CHAPTER V  ELECTRON PARAMAGNETIC RESONANCE AND
MAGNETIC SUSCEPTIBILITY

(A) ELECTRON PARAMAGNETIC RESONANCE

In the past, the phrase "optical precision" was considered
descriptive of the ultimate accuracy that could be attained in any
physical measurement. It had served as a high standard of excellence
that other methods of physical measurements might hope to equal but
never excel. Now-a-days a new branch of physics, called microwave
physics, which is really an extension of optical methods as applied
to electro-magnetic spectrum in general, has been developed which can
claim a comparable degree of precision. Because frequencies can be
measured with a high degree of precision, in the microwave region and
because the energy associated with a microwave photon is small, it has
become possible to measure certain molecular, atomic and nuclear
constants to a higher degree of precision than was hitherto possible.
As a result, theoretical speculations which were previously considered
purely abstruse mathematical calculations, have been brought within
the range of experimental verification. In some fields of physics,
microwaves are such a powerful tool that whole problems are being
investigated anew; in others, experimental evidence has already
been obtained that permits modification and extension of theories.

The techniques used are based on resonance phenomenon.
There are three resonance effects to be considered. These resonance
phenomena are shown at radio frequencies of a few mega cycles per
second by atomic nuclei possessing a resultant nuclear magnetic
moment; at frequencies of several thousand mega cycles by unpaired
electron spins as in paramagnetic substances; and at frequencies of
tens of thousands of mega cycles by ferromagnetic substances. The
first group of phenomena is called nuclear magnetic resonance (NMR),
the second electron paramagnetic resonance (EPR) or electron spin
resonance (ESR) and the third ferromagnetic resonance.

We are concerned here with the resonance absorption,
associated with reorientations of the magnetic moments of the metallic
ions of paramagnetic salts. As a first approximation, let us assume
that the ions are nearly free. In the absence of an external magnetic
field, all the ions then will exist in a common ground state. When a
static external magnetic field is applied, they will be distributed
among \(2J + 1\) equally spaced levels according to the Boltzmann
distribution. It is necessary to assume a slight interaction with
the lattice to insure that this equilibrium distribution will be
reached in a finite time (spin-lattice relaxation time). The
difference in energy between any two adjacent levels is given by

\[
\Delta E = gBH
\]

where \(g\) is the gyromagnetic ratio, \(B\) is the Bohr
magnetion, and \(H\) is the strength of the applied field. When a high
frequency transverse magnetic field of frequency \(\nu\) is introduced,
the transition probability of an ion from the level, it occupies to
an adjacent level is a maximum, when

\[
h\nu = gBH
\]

which is the well known magnetic resonance condition. The
transition probability to a higher level is identical with that to a
lower level, but the Boltzmann distribution insures that the lower levels are slightly more densely populated than the higher and a net absorption of energy from the alternating field occurs. In order for the rate of energy absorption at resonance to remain constant with the time, the amplitude of the high frequency magnetic field must not be so great that the Boltzmann distribution cannot be continually re-established. Such a condition would lead to the equalization of the level populations and hence to a disappearance of the absorption effect.

EPR 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.

5.1 Historical Development:

The great advantage in the development of microwave techniques during the early nineteen forties prompted several scientists to apply these techniques in observing resonant absorption between Zeeman levels in paramagnetic substances. The first report on the observation of this phenomenon came from Zavosyskiy (1,2), in the U.S.S.R. and was soon followed by reports from Cummerow and Halliday (3) in the U.S. and from Bagguley and Griffiths (4) in England. Since then the development has been rapid and the method has been applied successfully to numerous problems.

The Oxford group has discussed the main features of the method and given, results obtained for over hundred salts of the iron group. Even at that stage of development, the method readily
gave information about the fine structure (small splittings of the order of 1 cm.\(^{-1}\) and smaller) between the lowest (spin) levels of the paramagnetic ions, about the effective \(g\) value, about the presence of paramagnetic ions at different sites in the unit cell and about spin–spin and spin–lattice interactions.

The next step forward was the observation, made by Penrose (6), of nuclear hyperfine structure in magnetically dilute crystals. The observation of this phenomenon, which is due to the interaction of the nuclear magnetic moment and the magnetic moment of the electron spins, is quite important because it enables identification of the nuclei of the various isotopes of the elements. In this respect the interaction with the nuclear electric quadrupole moment (7) gives less information, because effect is often quite small.

