

User's Manual

ELECTRON SPIN RESONANCE SPECTROMETER

Model: ESR-105

(Rev : 12/01/2017)

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ISO 9001:2015
Certified Company

CONTENTS

Section	Page
1. Copyright, Warranty, and Equipment Return	1
2. Safety Information	2
• General Safety Summary	
• Symbols	
3. Unpacking and Inspecting the Instrument	4
4. Storing and Shipping the Instrument	4
5. Power Considerations	4
• Replacing the Fuse	
• Connecting to Power Line	
• Turning Power ON	
6. Cleaning the Instrument	6
7. Basics of Electron Spin Resonance	
i. Introduction	7
ii. Elementary Magnetic Resonance	7
iii. Electron Spin Resonance in Solids	7
iv. Relaxation and Saturation	8
v. Line Width, Spin-Spin and Spin Lattice Interaction	8
vi. Electron Paramagnetic Resonance and Spectroscopy	9
vii. General Consideration	10
viii. Experimental Technique	11
ix. Description of the ESR Spectrometer	12
8. Packing List	13
9. Installation	14
10. Operating Instructions	
i. Operation	14
ii. Origin of Four Peaks	14
iii. Determination of Magnetic Field	15
iv. Determination of Resonance Frequency	15
11. Calculations	15
12. Precautions	15
13. References	16
14. Appendix	
i. Sample Calculations	17
ii. Experimental Procedure	17
15. Technical support	18

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LIMITED WARRANTY

SES Instruments Pvt. Ltd warrants this product to be free from defects in materials and workmanship for a period of one year from the date of shipment to the customer. SES Instruments Pvt. Ltd will repair or replace, at its option, any part of the product which is deemed to be defective in material or workmanship. This warranty does not cover damage to the product caused by abuse or improper use. Determination of whether a product failure is the result of manufacturing defect or improper use by the customer shall be made solely by SES Instruments Pvt. Ltd. Responsibility for the return of equipment for warranty repair belongs to the customer. Equipment must be properly packed to prevent damage and shipped postage or freight prepaid. (Damage caused by improper packaging of the equipment for return shipment will not be covered by the warranty). Shipping costs for returning the equipment, after repair, will be paid by SES Instruments Pvt. Ltd.

EQUIPMENT RETURN

Should this product have to be returned to SES Instruments Pvt. Ltd, for whatever reason, notify SES Instruments Pvt. Ltd BEFORE returning the product. Upon notification, the return authorization and shipping instructions will be promptly issued.

Note : No Equipment Will Be Accepted For Return Without An Authorization.

When returning equipment for repair, the units must be packed properly. Carriers will not accept responsibility for damage by improper packing. To be certain the unit will not be damaged in shipment, observe the following rules:

1. The carton must be strong enough for the item shipped.
2. Make certain there is at least two inches of packing material between any point on the apparatus and the inside walls of the carton.
3. Make certain that the packing material can not displace in the box, or get compressed, thus letting the instrument come in contact with the edge of the box.

SAFETY INFORMATION

This Section addresses safety considerations and describes symbols that may appear on the Instrument or in the manual.

A **Warning** Statement identifies conditions or practices that could result in injury or death. A **Caution** statement identifies conditions or practices that could result in damage to the Instrument or equipment to which it is connected.



To avoid electric shock, personal injury, or death, carefully read the information in Table-1, “Safety Information,” before attempting to install, use, or service the Instrument.

GENERAL SAFETY SUMMARY

This equipment is Class 1 equipment tested in accordance with the European Standard publication EN 61010-1.

This manual contains information and warnings that must be observed to keep the Instrument in a safe condition and ensure safe operation.

To use the Instrument correctly and safely, read and follow the precautions in Table 1 and follow all safety instructions or warnings given throughout this manual that relate to specific measurement functions. In addition, follow all generally accepted safety practices and procedures required when working with and around electricity.

SYMBOLS

Table 2 lists safety and electrical symbols that appear on the Instrument or in this manual.

Table 2. Safety and Electrical Symbols

Symbols	Description	Symbols	Description
	Risk of danger. Important information. See Manual.		Earth ground
	Hazardous voltage. Voltage >30Vdc or ac peak might be present.		Potentially hazardous voltage
	Static awareness. Static discharge can damage parts.		Do not dispose of this product as unsorted municipal waste. Contact SES or a qualified recycle for disposal.

Table 1. Safety Information



To avoid possible electric shock, personal injury, or death, read the following before using the Instrument:

- **Use the Instrument only as specified in this manual, or the protection provided by the Instrument might be impaired.**
- **Do not use the Instrument in wet environments**
- **Inspect the Instrument in wet environments.**
- **Inspect the Instrument before using it. Do not use the Instrument if it appears damaged.**
- **Inspect the connecting lead before use. Do not use them if insulation is damaged or metal is exposed. Check the connecting leads for continuity. Replace damaged connecting leads before using the Instrument.**
- **Whenever it is likely that safety protection has been impaired, make the Instrument inoperative and secure it against any unintended operation.**
- **Have the Instrument serviced only by qualified service personnel.**
- **Always use the power cord and connector appropriate for the voltage and outlet of the country or location in which you are working.**
- **Never remove the cover or open the case of the Instrument before without first removing it from the main power source.**
- **Never operate the Instrument with the cover removed or the case open.**
- **Use only the replacement fuses specified by the manual.**
- **Do not operate the Instrument around explosive gas, vapor or dust.**
- **When servicing the Instrument, use only specified replacement parts.**
- **The equipment can remain Switched on continuously for five hours**
- **The equipment must remain Switched off for at least fifteen minutes before being switched on again.**
- **The equipment is only for the intended use**
- **Use the equipment only as specified in this manual.**

Unpacking and Inspecting the Instrument

Every care is taken in the choice of packing material to ensure that your Instrument will reach you in perfect condition. If the Instrument has been subject to excessive handling in transit, there may be visible external damage to the shipping container and packing material for the carrier's inspection.

Carefully unpack the Instrument from its shipping container and inspect the contents for damaged or missing items. If the Instrument appears damaged or something is missing, contacts the carrier and SES immediately. Save the container and packing material in case you have to return the Instrument.

Storing and Shipping the Instrument

To prepare the Instrument for storage or shipping, if possible, use the original shipping container alongwith thermocoal corners, as it provides shock isolation for normal handling operations. If the original shipping container is not available, use any good cardboard box which is at least 2-3 inches bigger than the instrument on all sides, with cushioning material (thermocoal or styrofoam etc) that fills the space between the instrument and the side of this box.

To store the Instrument, place the box under cover in a location that complies with the storage environment specification described in the "Environment Sections" below.

Environment

Temperature

Operating	0°C to 50°C
Storage	40°C to 70°C
Warm Up	15 min to full uncertainty specification

Relatively Humidity (non-condensing)

Operating	Uncontrolled (<10°C)
	<90 % (10°C to 30°C)
	<75 % (30°C to 40°C)
	<45 % (40°C to 50°C)
Storage.....	-10°C to 60°C <95 %

Power Considerations

The Instrument operates on varying power distribution standards found throughout the world and must be set up to operate on the line voltage that will power it. The Instrument is packed ready for use with a line voltage determined at the time of ordering.

