Chapter II

EXPERIMENTAL METHODS

II.1 The Instruments for the Measurement of Nuclear Relaxation Times

The electromagnet (Bruker B.E. 25c8) has been used to provide the d.c. magnetic field. The various parts of the instrument used for obtaining the nuclear relaxation times T_1, T_2 by the spin echo method are as follows,

Tektronix type 160A power supply ,
Tektronix type 162 wave form generator,
2 units of Tektronix type 163 pulse generator,
pulse amplifier ,
rf oscillator and gated rf transmitter[16,16a] ,
rf preamplifier ,rf amplifier ,
rf phase sensitive detector ,
sample cell ,
Tektronix type 549 storage oscilloscope ,
Tektronix type C12 scope camera .

The description of the pulse amplifier, rf preamplifier, amplifier and phase sensitive detector could be found elsewhere[17].

---

[16] R.J. Blume,"rf Gate with 10^9 Carrier Suppression," The Review of Scientific Instruments ,32(1961), 554.

[16a] W. Senghapan,"An Investigation of Spin-Lattice Relaxation Time of bcc Solid Helium-3,", Ph.D. Thesis, Boston University,1968 .

[17] P.Trivijitkasem," Spin Relaxation in PAA Liquid Crystal," M.Sc. Thesis, Chulalongkorn University,1972.

II.2 Sample Cell

Each of the commercial PCBAV and DADB was sealed in a cleaned 0.64 mm outside diameter and 0.14 mm wall thickness, pyrex tube. Since the sample was in the smectic phase in a range of temperature higher than room temperature,heating process was necessary.The hot oil with low viscosity from a thermostatic bath was used for this purpose. Thus the cylindrical copper chamber was designed in order that the sample in the pyrex tube had the minimum temperature gradient.

The cylindrical copper chamber consisted of the following parts.
(1) A cylindrical bar (which will later on be referred to as " the copper base") was 2.5 cm in diameter.It had a shallow hole centrally located at one end. The depth of the hole was about 0.5 cm . The copper base was wound around by a copper pipe 6 mm in diameter. Since the 6 mm copper pipe was the path of the oil used for heating the sample, the contact between the pipe and the copper base was very important. The 6 mm copper pipe was therefore connected with a 10 mm copper pipe which led to the thermostatic bath. The thermocouple was attached to this part for measuring the temperature of the sample.
(2) A 2.5 cm copper pipe, 1.5 cm wall thickness, was connected to the copper base. This pipe was 5.5 cm long. The rf coil about 2 cm long was placed in this part just above the copper base. The rf coil was at 0.5 cm above the copper base. The end of the wire of this end of rf coil was grounded. The other end of rf coil led to a preamplifier. This wire was supported by plastic along the brass pipe 1 cm in diameter. The brass pipe was surrounded by

insulating material to prevent heat loss .

(3) The copper lid.

The chamber was in the box made of insulating material.

II.3 Temperature Control and Measurement

The following apparatus was used for temperature control and measurement,

Techne model CTB thermostatic bath,
ballistic galvanometer,
standard cell,
chromel/alumel thermocouple,
vernier potentiometer.

II.3.1 Temperature control

The sample in the sealed pyrex tube was heated by means of hot oil[*] circulated in the copper pipe wound around the copper base. The part touching the copper base was only the bottom of the pyrex tube ,and grease was used to improve the contact. Since the pyrex tube was slightly touching the copper base, any specific temperature should be held for a long time to ensure that the whole sample was at exactly the same temperature as the copper base.

The oil was supplied from the thermostatic bath (TE-4/CTB), the temperature of which was controlled by means of an electronic unit. The desired temperature could be set through the dial.

---

[*] Although the heating system used in this experiment contained hot oil which was hydrocarbons,it was experimentally verified that the protons in hot oil did not interfere with the resonance in the sample since hot oil was completely shielded in the tube.