An extended discussion of the general theory of paramagnetic resonance and the use of the spin hamiltonian has been done by Pryce (8) and Abragam and Pryce (9). The authors assume the lattice to be perfectly ionic, so that the ions or water molecules surrounding the central paramagnetic ion could be regarded as point charges or dipoles having no overlap with the charge distribution of the central ion; in other words, it is assumed that crystal field theory was applicable.

However, partial covalent bonding of the central paramagnetic ion with its neighbours generally occurs and the first direct proof of the existence of covalent bonding was given by Owen and Stevens (10) in their observation of superhyperfine structure from
the chlorine nuclei in the complex (IrCl₆)²⁻. This effect of covalent bonding was then accounted for in the theory of paramagnetic resonance by applying the method of molecular orbits (11). With substances with complete covalent bonding, such as Si and Ge, yet another approach has been adopted. There the unpaired electron (or hole) may be weakly bound to the donor (or acceptor) impurity nucleus, in which case it moves in a quite large orbit, so its behavior is largely determined by the band structure and the dielectric constant of the host.

The electron-nuclear double resonance (ENDOR) technique (12) has proved to be very useful for obtaining quantitative information about the interaction of the unpaired electrons and the nuclear magnetic moment of the surrounding nuclei in cases in which this interaction is unresolved in the usual electron spin resonance (ESR) experiment.

Investigations by ESR of centers involved in the luminescence of inorganic solids were undertaken relatively early, when Hutchison (13) observed the resonances of F centers in LiF and KCl. This observation was soon followed by a paper of England and Schneider (14) dealing with ESR of divalent manganese in ZnS phosphors. Since then the ESR technique has been applied successfully to a number of problems in this field.

The application of the ESR technique to the study of optically induced valence changes of impurities in photoconducting phosphors such as ZnS and CdS (15, 16) is of special value in obtaining information about the structure of centers which are responsible for light induced processes in these materials. Often
this information cannot be obtained by studying the unexcited phosphors, because then the centers are not paramagnetic. However, they become paramagnetic if their valence is changed optically by transferring an electron from the center being studied, to an electron trap else where in the phosphor.

5.2 Advantages of Paramagnetic Resonance:

The advantages of EPR may now be enumerated. In the main, anisotropy arises from variation of the spectroscopic splitting factor of $g$ as the orientation of the field $H$ is changed with respect to the axes of the crystal field. In general, therefore, each type of ion in a salt will give its own spectrum, separate from those of other types. This means that impurities do not affect the results, a fact which is of great importance in substances such as the rare earths which are often costly or not available in highly purified condition. The experimental results yield precise information for a given level, and the quantity of material required is very small.

The frequencies used in magnetic resonance experiments range from $10^6$ to $10^{11}$ cps. These frequencies, situated below the limits of the infrared part of the spectrum, allow highly accurate investigation of energy level splittings, so small that they are inaccessible or almost inaccessible by optical methods.

The probability of spontaneous transition in the radio-frequency region is very small, as this probability is proportional to $v^3$. Therefore, in paramagnetic resonance studies one is forced to deal only with induced absorption and emission.

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.

The magnitude of paramagnetic resonance effect is exceedingly small; that 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. Thus $1 \text{ mw}$ corresponds to $n \approx 10^{20}$ photons per sec. at a frequency of $10^{10}$ cps.

In the optical frequency region the line width is always very small in comparison with the fundamental frequency, while the width of the EPR 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.

The most important factors determining the line width are magnetic dipole interactions, exchange forces, local electric fields created by neighbouring particles and finally thermal motion; the natural line widths of radio frequency spectra are completely negligible.

In contrast with optical experiments, in radiofrequency spectroscopy the radiation used is highly monochromatic and the general band of frequencies is incomparably narrower than the
absorption line width.

5.3. Unpaired spins in luminescence centers:

To be directly accessible to ESR work the luminescent centers must be paramagnetic; that is, they must contain one or more unpaired electron spins. This does not imply that all centers which have no unpaired electron spins are completely inaccessible to the ESR method, since by using different techniques one can study them also. The following cases can be coped with:

(1) Centers which contain in their ground state one or more unpaired electrons; examples are the ions of transition elements, such as \( \text{Cr}^{3+} \) in \( \text{Al}_2\text{O}_3 \) or \( \text{Mn}^{2+} \) in halophosphates, and lattice defects, such as the F center in alkali halides.

(2) Centers which have a ground state with no unpaired electrons but which have a sufficiently long lived excited state with unpaired electrons; an example is the M center in KCl.

(3) Centers which have no unpaired electrons but whose valence and at the same time, number of unpaired electrons can be changed in an easily controlled way; for example, the valence state of a number of centers of the transition elements in Si and Ge can be changed easily if the Fermi level is varied by introducing shallow acceptors or donors in addition to the transition elements.