Replacing the Fuses

The Instrument uses one fuse to protect the line-power input and two fuses to protect current-measurement inputs.

Line-Power Fuse

The Instrument has a line-power fuse in series with the power supply. Table 3 indicates the proper fuse for each of the four line-voltage selections. The line-power fuse is accessed through the rear panel.

1. Unplug the power cord.
2. Rotate the fuse holder cap to the right until the fuse POPS out.
3. Remove the fuse and replace it with a fuse of an appropriate rating for the selected line-power voltage. See Table 3.



To avoid electric shock or fire, do not use makeshift fuses or short-circuit the fuse holder.

Table 3. Line Voltage to Fuse Rating

Line Voltage Selection	Fuse Rating
220/ 240 V	0.3A, 250V (Slow blow)
100/ 120 V	0.6A, 250V (Slow blow)

Connecting to Line Power



To avoid shock hazard, connect the factory supplies three conductor line power cord to a properly grounded power outlet. Do not use a two-conductor adapter or extension cord, as this will break the protective ground connection. If a two conductor power cord must be used, a protective grounding wire must be connected between the ground terminal and earth ground before connecting the power cord or operating the Instrument.

1. Verify that the Line voltage is set to the correct setting.
2. Verify that the correct fuse for the line voltage is installed.
3. Connect the power cord to a properly grounded three-prong outlet. See Figure 3 for line-power cord types available from SES. Refer to Table 4 for description of the line-power cords.

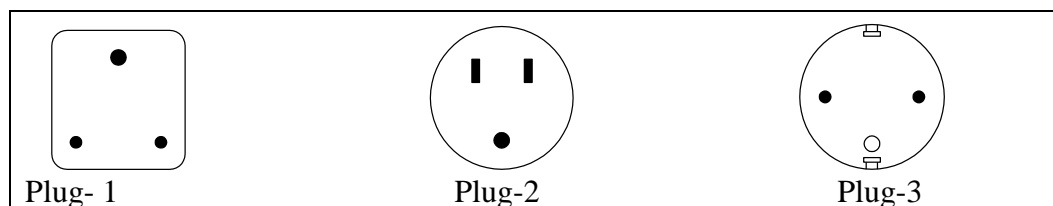


Figure 3. Line-Power Cord Types Available from SES

Table 4. Line-Power Cord Types Available from SES

Type	Voltage/Current	SES Model Number
India	240 V/ 5 A	Plug-1
North America	120 V/15 A	Plug-2
Universal Euro	220 V/16 A	Plug-3

Turning Power On

The On-Off switch on the front panel when points towards “ON” signs, indicates that the equipment has been switched on.

Cleaning the Instrument



To avoid electric shock or damage to the Instrument, never get water inside the Instrument.



To avoid damaging the Instrument’s housing, do not apply solvents to the Instrument.

If the Instrument requires cleaning, wipe it down with a cloth that is lightly dampened with water or a mild detergent. Do not use aromatic hydrocarbons, alcohol, chlorinated solvents, or methanol-based fluids when wiping down the Instrument.

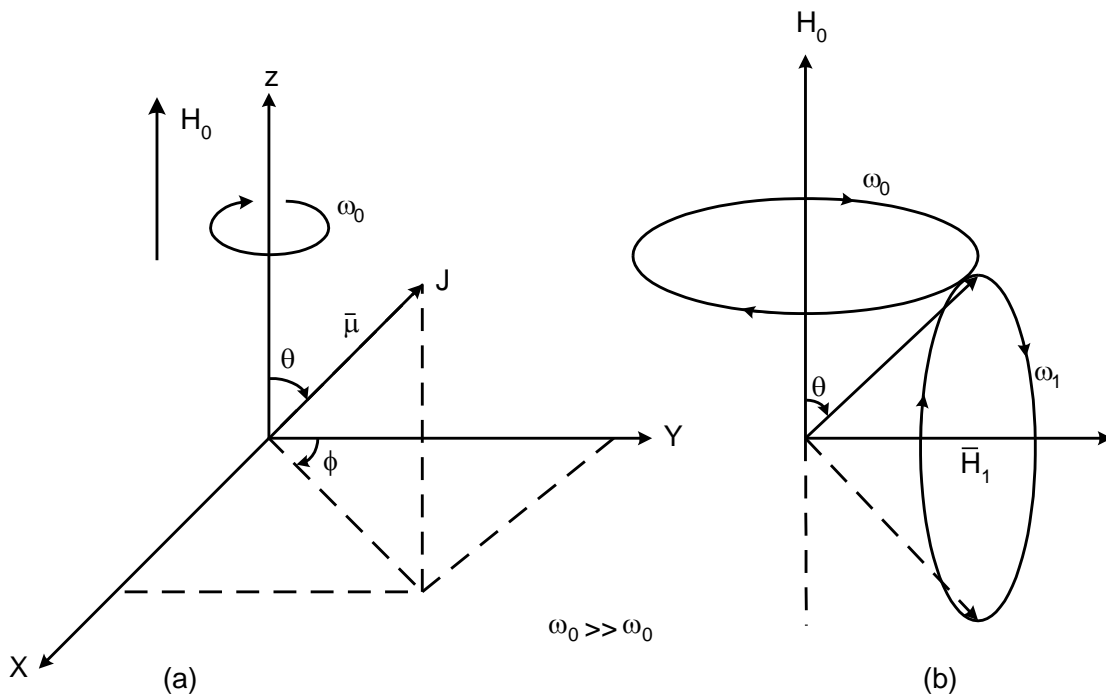


Fig. 1 : Precession of a magnetic moment $\bar{\mu}$ when placed in a magnetic field \bar{H}_0

- (a). The spin precesses with angular frequency $\omega_0 = \gamma H_0$; the angle θ is a constant of the motion.
- (b). In addition to \bar{H}_0 a weak magnetic field \bar{H}_1 is now also applied. \bar{H}_1 is rotating about the z axis with angular frequency ω_0 and therefore $\bar{\mu}$ precesses about \bar{H}_1 with angular frequency $\omega_1 = \gamma H_1$; θ is not any more conserved.

(i) INTRODUCTION

Zavoisky in 1945 performed the earliest magnetic resonance experiments in a solid. He observed strong electron spin resonance absorption in several paramagnetic salts. Applications of electron magnetic spin resonance in solid state physics are of great importance. It is a very sensitive technique and has been applied in many fields. The chief of these are :

- (a) Paramagnetic ions in crystals,
- (b) Unpaired electron in semi-conductors and organic free radicals,
- (c) Colour centres, and radiation damage centres,
- (d) Ferro and anti-ferro magnetic materials.

