CHAPTER II

EXPERIMENTAL TECHNIQUES

II.1 INTRODUCTION

Nuclear magnetic resonance can be studied by both cw and pulsed techniques. As this thesis is mainly concerned with T₁ measurements in certain diamagnetic solids, the details of the pulsed NMR spectrometer used in the study are described in this chapter. Several pulsed NMR spectrometers [1-6] have been reported in the literature. Microprocessor controlled [7,8] and PC controlled [9-12] spectrometers are also available.

The Block diagram of the spectrometer is shown in Fig. II.1. The main parts of the spectrometer are, (1) The Electro Magnet (2) Transmitter, (3) Matching network (probe), (4) Receiver (5) Data analysis set up. These are briefly described in the following sections.
Figure II.1. Block diagram of pulsed NMR spectrometer
II.2 PULSED NMR SPECTROMETER

II.2.1 ELECTROMAGNET:

The magnet provides the static magnetic field which should be stable and homogeneous.

A home made electromagnet with 12" diameter pole pieces and a gap of 2.5" provides the magnetic field \( H_0 \). The DC power supply to the electromagnet consists of a voltage regulator followed by current regulator. The current fluctuations are monitored across a constant resistance, maintained at constant temperature. The corresponding voltage fluctuations are fed to an error amplifier and compared against a steady reference dc voltage. The current regulator is a modified version of Cook et al [13]. The current in the magnet can be varied by varying the reference input to the current regulator. The field stability is of the order of 1 in \( 10^5 \) Gauss, which enables to observe stable FID signals.

VOLTAGE REGULATOR:

The series voltage regulator used for the magnet power supply is shown in Fig.II.2. It consists of a voltage regulator IC CA3085A working in a high voltage mode. Ten power transistors are connected in parallel at the output of CA 3085A to deliver the required current. To the emitters of these power transistors, 1 ohm resistors are connected which serve as current equalizers. The circuit provides a stable and regulated d.c. voltage up to 115V and up to 20 amps.
Figure II.2. Circuit diagram of voltage regulator.
CURRENT REGULATOR:

The current in the electromagnet is stabilised by a current regulator shown in Fig.II.3. This is a modified version of Cook et al [13]. The magnet coils (taken in series) and a standard resistance (SR) are connected in series with a bank of 2N 3442 power transistors. The current through the magnet coil is monitored by the standard resistance (0.3 ohm) maintained at constant temperature. The voltage drop across the standard resistance is compared with a reference voltage and the output of the error amplifier (μA 725 C) is used to regulate the current in the magnet coils. The standard resistance is immersed in an oil bath which is cooled by circulating water through the copper coils immersed in oil bath. The output of the error amplifier is connected to the base of a 2N 3442 mounted on an aluminium heat sink.

The error amplifier consists of μA 725C which has a low drift of 0.6μV/K and a high gain of 60 dB. The output of μA 725C is connected to the base of a 2N3442 which gives the base drive to the power transistors connected in parallel. A dry battery and a resistor network provide a clean and stable reference voltage to the error amplifier. If the reference input of the error amplifier is changed, it changes the base drive to the first 2N 3442 transistor which in turn changes the current in the magnet. The potentiometers provide coarse and fine variation of the magnet current. Any fluctuations in the magnet current are sensed across the standard resistance as voltage fluctuations and the error amplifier provides the appropriate base drive to the series transistors in such a way as to oppose the fluctuations in the current. To prevent any damage to the coils of the magnet from induced voltage in the event of sudden power failure, a high current diode IN 15 is connected.
Figure 11.3: Circuit diagram of current regulator.
the magnet coils in reverse biased mode.

II.2.2 TRANSMITTER:

The block diagram of the transmitter is shown in Fig.II.4. This consists of a radio frequency source, a programmable pulse generator, a double balanced mixer, a medium power amplifier and a high power amplifier.