(4) Centers which have no unpaired electron but which can be made to contain one by removing an electron or a hole from
one center by optical excitation and trapping this charge carrier at a different center; examples are the so-called self-activated and self-coactivated centers in ZnS.

5.4 EPR measurements related to other studies of luminescence:

The EPR method is especially well suited to giving in many cases a great deal of detailed information on isolated centers because of its extreme selectivity. However, the full power of the method in the field of luminescent centers is used only when the EPR results are related in the right way to the results of other studies of luminescence, such as optical absorption of the centers, photoconductivity, decay of the luminescence, and thermal glow, as shown in the following examples:

(1) The intensity of the EPR absorption of F centers in KCl has been related quantitatively to the strength of their optical absorption, and the optical absorption in turn has been related to the infrared emission of these centers.

(2) The decay of the EPR signal of a long-lived excited state of a luminescent center can be compared with the corresponding decay of the luminescence. A possible example is the long-lived excited state of Mn$^{2+}$ in CaF$_2$.

(3) The change in valence state of a transition element in Si or Ge, caused by the addition of shallow donors or acceptors, can be checked quantitatively by EPR measurements and can be related to the infrared emission associated with these valence states.

(4) The excitation spectra of the ultra-violet induced EPR of
the self-activated centers in ZnS and the self-activated emission of these centers can be compared quantitatively.

5.5 EPR Equipment used and results:

EPR equipment essentially consists of a source of radiation, a sample which absorbs the radiation, and a system to detect this absorption. Usually the source of radiation is a klystron, the frequency of which can be varied over only a narrow range, just enough to lock it to the absorption frequency of a high quality microwave cavity. This microwave cavity, containing the sample to be investigated, is situated between the poles of an electromagnet. The magnetic field is scanned over a large range of field intensities, so as to cause a variable splitting between the two Zeeman levels differing by one unit in their $M_S$ values is equal to the quantum of energy $\hbar\nu$ of the monochromatic microwave radiation. It is detected as a resonance line, which can be either displayed on an oscilloscope or recorded on graph paper. A very simple diagram, Fig. 5.1 illustrates the principle of the method. The klystron is connected to arm 1 of a microwave bridge. This bridge is designed in such a way that microwave power, the amount of which can be controlled by the attenuator, divides between arm 2, containing the microwave cavity and the sample, and arm 3, containing a matched load. When the bridge is balanced in an off resonance situation, no microwave power is detected in arm 4. When resonant absorption takes place, this causes an imbalance of the microwave bridge, which is now detected in arm 4. The modulation coils on the pole caps modulate the steady magnetic field so that a-c detection is
EPR EQUIPMENT

FIG 5.1

MATCHED LOAD

DISPLAY SYSTEM
DETECTION SYSTEM

ATTENUATOR

KLYSTRON

SAMPLE CAVITY

MAGNET
DEWAR

DETECTOR
possible. The modulation frequency is usually taken as high as possible, to give a good signal to noise ratio.

The block diagram of V-4502 EPR spectrometer used in the present work is shown in fig. 5.2. All measurements were taken at room temperature, and the phosphor powders were compressed into thin tablets, 1.4 cm. in diameter. Keeping the radiofrequency at 9500 mega cycles per sec., two successive runs were made in determining an absorption curve with scanning fields of 500 and 1000 oersteds. Each run began at high field, where magnetic absorption was zero and continued through the resonance region to zero field. The EPR spectrum was first observed on the oscilloscope and after adjusting the sensitivity and determining the resonance region, it was recorded with the help of an automatic recorder. Some of the recorded spectra are shown in fig. 5.3. The EPR spectrum of fired sample, which does not contain Gadolinium consist of six symmetrical lines, which are due to the presence of some paramagnetic impurity, probably manganese, as the EPR spectra of CaS:Mn phosphors also show six similar lines with hyperfine splitting due to nuclear spin. For all other phosphor samples, there is one more line in the center, which is due to Gadolinium. Gadolinium is expected to give either one or seven symmetrical lines. The value of 'g' as calculated from the magnetic resonance equation comes out to be 1.972. Similar spectra are obtained with the two scanning fields and there is no change with the change in activator concentration. Results are further discussed in chapter VI.
FIG. 5.2