(ii) ELEMENTARY MAGNETIC RESONANCE

The fundamentals of elementary magnetic resonance may be understood in terms of simple classical concepts. Suppose a particle having a magnetic moment $\vec{\mu}$ is placed in a uniform magnetic field of intensity \vec{H}_0 (Fig.1a). Then the moment $\vec{\mu}$ will precess around \vec{H}_0 with an angular Larmor frequency

$$\omega_0 = g \left(\frac{e}{2mc} \right) H_0 \quad (1)$$

g being the Lande' g -factor ($g=1$ for pure orbital momentum and $g=2$ for a free electron spin). For the case of anion in a crystal, the behaviour is modified by the environment and the g -factor may differ from the Lande' g -factor. This effective g -factor is known as the spectroscopic splitting factor.

We now introduce an additional weak magnetic field oriented in the xy plane and rotating about the z axis (in the same direction as the "Larmor precessing") with an angular frequency ω_1 . If the frequency ω_1 is different from ω_0 the angle between the field \vec{H}_1 and the magnetic moment $\vec{\mu}$ will continuously change so that their interaction will average out to zero. If, however, $\omega_1 = \omega_0$ the angle between $\vec{\mu}$ and \vec{H}_1 is maintained and net interaction is effective (Fig.1b). If we look at the system in a reference frame that is rotating about the z axis with the angular velocity ω_0 then the spin will appear to make an angle $\psi = 90^\circ - \theta$ with \vec{H}_1 , and according to the previous argument will start to precess (in the rotating frame) about \vec{H}_1 . This corresponds to a "nutation" and a consequent change of the angle which implies a change in the potential energy of the particle in the magnetic field. The change in θ is the classical analogy to a transition between sublevels with different m . We see that such transitions may take place only if the rotating field has an angular frequency $\omega_1 = \omega_0$.

Let us proceed to consider the quantum picture of elementary magnetic resonance. Suppose that the intrinsic angular momentum of the electron \vec{S} couples with the orbital angular momentum of electron \vec{L} to give a resultant \vec{J} . We know, that $J+1$ magnetic sublevels labelled by the magnetic field \vec{H}_0 by equal energy difference,

$$\Delta E = g\mu_0 H_0$$

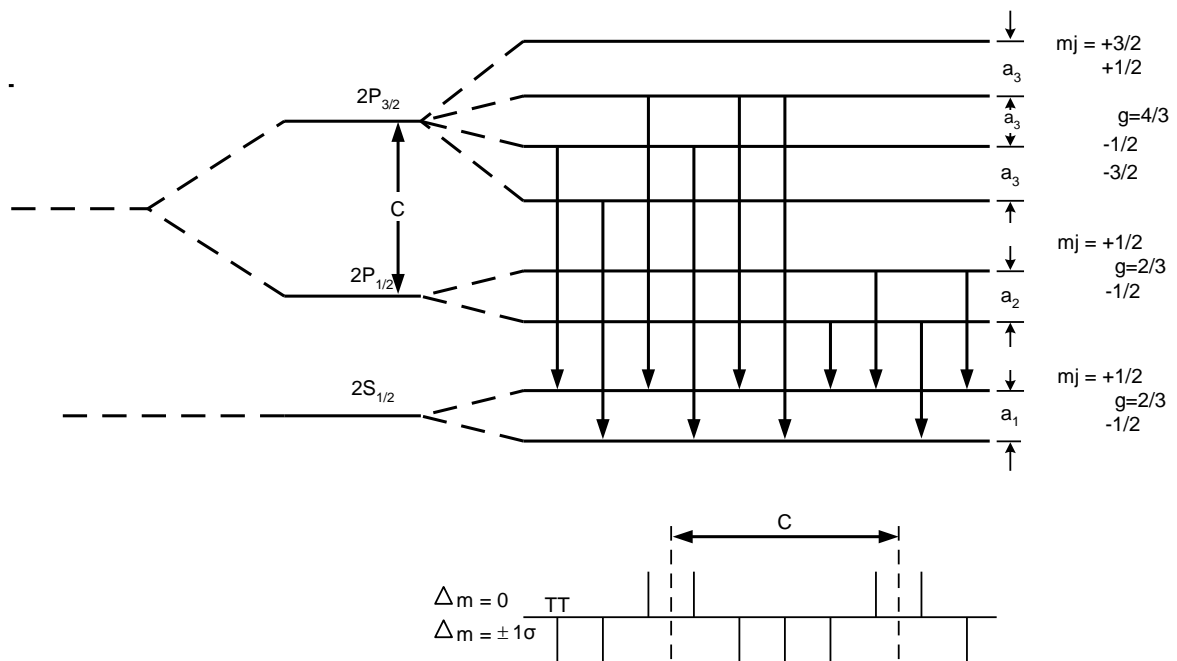


Fig. 2 : Energy levels of a single valence electron atom showing a P state and an S state. Due to the fine structure, the P state is split into a doublet with $j=2/3$ and $j = 1/2$. Further, under the influence of an external magnetic field each of the three levels is split into sublevels as shown in the figure where account has been taken of the magnetic moment of the electron. The magnetic quantum number m_i for each sublevel is also shown as is the g factor for each level. The arrows indicate the allowed transitions between the initial and final states, and the structure of the line is shown in the lower part of the figure.

between adjacent sublevels, where μ_0 is the Bohr magneton and g is the Lande' factor or g -factor whose correct quantum mechanical value is

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Now, if the particle is subjected to a perturbation by an alternating magnetic field with a frequency ν_1 such that the quantum $h\nu_1$ is exactly the same as the difference between the levels, ΔE and if the direction of the alternating field is perpendicular to the direction of the static magnetic field, then there will be induced transitions between neighbouring sublevels according to the selection rules $\Delta m = \pm 1$ for magnetic dipolar radiation.

Therefore, the condition for resonance is

$$\Delta E = g\mu_0 H_0 = h\nu_0 = h\nu_1 \quad (2)$$

Where ν_1 is the resonance frequency in cycles/sec. This requirement is identical with the classical condition $\omega_1 = \omega_0$.

In atomic spectroscopy, we do not observe the transitions between sublevels with different m (labelled a , a and selection rules $\Delta L = \pm 1$. Instead the splitting of a level is observed through small change in frequency of the radiation emitted in the transition between widely distant levels (Fig.2). It is clear that, if we could directly measure the frequency corresponding to a transition between the sublevels of the same state, a much more precise knowledge of the energy splitting would be obtained.

(iii) ELECTRON SPIN RESONANCE IN SOLIDS

Let us proceed from the treatment of an isolated magnetic particle to a macroscopic body. The behaviour of a paramagnetic substance in a magnetic field will depend on the interaction of the particles with one another and with the diamagnetic particles. There are mainly two types of interactions.

(a) **Spin - Spin:** In which the spin interacts with a neighbouring spin but the total energy of the spin system remains constant.

(b) **Spin - Lattice:** In which the electron spin interact with entire solid or liquid, transforming energy from the spin system to the lattice which act as a thermal reservoir. As a matter of fact it is the spin-lattice interaction that makes possible the observation of energy absorption from the radio- frequency field when the resonance frequency is reached.