RF SOURCE:

A sytronics (type 1103) signal generator, capable of generating up to 72 MHz is used as the rf source. There are two output ports available. (1) A direct output (unattenuated output of 1 Vpp into 50 ohm load) and (2) An attenuated output (variable from 0 to 1 V into 50 ohm load). The reference RF to the phase sensitive detector is taken from the direct output while the RF to the input of the gate is taken from the attenuated output.

PROGRAMMABLE PULSE GENERATOR:

The block diagram of the programmable pulse generator is given in Fig.II.5 and its sub-units are given in Fig.II.5a to Fig.II.5c. It can be programmed either through a PC or using the key pad on the front panel. Three sets of pulses can be generated using the ICs 8253 and 8254 (as count down counters), and a cascade of master clocks. The PPG is flexible and more versatile than those available in
Figure 11.4. Block diagram of gated transmitter.

Figure 11.6. Circuit diagram of Double Balanced Mixer.
the literature [14-17]. The required number of sets, the number of pulses in each set, the pulse width and the delay between the pulses within a set as well as delay between the sets of pulses can be programmed. The pulse width and the delay between pulses in a set can be varied from $1\mu\text{sec}$ to 1 msec. The delay between two sets can be varied from $1\mu\text{sec}$ to 100 sec and the repetition rate from 1 sec to 1 hour. With these options the pulse sequences required for our study could be generated.

Pulse parameters like the number of sets, number of pulses in a set (NS), width of the pulse and delay between the pulses in a given set, delay between the sets and the repetition time (R) can be fed to the appropriate Programmable Interval Timer IC's (PIT) 8253/8254. At the rate of one counter per parameter, five PITs are used in the PPG circuit. The repetition counter (R) working in the rate generator mode gives a narrow trigger pulse at every terminal count to the counter which controls the width of the pulses in the X-set. The cascade of counters and the accompanying hardware controls the pulse width, pulse delay and the number of pulses in the X-set. At the end of execution of X-set parameters the end of X-set trigger initiates the $D_{sz}$ counter which controls the delay between the X and Y sets. The end of $D_{sz}$ trigger initiates the Y-set and the process repeats to generate the Z-set.

Depending on the number selected (using a band switch), the "end of the set trigger" is routed to the clock of the set counter (NS) and a mono shot. The former counts the number of pulse sequences while the latter produces an end of sequence (EOS) pulse.

The pulses ($X_H$, $Y_H$, and $Z_H$) obtained at the output of the counters
Figure 11.5. Block diagram of Programmable Pulse Generator.
Figure II.5a. Diode matrix.
Figure II.5b. Schematic of key pad.
are inverted so that, the desired pulse sequence can be obtained at the output of a buffer after Nanding the outputs of $X_N$, $Y_N$, and $Z_N$ counters and are taken through a start-stop gate. The pulse input to the transmitter is taken through a protection window gate, which pulls the PPG output to logic "0", in the event the counter output get stuck up at logic "1" due to malfunctioning of the circuit and thus prevents the destructive pulse entering the transmitter.

The PIT's have to be mode programmed by writing a series of mode words into the IC's and then the pulse parameters are programmed by writing the proper parameter values in the form of count words to the corresponding count registers in the PIT's using front panel key pad interface and the built in auto programmer interface. The data bus, address bus and the control bus of the PIT are brought out from the PPG card and are connected to the programming interface card of the PC. The card performs the duties of channelling the desired interface to the data and control bus.

MEDIUM POWER AMPLIFIER:

A double balanced mixer (DBM) (UNITED SYSTEMS, type UDM 1C) is used as the gating unit. The circuit diagram of the DBM is given in Fig.II.6. It can take, up to 500mV RF input and provides an isolation of $> 40$ dB between the local oscillator (LO) and the RF ports.