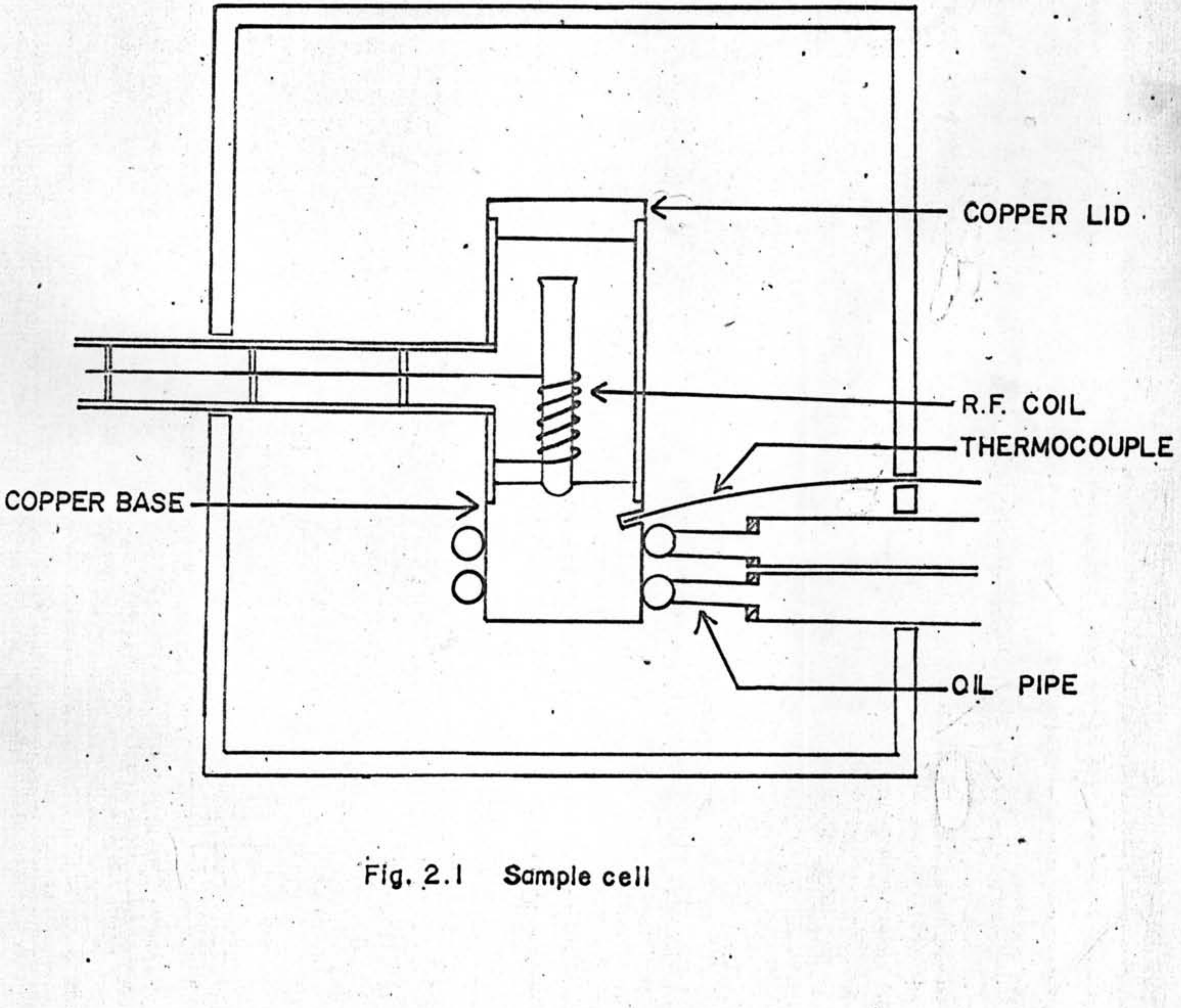

Fig. 2.1 Sample cell

" Shell Risela 17 " was used as the thermostatic fluid in this experiment because of its high boiling point and low viscosity. The advantage of low viscosity is for preventing heat loss in the flow of the fluid along the pipe.