To understand this last statement, consider a paramagnetic substance in a magnetic field $\overline{H_0}$ and say the equilibrium state has been reached. The population of individual energy levels will be determined by the Boltzmann distribution $e^{-g\mu_0 H_0 m / kT}$ where m is the magnetic quantum number. It can be seen that the population of the lower energy levels are greater than those of the upper levels and, therefore when a periodic magnetic field with a resonance frequency is switched on; the number of induced radiation events will be more and as a result the substance will absorb energy from the radio-frequency field. Thus, two opposing processes take place in ESR. The radio frequency field tends to equalise the population of various levels and the spin lattice interaction tends to restore the Boltzmann distribution by conversion of the energy absorbed from the radio-frequency field into heat.

(iv) RELAXATION AND SATURATION

In the preceding para, we see the mechanism through which the electron return from an excited state to the ground state or relax back to the ground state. This process in the field of magnetic resonance's (ESR, NMR, NQR ETC.) is known as relaxation and the time taken by the process is called the relaxation time. This complete process may be considered as two state process (provided the spin-spin interactions are much stronger than the spin-lattice interaction). First, the energy is absorbed from the radio frequency magnetic field and the equilibrium is established inside the 'spin system'. The time taken by this process is known as the spin-spin relaxation time and is a measure of the rate at which magnetic energy can be distributed within the spin system though total energy is conserved. Secondly, an exchange of energy occurs between the spin system and the lattice. The time taken is known as the **spin lattice relaxation time** and is a measure of the rate of transfer of energy from the spin system to the lattice.

In optical spectroscopy of the relaxation time is usually very short ($\sim 10^{-8}$ sec) so that the relaxation time does not impede the absorption rate. In radio frequency, on the other hand, typical relaxation times are in milliseconds or longer and the spin do not have time to relax if the energy is supplied at a faster rate. This situation is called the 'Saturation State'. In other words, no additional energy is absorbed, if the radio- frequency field power is increased beyond certain level.

(v) LINE WIDTH AND THE SPIN-SPIN AND SPIN-LATTICE INTERACTIONS

The effect of the spin-spin interaction is to slightly shift the exact position of energy level of any individual spin in the external field. This energy shift clearly depend on the relative orientation and distance of the spin and thus is different for each spin, resulting in apparent broadening of the energy level. Another way of thinking of the spin-spin interaction is that one electron spin produce a local magnetic field at the position of another spin. Thus, the width of absorption line due to spin-spin interaction may be estimated as $\frac{1}{T'}$, where T' is spin-spin relaxation time.

If the spin-lattice interactions are not weak the spin lattice relaxation time T will also be introduced. Let us consider the probability of a transition of an individual paramagnetic particle from one magnetic level to another under the influence of thermal motion. If the probability per second equal A , $T \sim \frac{1}{A}$ and the absorption line width would be of the order of $\frac{1}{T}$. In general case, however, the absorption line width may be estimated as $\frac{1}{T} + \frac{1}{T'}$.

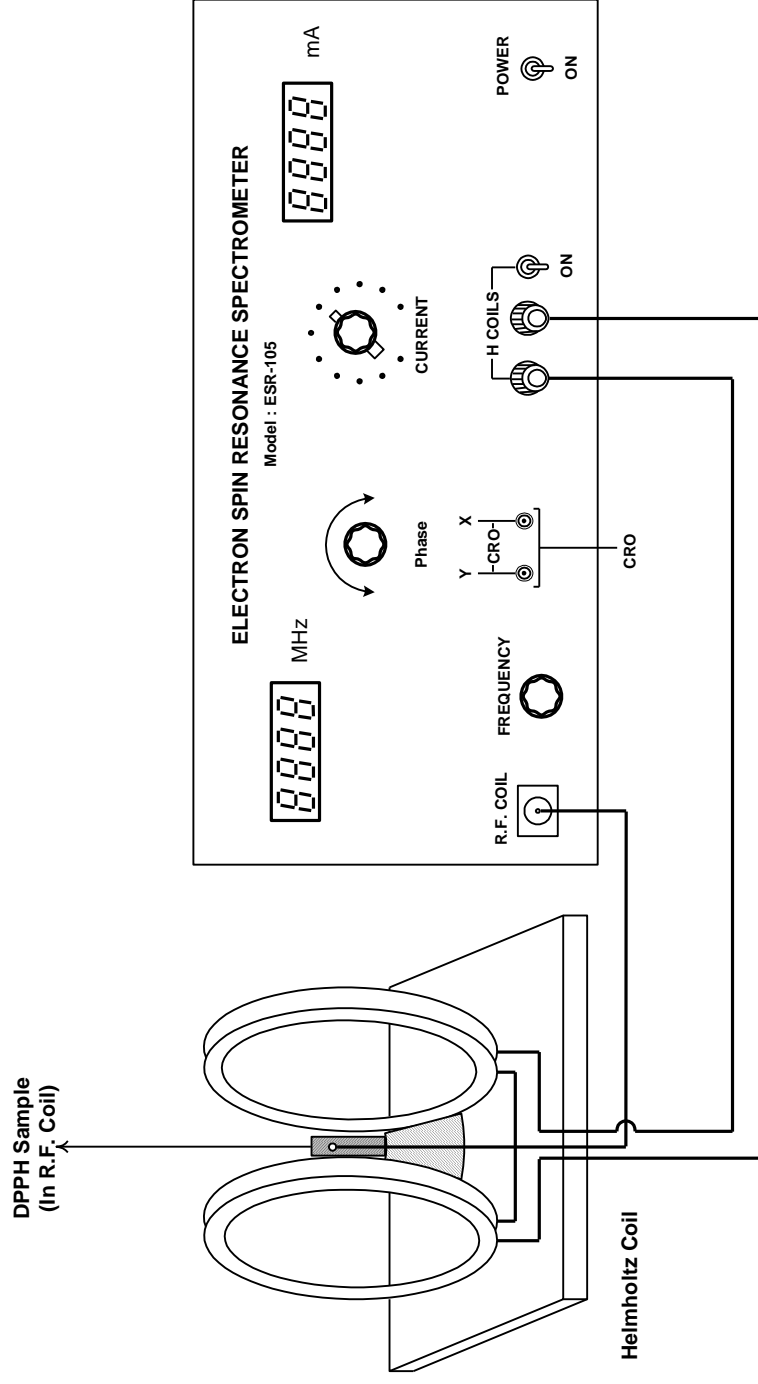
Thus, we see that from the width of absorption line it is possible to measure the relaxation time. In fact most of the research in this field involve the study of relaxation phenomena which in turn provide information about internal interactions in solids and liquids.

The position and number of lines of paramagnetic resonance absorption also depend on the internal interactions.

(vi) ELECTRON PARAMAGNETIC RESONANCE AND SPECTROSCOPY

Paramagnetic resonance is an integral part of spectroscopy, as it provides a means for determining the position of the energy levels of magnetic particles. It is interesting to consider the peculiar features of Paramagnetic resonance in comparison with optical spectroscopy.