The gated RF is amplified by the medium power amplifier to 20 V into 50 ohm load. The circuit diagram of the medium power amplifier is shown in Fig.II.7. It is a three stage cascaded amplifier built using NEC 2135 transistors. The
Figure 2.6 Circuit diagram of Double Balanced Mixer.
All resistors are in ohms
Capacitors - fractional values are in μF
others are in pF

Figure 2.7 Circuit diagram of medium power amplifier.
final stage uses a BLW 34 Philips transistor which has a power rating of 8W over a frequency range 1-100 MHz. The high pass response from the DBM is compensated by the \( \pi \) network provided at the input stage. A shunt series feed back mechanism \([18]\) is incorporated to match the input and output impedances to 50 ohms.

**HIGH POWER AMPLIFIER**:

The output of the medium power amplifier is further amplified by the high power amplifier built around RCA 3E29 double tetrode in push pull configuration as shown in Fig.II.8. Control grids of both the units of the tetrode are biased using a -150V DC to cut off the tube from conduction. The pulse amplifier converts the TTL output from the PPG and switches the grid biasing voltage from -150V to the conducting region during the pulse ON period. The output from the medium power amplifier is coupled to the control grids of both the units through a wide band (100KHz -100MHz) transformer (North Hills 0900 BB). The high power output is taken through a North Hills wide band transformer 1701.

**II.2.3 MATCHING NETWORK**

The matching network couples the transmitter power to the sample coil and then picks up the pulsed NMR signal from the sample coil to couple it to the receiver. The matching network described here is based on the design of Clark and McNeil \([19]\) which uses a single coil for both transmitting the rf pulses and receiving the signal from the sample (Fig.II.9). By appropriate tuning this can be used for a
Figure 2.8 Circuit diagram of 3E29 power amplifier.
Figure 2.9 Matching network (probe circuit)
The Probe consists of three sub units: the transmitter output circuit (R₁, L₁, C₁), the sample coil circuit (R₂, L₂, C₂), and the receiver input circuit (R₃, R₄, C₃, L₃). During the transmitter pulse the cross Diodes D₁, D₂ conduct. The rf pulse is applied to the series tuned combination of L₂ and C₂. Since L₂, C₂ and L₃, C₃ are series tuned, the induced voltage at L₂ appears at point F. This has high impedance to the ground which is necessary for the receiver. The sample coil L₂ is wound tightly over the sample tube and the resistance R₂ accounts for the losses in the components L₂ and C₂. The essential features of probe are (1) efficient conversion of the transmitter power into an intense homogeneous rf magnetic field in the sample coil and (2) fast recovery time after the pulse is off.

II.2.4 RECEIVER

The block diagram of the receiver is shown in Fig.II.10. The unit comprises of a low noise preamplifier, a high gain amplifier, a phase sensitive detector (PSD) and a video amplifier. The nuclear induction signal picked up by the sample coil is amplified by a high sensitivity, low noise preamplifier. The circuit diagram of the preamplifier is shown in Fig.II.11. It is a two stage amplifier using MOSFET 3N200. The first stage gives a gain of 5 while the second stage gives a gain of 2, over the band width 1 -100MHz. The crossed diodes protect the amplifier from RF overloading from the transmitter. The circuit has approximately 10 µsec recovery time.
Fig. 11.10. Block diagram of high gain amplifier
HIGH GAIN AMPLIFIER:

The main function of the receiver is to amplify and detect the signal without adding any distortion or additional electrical noise. Therefore the receiver should have sufficient bandwidth centered around the resonance frequency with a short recovery time to receive the signal. The high gain amplifier has a gain of 80dB with switchable 10dB attenuators with noise level <3dB having a band width 1-100MHz with selective band pass.

DATA ANALYSIS SETUP:

The second output of the power divider after suitable attenuation is used as the reference input to a Bruker broad band phase shifter BP-4 (1-100 MHz, 0-360° phase shift). The phase shifter output is given to the rf input port of a HP-10534 double balanced mixer used as PSD. The receiver output is given to L-port. The detected signal is taken from the X-port. The phase detected signal at the output of PSD is followed by a low pass filter. This is further amplified by a single stage video amplifier and given to a digital storage oscilloscope with signal averaging capability. Each stage is enclosed in a separate box to minimize external pick up and oscillation problems.