II.3.2 Temperature measurement

The temperature of the sample was measured by using the chromel/alumel thermocouple. One of the junction, grounded junction, was attached to the copper base, the other junction was held at fixed temperature 0°C. The thermal electromotive force corresponding to the specific temperature was measured by using a vernier potentiometer. The measured temperature in the range of this experiment had possible errors within about 0.3%.

II.4 The Principle of Measurement

An intense radiofrequency energy in the form of pulses was used instead of a continuous radiofrequency field. Each pulse lasted for a time which was short compared with the time in which the macroscopic magnetic moment could decay. After applying the following sequence of rf pulses,

(a) at $t=0$, a 90° pulse

(b) at $t=\tau$, a 180° pulse ,

the spontaneous nuclear induction signals were observed[18]. These echoes were due to a constructive interference of precessing macroscopic moment vectors after more than one rf pulse had been applied.

---

[18] E.L. Hahn , " Spin Echoes , " Physical Review ,80(1950),580.

The occurrence of the spin echo can be described as follows . The static field has an inhomogeneity of $\Delta H = H_z - H_{zo}$ where H_{zo} is considered as a center . With an increment dH_z , there is a corresponding incremental $d\vec{M}(H_z)$ which is the vector sum of the moments of all nuclei within the regions where the field strength is between H_z and $H_z + dH_z$. The equation of motion[19] of the incremental magnetic moment vector is

$$\frac{d}{dt}\left\{ d\vec{M}(H_z) \right\} = -\gamma \vec{H} \times d\vec{M}(H_z) \quad . \qquad (2.1)$$

Thus the incremental vector precesses with an angular frequency $\omega = -\gamma H$ about the direction of $\vec{H}$.

By transforming to a rotating coordinate system which rotates with an angular frequency $\vec{\Omega} = -\gamma H_{zo}\vec{K}$, Eq. (2.1) can be written as

$$\frac{\partial}{\partial t}\left\{ d\vec{M}(H_z) \right\} = -\gamma (\vec{H} + \frac{\vec{\Omega}}{\gamma}) \times d\vec{M}(H_z) \quad . \quad (2.2)$$

As a result, $d\vec{M}(H_z)$ precesses about $\vec{H}$ with small angular frequency

$$\vec{\omega}_\Delta = -(H_z - H_{zo})\vec{K} \quad , \qquad (2.3)$$

in the rotating coordinate system.

The radiofrequency magnetic field is applied perpendicular to the direction of the strong static field. The frequency of the rf field satisfies the resonance condition $\omega_{rf} = \gamma H_{zo}$. Breaking

---

[19] Charles Kittel , Introduction to Solid State Physics (John Wiley & Sons, Inc. New York , 1967).

the rf magnetic field into two rotating components, H_R and H_L

$$H_R = H_1 \left[\cos\omega t i + \sin\omega t j\right] , \qquad (2.4)$$

$$H_L = H_1 \left[\cos\omega t i - \sin\omega t j\right] . \qquad (2.5)$$

Only one of the two components plays a part in nutating the net magnetic moment[20]. The phase of the rotating system will be chosen such that the magnitude H_1 is along the x'-axis. With the rf field , the equation of incremental magnetic moments is

$$\frac{\partial}{\partial t}\left\{d\vec{M}(H_z)\right\} = -\left\{(\gamma\vec{H} + \vec{\Omega})\vec{k}\right\} \times d\vec{M}(H_z) . \qquad (2.6)$$

Thus the incremental magnetic moment vectors precess about the net magnetic field H ,

$$\vec{H} = \Delta H_z \vec{k}' + H_1 \vec{i}' . \qquad (2.7)$$

In a special approximation[21]., the net incremental moments precess about $H_1\vec{i}'$ during the presence of rf field. Consequently all incremental moments will rotate together as a single magnetic moment vector. After applying the rf pulse for a time t_ω the magnetic moment will rotate through an angle

$$\theta = \gamma H_1 t_\omega . \qquad (2.8)$$

---

[20] Charles P. Slichter ,<u>Principles of Magnetic Resonance</u> (Harper and Row.,New York: Evanston and London, 1963),p 18 .