1. Let us first note that the frequencies used in magnetic resonance experiments range from 10^9 to 10^{11} cps. These frequencies situated below the limits of the infrared part of the spectrum, allow highly accurate investigation of energy level splitting so small that they are inaccessible or almost inaccessible by optical methods.
2. The probability of spontaneous transition in the radio-frequency region is very small, since this probability is proportional to ν^3 . Therefore, in paramagnetic resonance studies one is forced to deal only with induced absorption and emission.
3. While in the great majority of cases optical spectra arise from electric dipole transitions between energy levels, the lines of paramagnetic resonance absorption arise exclusively from magnetic dipole transitions. Consequently, the Einstein coefficients for induced absorption and emission will, in the case of paramagnetic resonance, be smaller by roughly four orders of magnitude.
4. As a result, the paramagnetic resonance effect is exceedingly small; if it can be observed at all is due to the high sensitivity of electronic methods of detection and the enormous number of photons coming into play (1mW corresponds to $n \approx 10^{20}$ photons per sec at a frequency of 10^{10} cps).
5. In the optical frequency region the line width is always very small in comparison with the fundamental frequency. In paramagnetic resonance the relation between these quantities becomes quite different, since the interactions causing a broadening of the lines can be of the same order of magnitude as the energy splitting which determines the resonance frequency. Because of this the width of paramagnetic resonance lines is often comparable to the fundamental frequency and can be measured with great accuracy. This opens up wide possibilities for investigation of different types of interactions in paramagnetic substances by means of analysis of the shape and width of a paramagnetic resonance line and of the character of its dependence upon various factors.
6. The most important factors determining the line width are magnetic dipole interactions, exchange forces, local electrical fields created by neighbouring magnetic particles, and finally, thermal motion; the natural line widths of radio- frequency spectra are completely negligible.
7. In contrast with optical experiments, in radio-frequency spectroscopy it is customary to use radiation which is so monochromatic that the generated band of frequencies is incomparably narrower than the absorption line width.
8. Paramagnetic resonance spectra are not studied by varying the frequency of the incident radiation, but by varying the characteristic frequencies of the absorbing systems. This is achieved by varying the static magnetic field.



Panel Diagram of Electron Spin Resonance Spectrometer, ESR-105

(vii) GENERAL CONSIDERATIONS

For a free electron, by substituting the proper values of constants : $g=2.00$, $\mu_0=0.927 \times 10^{-20}$ erg / Gauss and $h=6.625 \times 10^{-27}$ erg.sec. in equation (2), we get,

$$\frac{\nu_0}{H_0} = 2.8 \text{ MHz/Gauss}$$

That is ESR can be observed at radio frequencies in a magnetic field of few gauss or otherwise in the microwave region in a magnetic field of a few kilogauss. The latter alternate has many distinct advantages :

- (a) For each transition the absorbed energy is much larger, and thus the signal-to-noise ratio is much improved.
- (b) A high magnetic field is used, thus providing separation between levels that are intrinsically wide and would remain partially overlapped at low fields.

Because of these advantages, ESR in microwave region is preferred for research purpose, though, it is very sophisticated and expensive.

The former is preferable, where simplicity, easy operation and cost factor are the main considerations and no high resolution is required **ideal for postgraduate level experiments.**

(viii) EXPERIMENTAL TECHNIQUES

In the radio frequency region, two types of methods are chiefly used:

1. The method of reaction on the generator
2. The method based on a determination of the change in a load factor of the oscillatory circuit due to paramagnetic loss.

The latter method has been used here. The sample under investigation is placed in an induction coil, which is the component of the tank circuit of the oscillator (generator). This is the Zavoisky's technique. It is based on the fact that under certain conditions such as absorption of power from generator, the watt load (Δw) on the generator changes. This change of Δw is proportional to the change in base current ΔI_b or collector current ΔI_c of the generator. The proportionality, however, holds only the power dissipated by the sample due to paramagnetic absorption is small in comparison to the total losses in the circuit. This change in ΔI_c is detected with the conventional circuits. To make the detection simple and more sensitive, the magnetic field and hence the Larmor frequency of the sample is modulated with a low frequency field 50Hz in the present set-up.

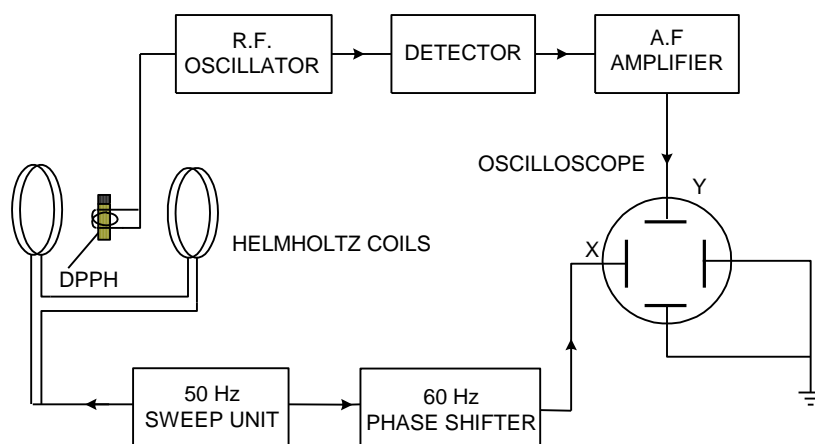


Fig. 3 : Block Diagram of the ESR Set

(ix) DESCRIPTION OF THE ESR SPECTROMETER

A block diagram of the ESR Spectrometer is given in Fig. 3 and panel diagram on the previous page.

1. Basic Circuit: The first stage of the ESR circuit consists of a critically adjusted (marginal) radio frequency oscillator having a frequency range of approximately 12–16MHz. A marginal oscillator is required here so that the slightest increase in its load decreases the amplitude of oscillation to an appreciable extent. The sample is kept inside the tank coil of this oscillator, which in turn, is placed in the 50Hz magnetic field, generated by the Helmholtz coils. At resonance, i.e. when the frequency of oscillation equal to the Larmor's frequency of the sample, the oscillator amplitude registers a dip due to the absorption of power by the sample. This obviously, occurs periodically - four times in each complete cycle of the Helmholtz coils supply voltage. The result is in amplitude modulated carrier (Fig. 4A) which is then detected using a diode detector and amplified by a chain of three low noise, high gain audio - frequency amplifiers of excellent stability. A sensitivity control is provided in the amplifier to suit the input requirement of any oscilloscope.

