ahead of the detector of the amplifier to allow the amplitude of a coherent 10.5-MHz reference signal to be measured relative to the amplitude of the nuclear signal. Knowing the ratio of these signals and the amplitude of the detected nuclear signal one can find the amplitude of the reference signal at the crystal detector. A reference signal of 1.5 V at the detector proved sufficient to bias it into the linear region.

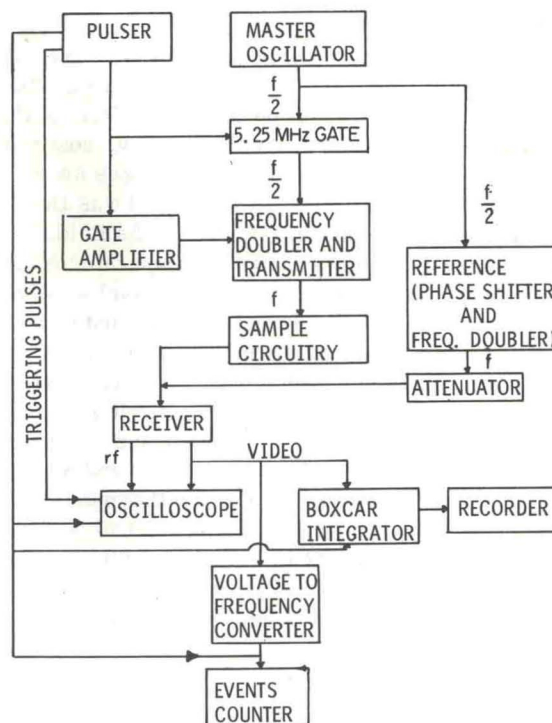


FIG. 1. Block diagram of the spin-echo apparatus.

Values of  $T_2$  were obtained from Polaroid multiple-exposure pictures of echo amplitudes for various values of  $t = 2\tau$ , or from the strip-chart output of a boxcar integrator.<sup>25</sup> The time between rf pulses was adjusted by a step switch and was measured by a Berkeley Universal Counter Model 7360R or a Hewlett Packard Counter Model 524D.

All of the measurements were made in a Harvey Wells 12-in. low-impedance electromagnet, Model L128, with a 3-in. air gap. The associated power supply (Harvey Wells HS-1050) has a current stability of  $10^{-5}$  at 5000 Oe. Additional details of the electronic instrumentation are contained in Ref. 26.

#### B. Pressure Equipment

The pressure generating equipment is essentially that described in Refs. 4 and 26. Full details are contained in the latter reference.

The design of the pressure vessel itself is rather conventional, and is shown in Fig. 2. The body of the vessel was machined of A286, a precipitation-hardenable stainless steel. This is a nonmagnetic alloy which retains its strength to above  $450^\circ\text{C}$ . The material was obtained from Republic Steel Corp. and hardened to Brinnell No. 321 by following the manufacturer's direction. The plug was machined of another high-temperature nonmagnetic stainless steel 19-9DL, also obtained from Republic Steel. This material is not hardenable by heat treatment.



The copper sealing rings flowed enough at high temperatures that it was often necessary to tighten the plug a few times with the vessel at about 200°C before a good seal could be obtained. Part of this difficulty no doubt came from the low viscosity of 3-centistoke silicone oil at temperatures near 450°C. The pressure fluid first used was Dow-Corning DC200, 200 centistokes. This fluid "crosslinked" at these elevated temperatures and upon disassembly of the pressure vessel was found to contain a puttylike substance composed of many small sticky translucent balls. This substance was probably very fluid at 400°C, but it would migrate along the pressure line, cool, and plug it. It was found that a simple test for an unplugged line was to increase the pressure at the intensifier and watch the galvanometer connected to the thermocouple imbedded in the vessel. If the temperature dropped within a few seconds it indicated that the pressure fluid was entering the pressure vessel.

Dow-Corning DC550 silicone fluid was also tried.

This lasted longer than DC200, 200 centistokes but it too would crosslink after prolonged time at high temperatures. Finally, Dow-Corning DC200, 3 centistokes was used successfully as a pressure fluid. The only disadvantage of this fluid was that it was difficult to contain. Although kept for several days at high temperatures, it never crosslinked or gelled. The only indication that it had been subjected to such treatment was a slight discoloration.