[21] H.Y. Carr and E.M. Purcell , " Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments," <u>Physical Review</u> ,94(1954), 630.

The 90° pulse and 180° pulse are the pulses which have been applied in time such that the angles of nutation are 90° and 180°, respectively. The spin-echo occurs after applying 90° pulse and 180° pulse. The formation of an echo can be shown in a simple diagram (Fig. 2.2).

II.5 Method for the Determination of T_1

The instruments were set as shown in the block diagram in Fig. 2.3. A 180° pulse was first applied. The total magnetic moment vector was inverted from the positive z-direction to the negative z-direction. According to the spin-lattice relaxation process, the total magnetic moment would return to the initial position after the removal of the 180° pulse. A 90° pulse was then applied at time τ after the 180° pulse, such that there would be no induction tail. The time τ that produced no induction tail is called τ null. The value of T_1 can be calculated directly from τ null by using the relation

$$\tau_{\text{null}} = T_1 \ln 2 \quad .$$

There is another aspect we would like to comment on here. In a smectic liquid crystal, the direction of the long axis of the molecule cannot be specified by the low external magnetic field as in a nematic liquid crystal. It has been suggested that the external magnetic field of about 20000 gauss should have enough power for alignment[21a]. In this experiment, the proton-spin lattice relaxation time of a smectic liquid crystal was studied at about 10.25 MHz. , which corresponded to the external magnetic field of about 2408 gauss. Since the magnetic field used in this experiment