BLOCK DIAGRAM V-4502 EPR SPECTROMETER

- REGULATED MAGNET POWER SUPPLY
- CAVITY
- R.F. WAVE GUIDE
- V-4500-41A MICROWAVE BRIDGE
- V-4500-20 POWER SUPPLY UNIT
- V-4500-10A EPR CONTROL UNIT
- 100 KC FIELD MODULATION UNIT
- SELECTOR PANEL
- GRAPHIC RECORDER
- 'SCOPE
- V-4260 POWER SUPPLY
  - EPR CONTROL UNIT
  - SWEEP UNIT
  - SWEEP AMPLIFIER
- V-4240/50
- V-4270 OUTPUT CONTROL UNIT
FIG. 5.3

EPR SPECTRA

FIRED POWDER

SCANNING FIELD = 1000 OERSTEDS
FIG. 5.3

EPR SPECTRA

SAMPLE 5

SCANNING FIELD = 1000 OERSTEDS
FIG. 5.3

EPR SPECTRA

SAMPLE 10

SCANNING FIELD = 1000 OERSTEDS
FIG. 5.3

EPR SPECTRA

SAMPLE 14

SCANNING FIELD = 1000 OERSTEDS
( B ) MAGNETIC SUSCEPTIBILITY

According to their susceptibilities, substances may be roughly divided into three classes: diamagnetic, paramagnetic and ferromagnetic.

'Paramagnetic substances' when placed in a magnetic field, get a feeble magnetism induced in the same sense as the external field. There is a greater concentration of the magnetic lines of force within the body of such substances than in the surrounding medium. In a non-uniform field, paramagnetic substances will experience an attractive force towards the strongest part of the field. For them permeability $\mu > 1$, and the susceptibility $k$ has a small positive value, which varies inversely as the absolute temperature of the material.

'Diamagnetic substances' on the other hand, acquire a feeble induced magnetism in a direction opposite to the external field, when placed in it. They have a tendency to move from stronger to weaker parts of the field and are characterised by negative susceptibility. There is thus a lesser number of lines of force through them than in the outside field i.e. $\mu < 1$.

'Ferromagnetic substances' are distinguished by a large value of magnetic permeability and are consequently capable of high degree of magnetisation. In general these substances are capable of developing north and south poles, when placed in a magnetic field and the induced magnetisation is not proportional to the magnetising force.
The intensity of magnetisation I for any material is proportional to the magnetising field H, i.e.

\[ I \propto H = kH \]

or \[ k = I/H \]

The ratio I/H or k is termed the 'magnetic susceptibility'. The susceptibility per unit volume or the intensity of magnetisation per unit field, which is the quantity most commonly measured directly by experiment is usually denoted by k. The specific susceptibility or the susceptibility, per unit mass, a quantity frequently required in theoretical discussions, is denoted by \( X \), and is equal to \( k/p \), where p is the density of the substance. The atomic or molar susceptibility \( X_A \) or \( X_M \) is respectively equal to the product of \( X \) and the atomic or molecular weight.

Magnetic behaviour has been explained in terms of 'elementary magnets', even in the older magnetic theories. These, in turn have been attributed to electrical 'molecular currents' i.e. the circulation of electricity within the atom. With the development of atomic theory, these ideas have been given precise meaning, in that the molecular currents are identified with the orbital motion and spin of the electron. The electrons within any one atom can diminish or augment each other's effects, according as their individual moments are oppositely or similarly oriented. If their resultant effect is zero, the substance is diamagnetic, in other case it is paramagnetic.
5.6 Magnetic susceptibility and luminescence:

Magnetically speaking, the luminescent sulphides generally consist of a diamagnetic material like CaS, together with some diamagnetic fluxes like Na$_2$SO$_4$ in which paramagnetic atoms, such as Gadolinium or diamagnetic atoms like copper (Cu) are embedded. The difficulties encountered in the resonance measurements, in being unable to distinguish between diamagnetism and paramagnetism which result in a very broad absorption spectrum, are absent in the measurement of static susceptibility.

Rupp (17) has taken into consideration the magnetic behaviour of sulphide phosphors and has attempted to correlate the magnetic susceptibility with other factors such as the formation of complex molecular groups, nature of emitted radiations and the influence of temperature. He concluded that:

(i) The groups of molecules of the basic materials - Ca - S and -Ca-O are more paramagnetic than the simple CaS or CaO.

(ii) Even the luminescent substances containing ZnS are more paramagnetic when they exhibit phosphorescence than when they are non-excited.

(iii) When diamagnetic metals like Bi, Cu and Ag are added in small quantities in the production of the luminescent sulphides, their susceptibilities become about 1000 times more than their normal mass susceptibility.