The entire pressure vessel was contained in a cylindrical oven which was insulated with asbestos on the outside to prevent heating of the magnet pole pieces. The noninductive heater of this oven was dc powered. Under the usual operating conditions, temperatures remained constant to  $\pm 1^\circ\text{C}$  without control, however, for some runs a conventional proportioning type controller circuit was used, employing the signal from one of the thermocouples embedded in the pressure vessel (see Fig. 2).

### C. Sample Preparation

Two sources of 99.99% aluminum were used. One source was a single-crystal rod of aluminum purchased from the Monocrystals Co. The rf penetration depth in aluminum is  $28\ \mu$  at 10.5 MHz and room temperature, and increases as the temperature is increased. To ensure reasonably uniform penetration the samples used in the pressure dependence study consisted of filings less than 325 mesh ( $44\ \mu$ ) obtained from this crystal bar. Ferromagnetic particles were removed from the sample by repeatedly passing a test tube containing small amounts of loosely packed sample through a 5000-G magnetron magnet. These aluminum filings were put in a Pyrex glass tube, 9 mm o. d. and about 3 cm in length, and mixed with Dow-Corning 550 silicone fluid. A loose fitting glass piston was placed in the tube on top of the filings. One sample in which the filings were mixed with Dow-Corning DC200, 3 centistokes silicone fluid sintered at high temperature and pressure.

The other source of samples was a piece of aluminum from an ingot which was part of the Ames Laboratory pure metals stock. This piece was filed, and the filings were sieved and cleaned of ferromagnetic particles. Samples from this source were used only in a temperature dependence study.

## IV. EXPERIMENTAL RESULTS

### A. Previous NMR Work on Aluminum

Spokas<sup>6,7</sup> employed the spin-echo technique to measure the spin-lattice relaxation time  $T_1$  and the inverse linewidth relaxation time  $T_2$  in 99.99% aluminum foil as a function of temperature from 77°K to above the melting point. The objective was to

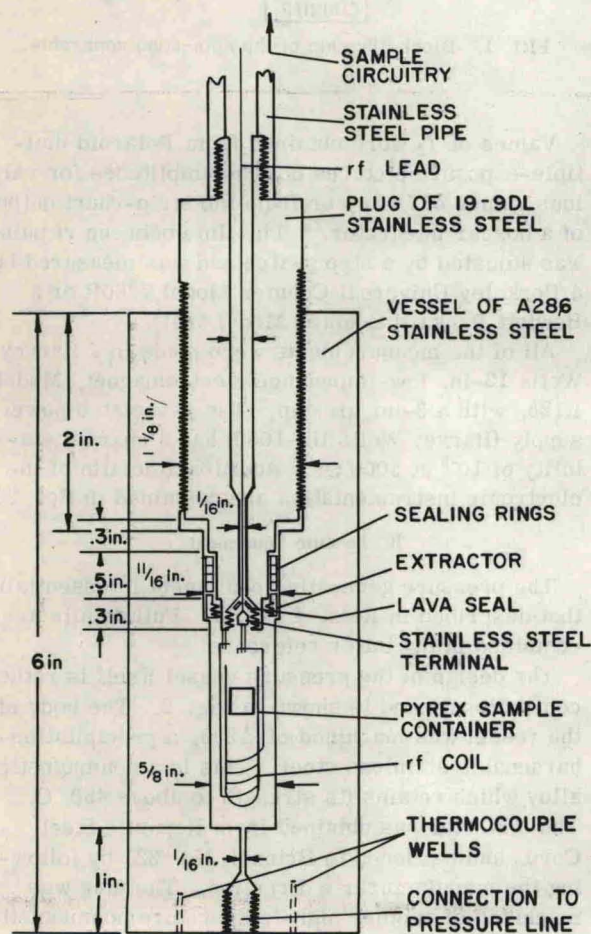


FIG. 2. Stainless-steel pressure vessel used for spin-echo measurements. Outside diameter of the vessel is  $2\frac{1}{8}$  in.