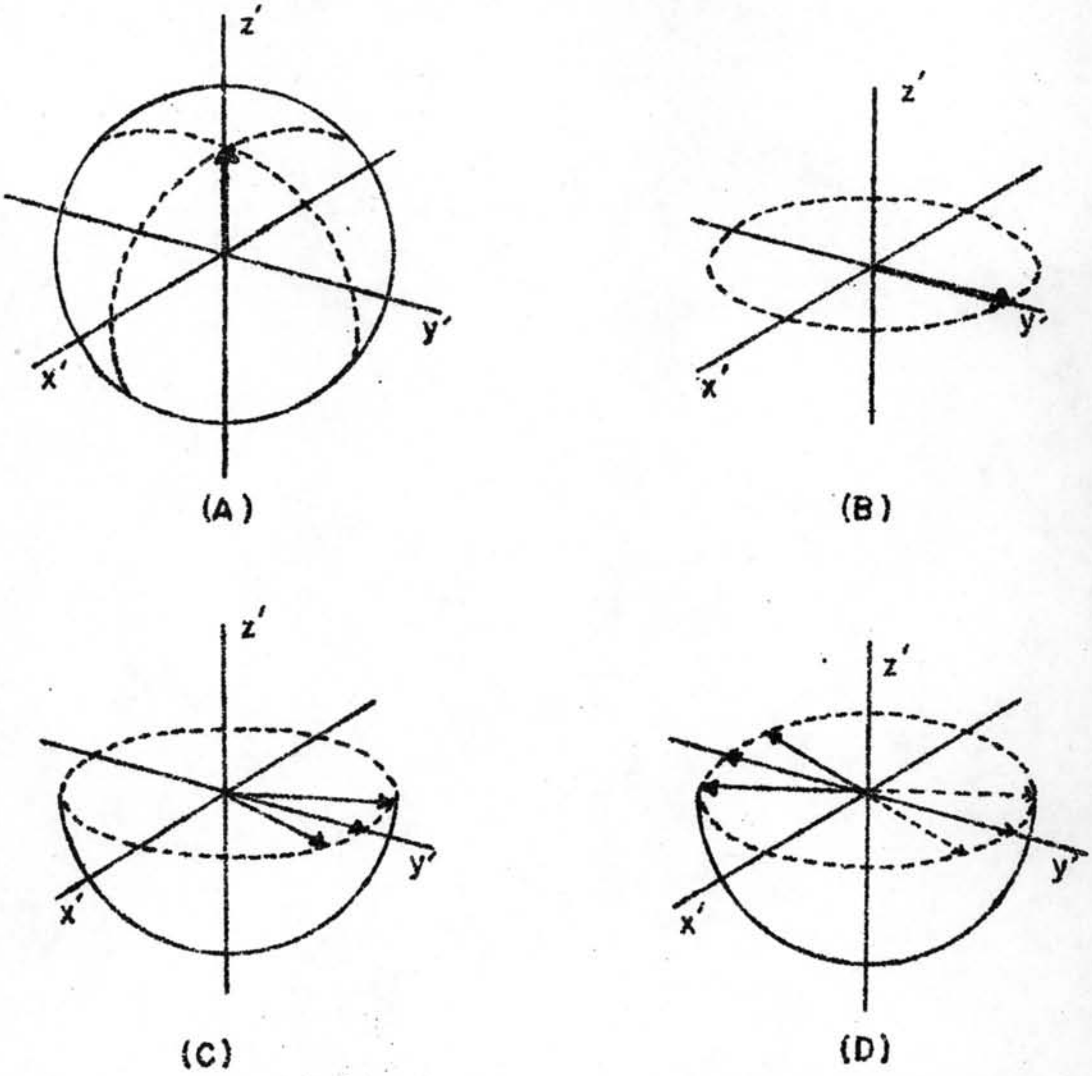

Fig. 2.2 The formation of an echo in the rotating frame

(A) The total magnetic moment is in its equilibrium position.

(B) After applying a 90° pulse, the total magnetic moment is in the xy plane.

(C) The incremental magnetic moments begin to fan out due to the inhomogeneity of the static field.

(D) After applying a 180° pulse, the incremental magnetic moments are inverted.

could not align the smectic molecules , the substance should be heated up to the temperature that was slightly higher than the smectic-isotropic transition temperature. In this way the smectic molecule could be aligned parallel to the magnetic field. Maintenance of a slow repetitive rate prevented heating the sample by the rotation field pulse.

II.6 Method for the Determination of T_2

The instruments were set as indicated in the block diagram in Fig. 2.4 . A 90° pulse was first applied. The total magnetic moment was tipped into the xy plane , and a 180° pulse was then applied at time $t=\tau$. The echo appeared at $t=2\tau$. When a 180° pulse was applied at $t=3\tau$, the second echo was formed at $t=4\tau$. In this method a sequence of 180° pulses were applied after the 90° pulse until there was no further echoes observed. The envelope of these echoes indicates the decay of the magnetic moment in the xy plane.

This spin-spin relaxation time T_2 of the substances used in the present investigations was generally so short that an echo experiment could not be performed. So T_2 was deduced from the line width by using the relation.

$$T_2 = \frac{T_{1/2}}{\ln 2}$$

where $T_{1/2}$ = the half width of the induced signal of the 90° pulse .

[21a] D.L. Uhrich , J.M. Wilson and W.A. Resch," Mössbauer Investigation of the Smectic Liquid Crystalline State ," Physical Review Letters., 24(1970),355.