II.3 VARIABLE TEMPERATURE ASSEMBLY

The sample coil is encircled by a slotted copper cage to suppress the external pick-ups. This is inserted in a L-shaped double walled glass dewar open at both the
ends and is placed in between the pole pieces of the magnet (Fig.II.12). The other end of the dewar is connected to a 25 litre liquid nitrogen container. A heater is immersed in liquid nitrogen to boil nitrogen. Various temperatures are obtained by controlling the rate of boiling of the liquid. This is done by adjusting the voltage applied to the heater. The cold gas from the storage dewar rises along the column of the evacuated glass cryostat, cooling the sample. The temperature stabilizes in about 30 to 45 minutes after the setting of corresponding voltage. Temperatures from 300 to 135K can be obtained in this way.

Further to vary from 135 to 77K a modified stainless steel cryostat is used which consists of two additional control valves by means of which the pressure of liquid nitrogen can be adjusted which facilitates the required amount of nitrogen gas to arrive at a desired temperature. The temperature of the sample above room temperature from 300 to 450K can be varied by heating the sample indirectly through heating the cage surrounding the sample coil, using heating elements.

II.4 MEASUREMENT OF SPIN LATTICE RELAXATION TIME IN SOLIDS

Proton spin lattice relaxation time ($T_1$) in the laboratory frame has been measured at a Larmor frequency of 10 MHz, using the inversion recovery and saturation burst methods.

Prior to the measurement of the relaxation time it is necessary to optimize the pulse widths of $\pi$ and $\pi/2$ pulses. For this purpose a single pulse sequence
1. Glass dewar
2. Thermocouple
3. RF Shield
4. Sample
5. Heating coil
6. Liquid nitrogen
7. Dimmerstat

Figure 2.12 Nitrogen gas flow assembly.
is used. The width of the pulse for which the FID amplitude becomes zero is the π pulse, and the π/2 pulse is half in width.

(1) INVERSION RECOVERY METHOD:

This technique with pulse sequence π - τ - π/2 is suitable when the $T_1$ values are short say about less than 500 msec. The macroscopic magnetization is inverted to the -z direction by the π pulse. The spins are then allowed to relax to the lattice in the absence of the $H_1$ field for a time τ. During the time τ, the macroscopic magnetization grows in z direction. The extent of growth depends on τ as well as $T_1$. At the end of the delay time τ, the z component of the magnetization $M_z$ is brought to the xy plane by a π/2 pulse and FID is observed. The height of the FID is measured. This is repeated for different values of τ. The behaviour of the magnetization in the inversion recovery method is shown in Fig.II.13. The growth of magnetization follows the equation [20]

$$\frac{dM_z}{dt} = \frac{(M_z - M_0)}{T_1}$$ .... II.1

Integration of this equation with $M_z = -M_o$ at $\tau = 0$ yields,

$$M_z(\tau) = M_o(1 - 2exp(-\tau/T_1))$$ .... II.2

$M(\tau)$ is the amplitude of FID for a given $\tau$. $M_o$ is the equilibrium value of the amplitude of FID. A plot of $\ln [2M_o/(M_o-M_z(\tau))]$ versus $\tau$ gives $T_1$ as the inverse
Fig. II.13. $T_1$ measurement (a) by inversion recovery method (b) by saturation recovery method.
Experimental Techniques

slope. $T_1$ is determined by non linear least square fitting to equation II.2. The pulse sequence is repeated after a time longer than $5T_1$ to allow the equilibrium magnetization to be reached after each sequence. It is seen from equation that

$$M(\tau) = 0 \text{ for } \tau = T_1 \ln 2 = 0.69T_1 \quad \ldots \quad \text{II.3}$$

Thus $T_1$ can be found from the pulse spacing $\tau$ that results in no free induction signal following $90^\circ$ pulse. This procedure is known as zero-crossing method and is useful to obtain approximate value of $T_1$.