Magnetic susceptibility changes accompanying excitation have been reported by Sibaiya and Venkataramiah (18) for sulphide
phosphors. In such materials the apparent long life of the excited state results from the trapping of electrons; therefore, the susceptibility change is a property of the difference in magnetic character of the unexcited and the trapped electrons. Johnson and Williams (19) studied the changes in susceptibility on excitation of ZnF$_2$:Mn phosphors. Specific susceptibility measurements indicated that the unexcited Mn$^{2+}$ was in the state of maximum multiplicity $^6S$ with five unpaired electron spins in the 3d shell. It was expected that if the emitting state had different multiplicity as compared to the ground state of the activator, then paramagnetic susceptibility should decrease on excitation. After taking into account the possible effects produced by heating consequent on excitation, the change in susceptibility was found to be about one Bohr magneton. This indicated a lower multiplicity, probably $^4G$, where one of the spins of 3d$^5$ electron is reversed.

Johnson and Williams (20) have also studied the change in degree of interaction in ZnF$_2$:Mn phosphors with activator concentration. The Weiss constant is a direct measure of interaction energy. A study of variation of Weiss constant with temperature suggested that there was negligible exchange demagnetisation of adjacent paramagnetic activator ions and that the manganese ions were distributed at random over the cation sites.

Larach and Turkevich (21) studied the magnetic susceptibility of manganese activated Zinc-orthosilicate phosphors as a function of manganese content. It was found that the effective magnetic moment decreased monotonically with increasing manganese content. Extrapolation to the region of infinite manganese dilution
yielded the value of 5.9 Bohr magnetons as against the theoretical 'spin only' value of 5.82 B.M. for Mn$^{2+}$. This gave direct evidence for the state of ionization of the luminescent centers. The increase in Weiss constant with concentration was interpreted as an increase in mutual interaction between different luminescent centers. The decrease in luminescence intensity with concentration also suggested greater interaction leading to increased probability of radiationless transitions.

Using magnetic methods, Larach and Turkevich (29) have investigated the effective role of the flux, added in the preparation of phosphors and have verified Kroger's (23) theory of charge compensation. Jensen (24) has measured the paramagnetic susceptibility of trapped electrons in alkali halides. Lewis (25) and coworkers have shown that multiplicity changes are active in the luminescence of organic phosphors.

5.7 General theory of susceptibility measurements:

Magnetic susceptibility determination involves the measurement of the mechanical forces acting on a body in a magnetic field. The force can be regarded as superposition of: first, the forces acting on the body in virtue of its permanent magnetism, and secondly, the forces acting on the body in virtue of its induced magnetism.

For the value of $F_x$, the $x$ - component of the mechanical force per unit volume, Jeans (26) gives the equation in the form

$$F_x = -p \frac{\mathrm{d}V}{\mathrm{d}x} - \frac{d^2}{\delta^2} \frac{\mathrm{d}u}{\mathrm{d}x} + \frac{d}{\delta^2} \frac{d}{\mathrm{d}x} \left( \frac{H^2}{\delta^2} \frac{\mathrm{d}u}{\mathrm{d}r} \right) \ldots (5.1)$$

where $p$ is the density of magnetic poles, $V$ is the
magnetic potential and \( \tau \) is the density of the magnetic fluid, \( u \) and \( H \) are permeability and field respectively.

Equations similar to (5.1) can be written for the mechanical forces along the \( y \) and \( z \) components.

For a body which has no permanent magnetism, the first term of equation (5.1), \(- p \frac{dV}{dx}\), vanishes so that the equation reduces to

\[
F_x = - \frac{H^2}{8\pi} \frac{du}{dx} + \frac{d}{dx} \left( \frac{H^2}{8\pi} \tau \frac{du}{d\tau} \right) \quad \ldots \ldots (5.2)
\]

It can, further, be shown that, in general, \((u - 1)\) is proportional to \(\tau\), and consequently we can write

\[(u - 1) = c\tau\]

where \(c\) is a constant. Also if the medium is isotropic \(\frac{du}{dx} = 0\) and the equation (5.2) may be put in the simpler form

\[
F_x = \left( \frac{u - 1}{8\pi} \right) \frac{d}{dx} \left( H^2 \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots (5.3)
\]

Also, there will be similar equations for the forces along \( y \) and \( z \) axes i.e.

\[
F_y = \frac{u - 1}{8\pi} \frac{d}{dy} \left( H^2 \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots (5.4)
\]

and

\[
F_z = \frac{u - 1}{8\pi} \frac{d}{dz} \left( H^2 \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots (5.5)
\]