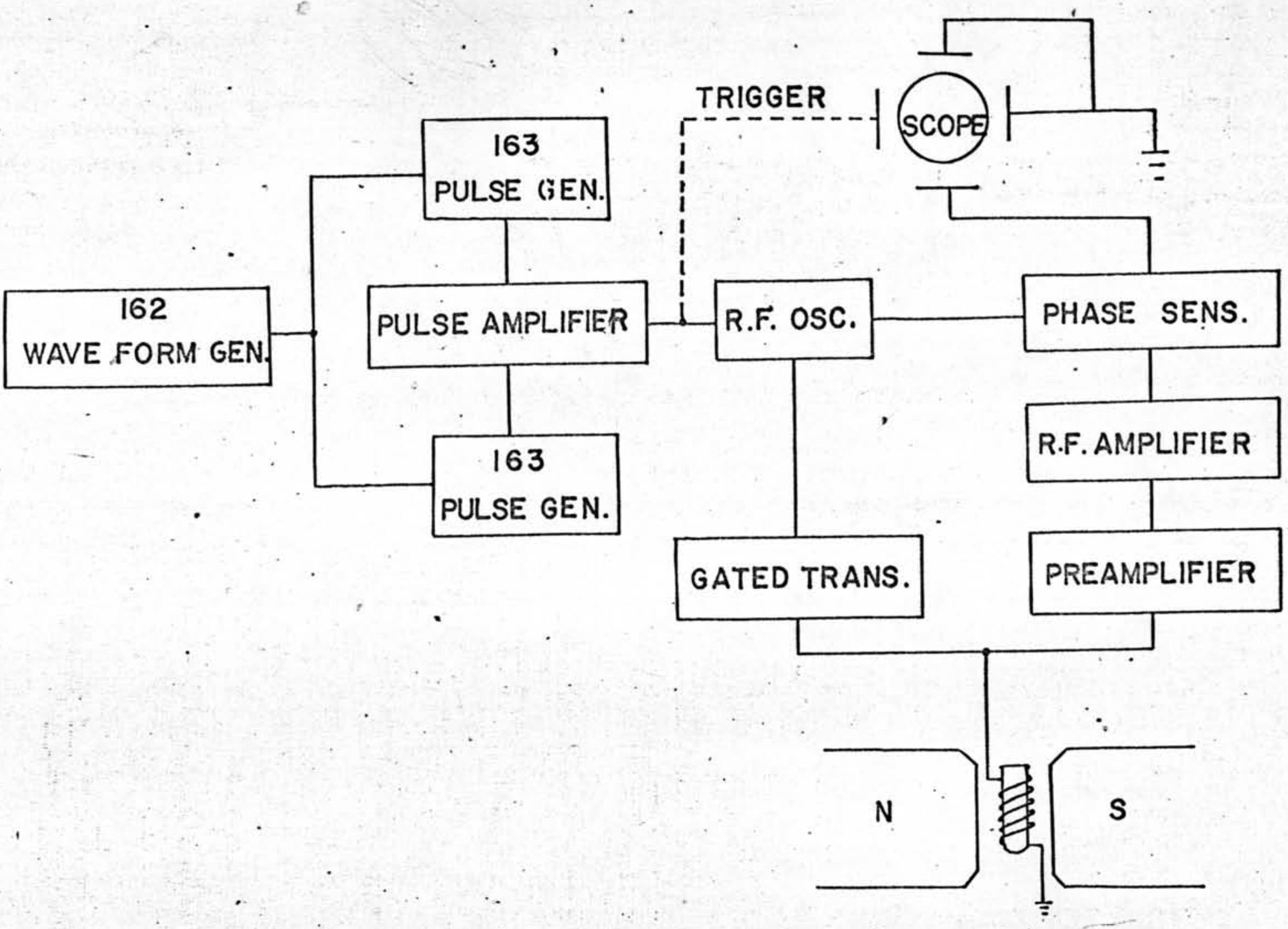

Fig. 2.3 Block diagram for measuring T_1