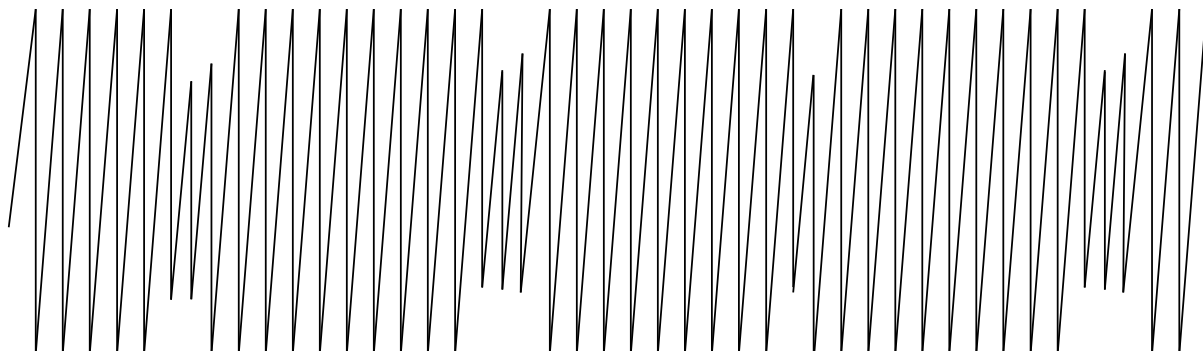
2. Phase Shifter: In order to make it possible to use an ordinary displaying type oscilloscope, instead of a measuring oscilloscope which preserve the phase between X and Y plates signals, a phase shifter is provided. This can compensate the phase difference which is introduced in the amplification stage of the ordinary oscilloscope.

The circuit diagram of the phase shifter is shown in Fig.4(B). The primary of the transformer is fed from the 220V, 50Hz (or 110V, 60Hz) mains and the secondary is centre tapped developing V_1 -0- V_1 (say). The operation of the circuit may be explained with the help of the vector diagram shown in Fig.4(B). The vectors OA and BO represent the voltage developed in the secondary, in phase and magnitude. The current flowing in the circuit ADB leads the voltage vector BA due to the presence of capacitor C and is shown in the diagram as I. Voltage developed across resistance R, i.e. V_R is in phase with the current I, and the voltage across capacitor V_c is 90° (lag) out of phase with the current. The vector sum of V_c and V_R is equal to $2V_1$. These are also plotted in the diagram. It is clear from the diagram that as R is varied, V_R will change and the point D will trace a semicircle, shown dotted. The vector OD, or the voltage across points O and D, will, therefore, have a constant magnitude equal to V_1 and its phase, variable from 0 to 180° . This is the voltage which is fed to the X-amplifier of the oscilloscope to correct for any phase change which might have taken place in the rest of the circuit.

3. 50 Hz Sweep Unit : For modulation with a low frequency magnetic field, a 50 Hz current flows through the helmholtz coils. As the resonance in this frequency range occurs at low magnetic fields, no static D.C. magnetic field is required.

4. Power Supplies :

- a) D.C. Power Supply : The ESR circuit requires a highly stabilised almost ripple free voltage. These are obtained using integrated circuit regulator.
- b) Helmholtz Coils Power Supply : The Helmholtz coils power supply consists of a step down transformer (220 to 35 V AC). Variable coil current is provided in 10 steps using a band switch, while the current is displayed on a $3\frac{1}{2}$ digit panel meter. The output is taken from the two terminals provided on the panel.



At A



At B

Fig. 4 (A)

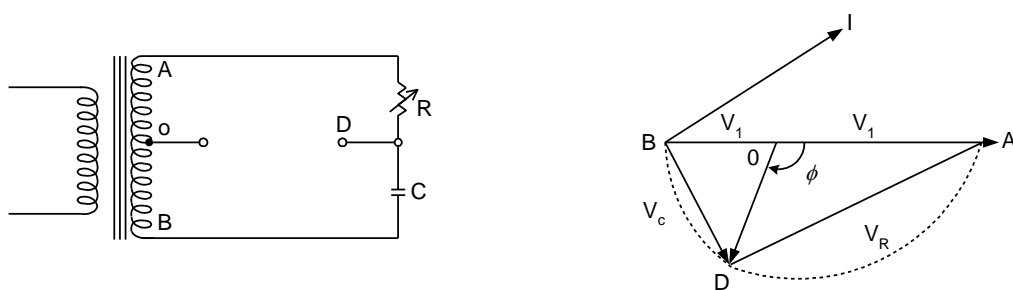


Fig. 4 (B)

5. Helmholtz Coils : There are two coils exactly alike and parallel to each other, so connected that current passes through them in the same direction. The two coils increase the uniformity of the field near the centre.

Number of turns	:	500 in each coil
Diameter of the Windings	:	15.4 cm
Separation of the coil	:	7.7 cm

In the centre of the coils, an attachment is provided to keep the sample in place and to minimise shocks and vibrations.

6. Test Sample: A test sample, Diphenyl Picryl Hydrazyl (DPPH) (Fig. 5) is placed in a plastic tube, which itself is in the induction coils. This increases the filling factor to the maximum. DPPH is a free radical and widely used as a standard for ESR measurements.

8. Controls & Terminals : (Please refer to Panel Diagram)

- (1) Mains : To switch 'ON' or 'OFF' the ESR Spectrometer.
- (2) Phase : To adjust the phase between X and Y plates signals.
- (3) Current : To control current in Helmholtz coils.
- (4) 'H' Coils : Terminals and switch for Helmholtz coils.
- (5) Frequency : To adjust the frequency of the Oscillator.
- (6) X,Y,E : For X, Y and Earth terminals of the Oscilloscope.

9. Oscilloscope: As the Oscilloscope is not supplied with the spectrometer, it is presumed that the worker is already familiar with the control knobs and functioning of the Oscilloscope in question.

Any Oscilloscope, normally available in the laboratory of the following specifications or better, will be quite suitable for the observation of ESR resonance :

- Screen diameter : 12.5 cm
- Vertical amplifier sensitivity : 50 mV/cm

PACKING LIST

- i. ESR Spectrometer, ESR-105: One
- ii. Helmholtz coils fitted with R.F. Coil: One
- iii. Sample - DPPH (inside R.F. Coil)

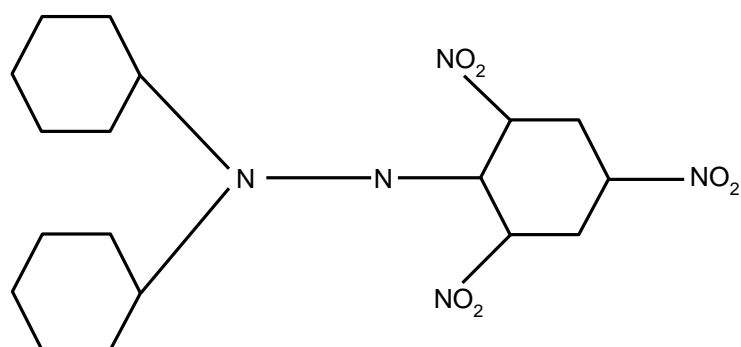


Fig 5.: Chemical structure of DPPH (2,2-Diphenyl-1-picrylhydrazyl, (free radical, 95%))

INSTALLATION

Now for installation proceed as follows :

- 1) Connect the Coaxial cable of the induction coil to the Oscillator through the socket.
- 2) Connect the Helmholtz coils to the terminal marked 'H' coil.
- 3) Connect the terminal marked X,Y, and E on the ESR Spectrometer to the X plate, Y plate input and earth of the Oscilloscope respectively and switch the Oscilloscope.
- 4) Connect the spectrometer with the AC mains $220 \pm 10\%$ Volts, 50 Hz and switch - on the power. Ensure that the equipment is properly earthed.