For practical applications the equations (5.3), (5.4) and (5.5) can be further simplified by taking the field along the \( y \) - direction, its gradient along the \( x \) - direction and supposing the field uniform along \( y \) and \( z \) axes. Consequently, equations (5.4) and (5.5) reduce to zero.
If a body having a volume $v$, with a permeability $u_1$, is suspended in a medium of permeability $u_2$, we can rewrite the equation (5.3)

$$F_x = \frac{u_1 - u_2}{4\pi} v \frac{dH_y}{dx} \quad \cdots \cdots \cdots \quad (5.6)$$

Or since $u = 1 + 4\pi k$ where $k$ is the volume susceptibility, we have

$$F_x = (k_1 - k_2) v H_y \frac{dH_y}{dx} \quad \cdots \cdots \cdots \quad (5.7)$$

Further, we can consider the case where the field is uniform, but the body is in the form of a long uniform cylinder with its axis lying, say, along the $x$-axis so that its one end is in a field of strength $H_1$ and the other end lies in a region of field $H_2$. Inside the body there would, then, be a field gradient with $H = H_1$ at $x = 0$ and $H = H_2$ at the other extremity. Consequently we get on integration from equation (5.3)

$$F_x = \frac{u - 1}{8\pi} (H_1^2 - H_2^2)$$

Substituting $u = 1 + 4\pi k$ and remembering that equation (3) refers to a unit volume,

$$F_x = \frac{1}{2} (k_1 - k_2) A H^2 \quad \cdots \cdots \cdots \quad (5.8)$$

Where $A$ is the area of the cross-section of the cylindrical specimen.

The equations (5.7) and (5.8) are of fundamental importance from the point of view of practical susceptibility measurements and all the present methods of measurement depend
on one or the other of these.

According to the theory developed above, the methods of measurements of magnetic susceptibilities can be broadly put under two main divisions:

(1) Non-uniform field methods.
(2) Uniform field methods.

The earliest application of the non-uniform field method to practical susceptibility measurements is due to Faraday (27) and the method is known after him. The uniform field method for solids is known after Gouy (27), although this method was applied for liquids by Quincke (28) in 1885.

5.8 Experimental methods:

(i) The Gouy Method: If a cylindrical sample of matter is suspended between the poles of a magnet so that one end of the sample is in a region of large field strength and the other in a region of negligible field, then the force acting on the sample, as shown in previous equation, is given by

\[ f = \frac{1}{2} k H^2 A \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (5.9) \]

where \( A \) is the cross-section area of the sample. If the atmosphere surrounding the sample have a susceptibility \( k_0 \) and the field at the outer end of the sample is \( H_0 \), then the equation becomes -

\[ f = \frac{1}{2} \left( k - k_0 \right) \left( H^2 - H_0^2 \right) A \quad \ldots \ldots \quad (5.10) \]

In practice \( H_0 \) may be made negligible and, by using hydrogen or
nitrogen for the surrounding atmosphere, \( k_0 \) may also be made negligible. It is convenient to measure \( f \) by suspending the sample from a balance, in which case

\[
f = g \Delta w = \frac{1}{2} k H^2 A \quad \ldots \ldots \ldots \quad (5.11)
\]

where \( g \) is the gravitational constant, and \( \Delta w \) the apparent change in weight of the sample on application of the magnetic field.

For many types of investigations it is convenient to use a magnetic field of from 5000 to 15,000 oersteds. For strongly paramagnetic samples \( \Delta w \) may then be of the order of several tenths of a gram, if the cylindrical sample has a diameter of 5 to 10 mm. An ordinary analytical balance therefore gives a sufficient degree of accuracy for some purposes. A refinement in which the weighing is done by electrodynamic balancing is described by Hilal and Fredericks (29).

Other methods are available for obtaining \( f \). For instance, the sample may be observed with a microscope, or interferometrically (30). Sucksmith (31) has described an optical method based on the distortion of a phosphor bronze ring. The sample may also be suspended horizontally, from a torsion (32) or bifilar suspension (33, 34).

Powdered samples may be measured by packing them into cylindrical glass sample tubes. Correction must be made for the susceptibility of glass, which is generally diamagnetic with a slight temperature coefficient. The accuracy of measurements on powdered samples is severely limited by the uniformity and reproducibility of
packing. It is difficult to exceed an accuracy of \( \pm 1\% \). However, some methods for improving the precision are described by French and Harrison (35).

(B) The Faraday Method: If the poles of a magnet are inclined towards each other, there is produced a non-homogeneous field with an axis of symmetry. A non-homogeneous field may also be found between appropriately shaped polepieces or near the edges of plance poles. If now a substance of susceptibility other than zero is placed in a region where the strength of the field \( H \) changes with displacement along the axis of symmetry \( S \), then the substance will be subjected to a force along the axis.

\[
f = m X H \frac{dH}{ds} \quad \ldots \ldots (5.12)
\]

where \( m \) is the mass of the sample, \( X \) the mass susceptibility, \( H \) the field strength, and \( \frac{dH}{ds} \) the field gradient along the \( s \)-axis.