(2) SATURATION BURST METHOD:

This technique with pulse sequence $n\pi/2-\tau-\pi/2$ is suitable when the $T_1$ values are long say greater than 500msec. It makes use of a number of $\pi/2$ pulses separated from one another by a time greater than $T_2$ and much less than $T_1$. The monitoring $\pi/2$ pulse is applied after a delay time $\tau$. The set of $\pi/2$ pulses, tip the magnetization successively from $z$ to $y$ direction and randomize the spin system completely in the $xy$ plane. The randomized spins are left in the static field where they exchange their energy with the lattice and growing in the $z$ direction. After a delay $\tau$, the monitoring $\pi/2$ pulse tips the $z$ component of magnetisation into the $xy$ plane and a FID is observed. The FID amplitude is measured as a function of $\tau$ for increasing $\tau$ values till a constant $M_o$ is reached.

$$M_s(\tau) = M_o[1 - \exp(-\tau/T_1)] \quad \ldots \quad \text{II.4}$$
The pulse width in the burst of pulses need not be 90°. If the angle tipped is $\alpha$, the amplitude $M$ is given by the relation [21]

$$M = M_o[1 - (1 + \cos \alpha)\exp(-\tau/T_1)]$$  \hspace{1cm} \text{... II.5}

or

$$\ln \left[ \frac{M_o - M_z}{M_o} \right] = \ln(1 + \cos \alpha) - \left[ -\frac{\tau}{T_1} \right]$$  \hspace{1cm} \text{... II.6}

It is apparent that this does not affect the slope $T_1$. However $\pi/2$ is convenient because this ensures maximum signal that there is no magnetization present along $+z$ direction.

II.5 OPERATION OF THE SPECTROMETER

The following steps are adopted to operate the spectrometer.

(1) First the probe is tuned to 10MHz as per the procedure.

(2) The pulse programmer is switched ON and the pulses are monitored on the oscilloscope.

(3) The gated transmitter is switched ON in stages. After ensuring the various power supplies ($\pm15V$, $-150V$, $\pm12V$) are functioning properly, the gate
input is given from the pulse programmer. The pulse amplifier output is monitored for -150V to 0V. Then the rf input of the transmitter is connected to the signal generator output. The medium power amplifier output is checked for 20V peak to peak.

(4) The high voltage power supply for the transmitter is then switched ON and the output of 3E29 tube is checked for 400V peak to peak on the oscilloscope (terminated with 50 ohms).

(5) The output of the video amplifier is monitored on the Oscilloscope. The magnetic field is switched ON and the field is adjusted to get the resonance signal. With fine current variation the free induction decay (FID) signal is observed. The \( \pi/2 \) pulse width, phase are optimised to maximise the FID amplitude. The approximate T\(_1\) is measured with zero crossing technique and repetition rate is given as \( 5 \times T_1 \).

(6) Alternate adjustment of the field and the probe tuning is done until one obtains the maximum FID with respect to changes in the magnetic field.

(7) The FID signal obtained is averaged by using a Digital Storage Oscilloscope (Tektronics 2230).
REFERENCES


2. Mansfield.P. and Powels.J.G.,


4. Clark.W.G.,

5. Karlicok.R.F. and Lowe.I.J.,

6. Shency.R.K., Ramakrishna.J. and Jeffrey.K.R.,


8. Geiger.A. and Holz.M.,


10. Wright. D.A. and Rogers.M.T.,

11. Huang.S.G. and Rogers.M.T.,


13. Cook.J.B., George.R.E. and Grant.E.H.,
14. Lind. A. C.,

15. Franconi. C. and Terenzi. M.,


17. Cantor. D. M. and Jonas. J.,

18. Application information for thin film cascadable amplifiers, RF signal processing components.


20. Farar. C. T. and Becker. E. D.,

21. Fukushima. E. and Roeder. B. W. S.,
   *Experimental Pulse NMR : A Nuts and Bolts approach.*, Addison Wesley, Tokyo, (1980).