OPERATING INSTRUCTIONS

(i) OPERATION

- (1) Switch on 'H. COIL' power and adjust the current at 150 mA.
- (2) Set the front panel controls of ESR Spectrometer as follows
Frequency : Centred
Phase : Centred
- (3) Observe four peaks on the Screen of CRO. Now adjust the FREQUENCY of the Spectrometer and SENSITIVITY of the CRO to obtain the best results (i.e. sharp peaks and good signal to noise ratio).
- (4) Adjust the PHASE knob to coincide the two peaks with the other two as far as possible.
- (5) Adjust the orientation of Helmholtz coils with respect to the main unit for best overlap of base lines.

(ii) ORIGIN OF FOUR PEAKS

The observed peaks are in fact absorption dips, because the sample absorb power from the induction coil, reasons explained in Chapter 1. The reason for getting peaks is due to odd number of amplifying stages in the circuitry.

The spin precesses with Larmor's frequency ($\omega_0 = \frac{eH_0}{2mc}$) and hence varies in magnitude and direction due to variation of magnetic field $\overline{H_0}$ which is due to an alternating current in the Helmholtz coils. Now if the radio frequency field, ω_1 falls in the range of ω_0 the resonance occurs. The positions of the four peaks can be understood with Fig. (3).

If the X plate signal (50Hz) and Y plate signal (ESR output) are in phase the I and II peaks and III and IV peaks will coincide. The coincidence of peaks on the x-scale needs to be calibrated for magnetic field measurements. The coincidence ensures that the magnetic field is zero at the centre and has the peak values at the two ends. Complete merger of the peaks on y- scale may not occur due to many reasons such as 50Hz pick-ups, ripples in the power supply etc. Though, every effort has been made to minimise these factors but the large amplification ($\cong 4000$) in the circuitry make them substantial. However, any non- coincidence on the y-scale is immaterial as neither any measurement of the y-scale is involved in the calculation of g- factor nor any measurement is made on it.

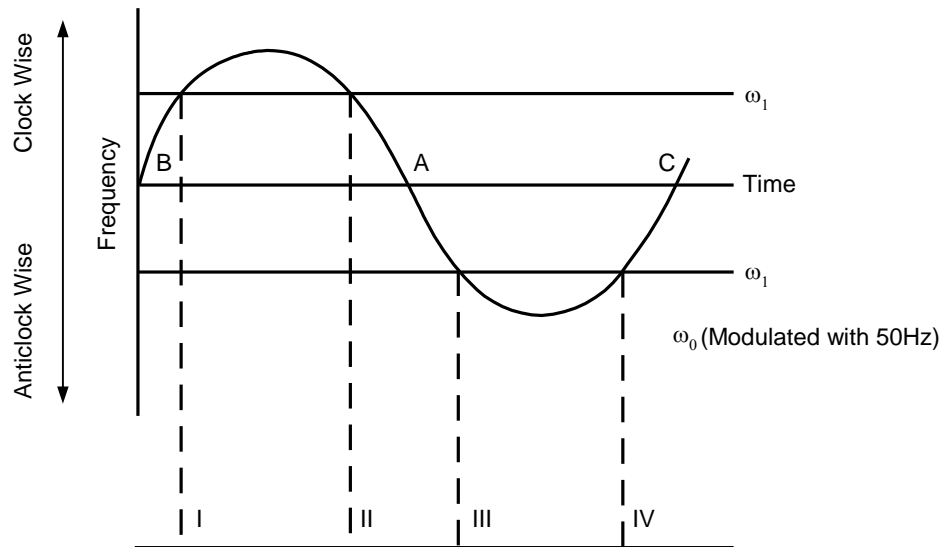


Fig. 6 : The radio frequency is linear by polarised, which can be regarded as two circularly polarised fields of opposite direction (say clockwise and anti clockwise). Further magnetic field H_0 also changes direction. Thus resonance occurs when the two frequencies (ω_1 and ω_0) becomes equal in magnitude as well as direction i.e. four times in one full cycle of H_0 .

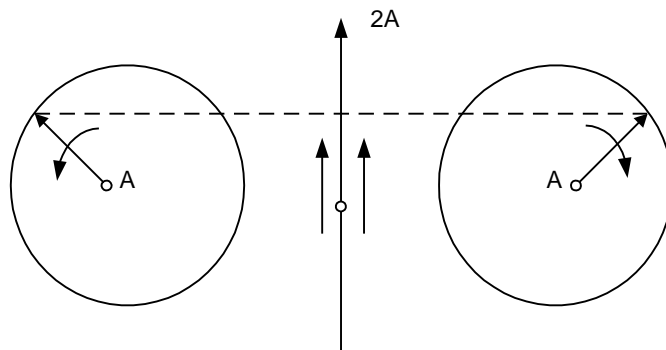


Fig. 6 : A linearly field of frequency is equivalent to two fields rotating in opposite direction with the same frequency ω

(iii) DETERMINATION OF MAGNETIC FIELD

To calibrate the X-plate of CRO in terms of magnetic field proceed as follows :

1. Adjust the X amplifier (CRO) to obtain the maximum X deflection (say 'P' divisions).
2. Read current flowing in Helmholtz coils and calculate the magnetic field.

$$H = \frac{32 \pi n}{10 \sqrt{125} \cdot a} \cdot I$$

Where 'n' is the number of turns in each coil

'a' is the radius of the coils

'I' is the current (in amp) flowing through the coils.

This is the root mean square (rms) field. The peak to peak field will be $2\sqrt{2} \cdot H$ and represents 'P' division of the CRO X plate. The zero field is at the middle point.

3. Measure the positions of the two peaks. These should be at equal distances from the middle point (say 'Q' division). The magnetic field at the resonance is thus

$$H_0 = \frac{2\sqrt{2} \cdot H}{P} \cdot Q \text{ gauss}$$

CALCULATIONS

From equation (2)

$$h\nu_1 = g \mu_0 H$$

or
$$g = \frac{h \nu_1}{H_0 \mu_0}$$

Substitute the measured values of H_0 and ν_1 universal constants $h=6.625 \times 10^{-27}$ erg.sec and $\mu_0=0.927 \times 10^{-20}$ erg/gauss to get the g factor.

PRECAUTIONS

1. Experiment should be set up at a quite place free from mechanical and electrical disturbances.
2. Y - output from the ESR Spectrometer should be taken through shielded cable to minimise external pick-ups.
3. X and Y plates sensitivities of the Oscilloscope should be adjusted such that they should be in the linear range only.
4. Since the Helmholtz current is unstabalised, care should be taken that it should remain constant during the observation.
5. High currents (~ 200 mA) should not be allowed to flow through the Helmholtz coils for an extended period. This will unnecessary heat the coils which may get damaged after some time.
6. If the peaks do not coincide on the x-scale, check the sinusoidal wave form of the mains voltage which may be distorted due to overloading of the main line due to other heavy gadgets working on the same line.