This method is convenient and sensitive. Small amounts of materials are needed, and no separate determination of density is required. The method was used by P. Curie (36) in his classical studies, and has been used and developed by many investigators since then. The sample may conveniently be mounted on a torsion arm. Displacements may be observed directly, or by a mirror, lamp and scale arrangement. The sample is generally restored to its original position with the aid of a torsion head. The electrical torsion head is satisfactory for this purpose (37).

Many observations, using the Faraday method, have been made at both, high and low temperatures. The method is a strong competitor of the Gouy method for many types of investigations.
Refinements, some of them of quite extraordinary sensitivity, have been described by many workers (38-43).

5.9 Method used and experimental results:

In the present investigation, the Gouy method was used to measure the magnetic susceptibility of CaS:Gd phosphors. The phosphors were nicely packed upto a fixed mark (13 cm.) in a thin-walled pyrex glass tube of diameter 1 cm. The tube was suspended by a nylon thread from one pan of a specially designed analytical balance (design by Prof. A. Mukerji of Burdwan University) having a sensitivity of 0.2 milligram. The thread is surrounded by a glass tube to avoid air currents. A large electromagnet of 3 cm. pole pieces gave a steady field of 5000 oersted with 3 amp. of current. A current of 3 amp. passed for ten minutes did not heat the coils to any sensible degree. The current was adjusted by a system of rheostats. Before each reading the current kept at a low value, was reversed sufficient number of times in order to bring the iron core to cyclic state. Current of 3 amp. was always used and the field was always reproducible.

The simplified Gouy equation requires that the field be a maximum at one end of the sample and negligible or almost zero at the other end. Field strength as a function of vertical distance was determined using Bismuth spiral and is shown in fig. 5.4 As the squares of the field strength are involved, it is seen that samples longer than 13 cm. can be treated as having negligible field at the upper end.

If the difference in weight of the sample, with and
FIG. 5.4

VERTICAL DISTANCE (cm)

FIELD

6000
5000
4000
3000
2000
1000
0

3 AMP.

4 AMP.
without magnetic field, is \( g \Delta w \), then the force \( f \) on a sample is given by:

\[
f = \frac{g \Delta w}{2} (k - k_0) H^2 A \hspace{1cm} (5.13)
\]

where \( k \) and \( k_0 \) are volume susceptibilities of the sample and the surrounding atmosphere respectively; and \( A \), the cross-sectional area of the sample. Calculations for volume susceptibility were made by using the formula

\[
\frac{\Delta w}{\Delta w_{\text{standard substance}}} = \frac{k - k_{\text{air}}}{k_{\text{standard substance}} - k_{\text{air}}} \hspace{1cm} (5.14)
\]

As suggested by Selwood (44), cane sugar was used as a standard substance. The calculated value of susceptibility of Benzene, taking cane sugar as standard, gave satisfactory results. Three sets of observations taken for every sample, gave almost consistent readings. Some samples were also run at different field strengths and were found to give fairly consistent results. All readings were taken at room temperature.

To make corrections for the diamagnetic susceptibility of the glass tube, weights were taken four times (Table 5.1) i.e. weight of empty tube with \( (A) \) and without \( (B) \) magnetic field and weight of sample tube, filled with phosphor, with \( (C) \) and without \( (D) \) magnetic field. The difference \( (C - A) - (D - B) \) directly gave the apparent change in weight \( \Delta w \) of the sample in magnetic field and the correction for the glass tube is automatically avoided. This change in weight \( \Delta w \) for each sample is substituted in
the equation to calculate the value of volume susceptibility, which is then converted to mass susceptibility. Corrections for the diamagnetic susceptibility of the host material are made by determining the mass susceptibility of the fired powder sample, in which activator is not added. Subtraction of this mass susceptibility of the host material from the mass susceptibility of phosphor sample, gives the value of mass susceptibility of Gadolinium for a particular concentration of it, which is then converted for its unit mass. Finally it is multiplied by molecular weight of Gadolinium \((M = 157.25)\) to obtain molecular susceptibility. Molecular susceptibility vs. concentration of Gadolinium is shown in fig. 5.5. The concentration of Gadolinium is taken on logarithmic scale. For lower concentrations, the susceptibility is paramagnetic. As the concentration of Gadolinium in Gypsum reaches 0.02% and above, susceptibility changes to diamagnetic. Results are further discussed in chapter VI.
TABLE 5.1 (A)
Magnetic Susceptibility for CaS:Gd Phosphors