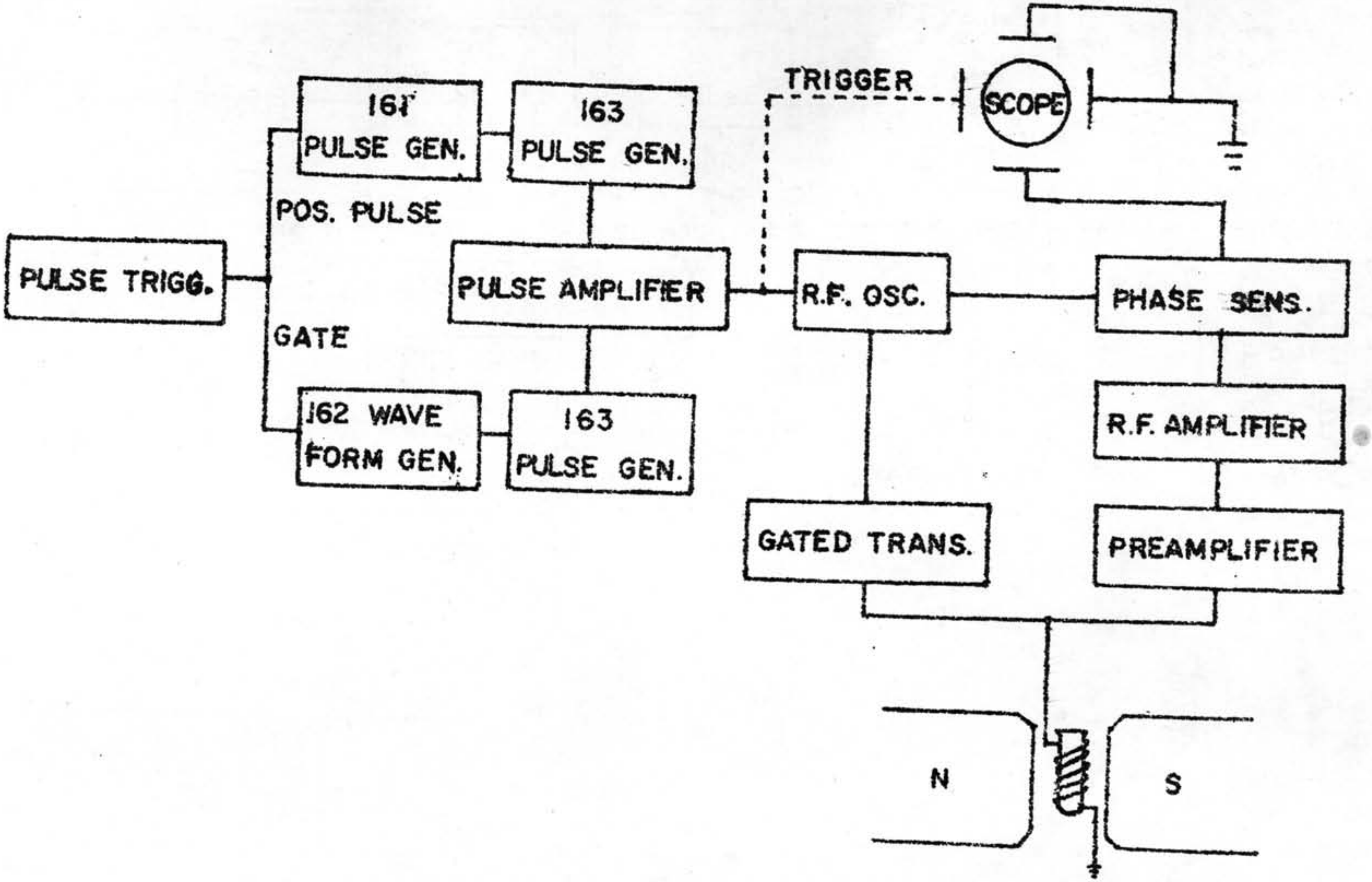

Fig. 2.4 Block diagram for measuring T_2