7. Do not use AC Stabiliser as it is likely to distort the sinusoidal wave form. If necessary use the variac.

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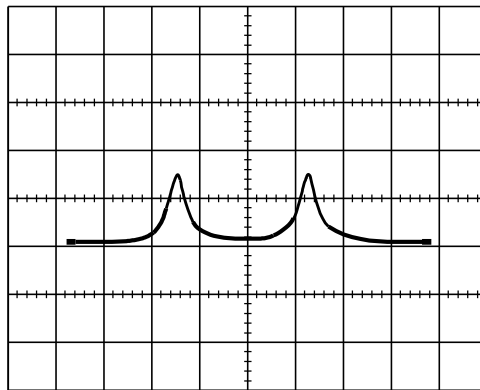
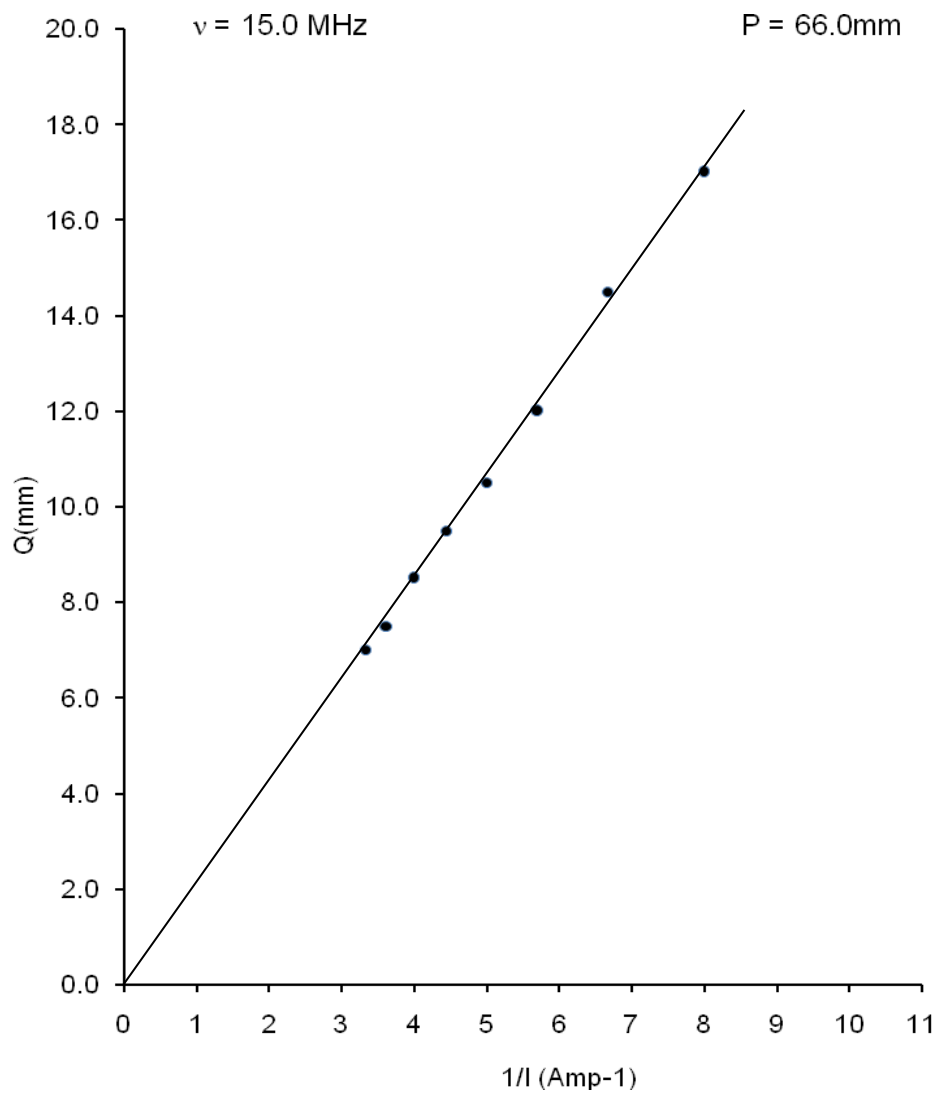


Fig. 8 Line Sketch of the Resonance Peak



Graph between $1/I$ Vs Q

APPENDIX

(i) SAMPLE CALCULATIONS

Magnetic field at the centre of a Helmholtz coil is :

$$H_0 = \frac{32 \pi n}{10 \sqrt{125} \cdot a} \cdot I = KI \text{ gauss}$$

Where I is the current in amperes and other symbols have their usual meaning. Since the current measured is rms the magnetic field is also rms. The peak to peak magnetic field will be :

$$H_{PP} = 2\sqrt{2} H$$

The H_{PP} corresponds to the total X-deflection on the oscilloscope with zero field at the centre. Substituting the values $a=7.7\text{cm}$; $n=500$, we obtain

$$H_{PP}=165.25 \text{ gauss/amp}$$

Let us take a typical observation (Fig. 8). The measured values are :

$$\nu_0=14.00 \text{ MHz}; I=200 \text{ mA}; P=100 \text{ mm and } 2Q=30 \text{ mm}$$

Since P corresponds to H_{PP} , the magnetic field per mm of the X-deflection will be H_{PP}/P and hence the magnetic field for either resonance is

$$H_0 = \frac{H_{PP}}{P} \cdot Q = \frac{165.25 \times 0.2 \times 15}{100} = 4.96 \text{ gauss}$$

Substituting the values in the relation

$$h\nu_0=g\mu_0H$$

$$g = \frac{h \nu_0}{\mu_0 H_0} = \frac{6.625 \times 10^{-27}}{0.927 \times 10^{-20}} \times \frac{14.00 \times 10^6}{4.96} = 2.04$$

(ii) EXPERIMENTAL PROCEDURE

1. Increase the horizontal sensitivity of the Oscilloscope to the maximum **within the linear range**.
2. Obtain the best possible resonance peaks by varying the frequency, detection level and vertical sensitivity of the oscilloscope, keeping the current at 150 mA (say).
3. Keep the frequency fixed but vary the current flowing through the coils and measure the corresponding horizontal separation between the two peaks (2Q) after adjusting the phase. Take five to six sets of observations.
4. Draw a graph in $1/I$ Vs Q which should be a straight line. Calculate the g-factor using the QI value from the graph.
5. Repeat the experiment with different frequency.

The reason for drawing graph between $1/I$ and Q with fixed is that the measurements of I and Q are likely to contain some random errors.

TECHNICAL SUPPORT

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Model number and Revision (listed by month and year on the front cover).
Have the manual at hand to discuss your questions.