Current = 3.0 Amp.                       Room Temperature = 22°C
Length of Sample = 13 cm.                 Radius = 0.28 cm.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Wt. of empty tube in gms.</th>
<th>Wt. of (tube + sample) in gms.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without any field (A)</td>
<td>With the field on (B)</td>
</tr>
<tr>
<td>1</td>
<td>13.2889</td>
<td>13.2847</td>
</tr>
<tr>
<td>2</td>
<td>13.2890</td>
<td>13.2852</td>
</tr>
<tr>
<td>3</td>
<td>13.2892</td>
<td>13.2854</td>
</tr>
<tr>
<td>4</td>
<td>13.2892</td>
<td>13.2854</td>
</tr>
<tr>
<td>5</td>
<td>13.2897</td>
<td>13.2859</td>
</tr>
<tr>
<td>7</td>
<td>13.2904</td>
<td>13.2866</td>
</tr>
<tr>
<td>8</td>
<td>13.2900</td>
<td>13.2862</td>
</tr>
<tr>
<td>10</td>
<td>13.2900</td>
<td>13.2862</td>
</tr>
<tr>
<td>12</td>
<td>13.2900</td>
<td>13.2862</td>
</tr>
<tr>
<td>13</td>
<td>13.2902</td>
<td>13.2864</td>
</tr>
<tr>
<td>15</td>
<td>13.2903</td>
<td>13.2865</td>
</tr>
<tr>
<td>Host material</td>
<td>13.2898</td>
<td>13.2860</td>
</tr>
</tbody>
</table>

continued ...............
### TABLE 5.1 (B)

**Magnetic Susceptibility for CaS:Gd Phosphors**

(After refilling the tube)

<table>
<thead>
<tr>
<th>Current = 3.0 Amp.</th>
<th>Room Temperature = 22°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of Sample = 13 cm.</td>
<td>Radius = 0.28 cm.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Wt. of empty tube in gms.</th>
<th>Wt. of (tube + sample) in gms.</th>
<th>Increase in wt. mean ( \Delta W ) in gms.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without any field (A)</td>
<td>With the field on (B)</td>
<td>Without any field (C)</td>
</tr>
<tr>
<td>1</td>
<td>13.2887</td>
<td>13.2849</td>
<td>15.4199</td>
</tr>
<tr>
<td>2</td>
<td>13.2891</td>
<td>13.2852</td>
<td>15.3157</td>
</tr>
<tr>
<td>3</td>
<td>13.2896</td>
<td>13.2856</td>
<td>15.2372</td>
</tr>
<tr>
<td>4</td>
<td>13.2892</td>
<td>13.2854</td>
<td>16.0053</td>
</tr>
<tr>
<td>5</td>
<td>13.2897</td>
<td>13.2859</td>
<td>15.5216</td>
</tr>
<tr>
<td>7</td>
<td>13.2896</td>
<td>13.2858</td>
<td>15.5039</td>
</tr>
<tr>
<td>8</td>
<td>13.2900</td>
<td>13.2862</td>
<td>15.4158</td>
</tr>
<tr>
<td>9</td>
<td>13.2900</td>
<td>13.2862</td>
<td>16.2692</td>
</tr>
<tr>
<td>10</td>
<td>13.2900</td>
<td>13.2862</td>
<td>15.3946</td>
</tr>
<tr>
<td>12</td>
<td>13.2900</td>
<td>13.2862</td>
<td>15.5364</td>
</tr>
<tr>
<td>13</td>
<td>13.2902</td>
<td>13.2864</td>
<td>15.3452</td>
</tr>
<tr>
<td>14</td>
<td>13.2900</td>
<td>13.2862</td>
<td>16.2450</td>
</tr>
<tr>
<td>15</td>
<td>13.2903</td>
<td>13.2865</td>
<td>15.8440</td>
</tr>
<tr>
<td>Host material</td>
<td>13.2898</td>
<td>13.2860</td>
<td>15.9751</td>
</tr>
</tbody>
</table>
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CHAPTER VI  DISCUSSIONS AND CONCLUSIONS

6.1 Decay studies  119
6.2 Thermoluminescence  122
6.3 Fluorescence  128
6.4 Electron Paramagnetic Resonance  136
6.5 Magnetic Susceptibility  139
6.6 Site occupied by activator and charge compensation  140
6.7 Conclusions  142
6.8 References  144