

## MAGNETIC PROPERTIES OF RARE EARTH HYDROGEN SELENITE CRYSTALS

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### 7.1 Introduction

This chapter deals with the magnetic properties of the rare earth hydrogen selenite crystals. The magnetic properties of mono and mixed rare earth hydrogen selenite crystals of different stoichiometry are observed and are quite interesting. Yet, no work seems to have been reported in the literature about the magnetic properties of rare earth hydrogen selenite crystals.

A great deal of work has been reported recently on the magnetic properties of rare earths and its compounds<sup>1,2,3</sup>. Large number of crystals of rare earth has been grown by using different techniques<sup>4,5</sup>. Recently data on the growth and magnetic properties of rare earth oxalate crystals has been reported<sup>6</sup>.

Materials are classified according to their bulk susceptibility as diamagnets, paramagnets and ferromagnets. For the first group of materials, for which the susceptibility is small and negative ( $\chi \approx -10^{-5}$ ). These materials are called



diamagnetic as their magnetic response opposes the applied magnetic field. Copper, silver, gold, bismuth, beryllium etc. belong to this class. Superconductors form another group of diamagnets for which susceptibility ( $\chi$ )  $\approx$  -1.

Another major group of materials are paramagnets. They have susceptibility  $\chi$  small and positive, typically  $\chi \approx 10^{-3}$  to  $10^{-5}$ . The magnetisation of the paramagnets is weak but aligned parallel to the direction of the magnetic field. Most of the rare earth elements fall in this category.

The most widely recognised materials are the ferromagnetic solids for which the susceptibility is positive, and very large typically 50 to 10000. Iron, cobalt, nickel and some alloys containing rare earth elements belong to this class.

This chapter reports the theory of the magnetic properties, methods of measurements, and the experimental determination of magnetic moment of mono (single) and doubly mixed rare earth hydrogen selenite crystals.

## 7.2 Theories of atomic paramagnetism

Most of the rare earth elements are paramagnetic in nature. In the case of an atom, it may or may not have permanent magnetic moment. If it has not, application of a magnetic field to the atom leads to an induced moment of sign opposite to that of the applied field, and the atom is said to be diamagnetic. But if the atom has a permanent magnetic moment, application of a field leads to orientation of the moment and the atom is said to be paramagnetic. An atom will have a permanent magnetic moment, if it has an odd number of electrons or all the electrons are not paired off in respect of their spins. All atoms are subjected to induced magnetisation, but when paramagnetism is present, it is at least 10 times greater than the diamagnetism.

The classical theory of paramagnetism was developed by Langevin<sup>7,8</sup> under the assumption that each atom is a little permanent magnet and that the atomic magnets tend to line up parallel to an applied magnetic field. The alignment is resisted by the



thermal agitation of the atoms. There is an obvious identification of the hypothetical atomic magnet with the magnetic moment caused by orbital electronic motion<sup>9</sup>.

In any element, particularly in the case of rare earths, associated with the paramagnetism, there is a contribution due to the diamagnetism also. Diamagnetism is associated with the tendency of electric charges partially to shield the interior of a body from an applied magnetic field.

When the flux through an electrical circuit is changed an induced current is set up in such a direction as to oppose the flux change. In an electron orbit within an atom, the induced current persists as long as the field is present. The magnetic field of the induced current is opposite to the applied field and the magnetic moment associated with the current is a diamagnetic moment. Even in a normal metal there is a diamagnetic contribution from the conduction electrons, and the diamagnetism is not destroyed by collision of the electrons<sup>10</sup>.

The Larmor theorem is concerned about effect of a magnetic field on the orbital motion of an electron. In a magnetic field the motion of the electrons around a central nucleus is to the first order in  $B$ , the same as a possible motion in the absence of  $B$  except for the superposition of a precessional motion with angular frequency,

$$\omega = \frac{eB}{2m}$$

If the field is applied slowly, the motion in the rotating reference system will be the same as the original motion in the rest frame of the system before the application of the field. If the average electron current around the nucleus is zero initially, the application of the magnetic field will cause a finite current around the nucleus. The current is equivalent to a magnetic moment opposite to the applied field. The Larmor frequency is much lower than the frequency of the original motion in the central field.

The Larmor precession of  $Z$  electrons is equivalent to an electric current



$I = (\text{charge}) (\text{revolutions per unit time})$

$$= -Ze \frac{1}{2\pi} \frac{eB}{2m}$$

The magnetic moment  $\mu$  of a current loop is given by the product of current and area of the loop.

The area of a loop of radius  $\rho$  is  $\pi\rho^2$ . Thus, the magnetic moment is given by

$$\mu = \frac{-Ze^2 B}{4m} \langle \rho^2 \rangle$$

Where  $\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$  is the mean square of the perpendicular distance of the electron from the field axis through the nucleus. The mean square distance of the electrons from the nucleus is

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$$

For a spherically symmetric distribution of charge;  $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$ ;

so that  $\langle r^2 \rangle = 3/2 \langle \rho^2 \rangle$

If  $N$  is the number of atoms per unit volume, the diamagnetic susceptibility per unit volume is,

$$\chi = \frac{\mu_0 N \mu}{B} = -\frac{\mu_0 N Z e^2}{6m} \langle r^2 \rangle$$

This is the classical Langevin result. The diamagnetic susceptibilities per gram ion of the rare earths which are relevant in the current study are given in table 7.1<sup>9</sup>

### 7.3 Paramagnetism

The magnetic moment of an atom or ion in free space is given by

$$\mu = \gamma \hbar J = -g \mu_B J$$

7.1



where the total angular momentum  $\hbar J$  is the sum of the orbital  $\hbar L$  and spin  $\hbar S$  angular momenta,  $\gamma$  is called the gyromagnetic ratio (ratio of the magnetic moment to the angular momentum). For electronic system 'g' is called the g factor or the electronic splitting factor and is defined by

**Table 7.1 Diamagnetic susceptibility per gram ion of the elements and groups used for crystallisation.**

Ion of element	Diamagnetic susceptibility per gram ion ( $-\chi \times 10^{-6}$ )
Pr <sup>3+</sup>	20
Pr <sup>4+</sup>	17
Nd <sup>3+</sup>	20
Sm <sup>2+</sup>	23
Sm <sup>3+</sup>	20
SeO <sub>3</sub> <sup>2-</sup>	41
Se <sup>3+</sup>	6

$$g\mu_B = -\gamma\hbar \quad 7.2$$

For an electron spin,  $g = 2.0023 \cong 2.00$ . For a free atom the g factor is given by the Lande equation

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad 7.3$$

The Bohr magneton  $\mu_B$  is defined as  $e\hbar/2m$ . It is closely equal to the spin magnetic moment of a free electron.

The energy levels of the system in a magnetic field are

$$U = -\mu \cdot B = m_j g \mu_B \cdot B \quad 7.4$$

Where  $m_j$  is the azimuthal quantum number and has the values  $J, J-1, \dots, -J$ . For a single spin with no orbital moment, we have  $m_j = \pm 1/2$  and  $g = 2$ , whence  $U = \pm \mu_B \cdot B$ . The splitting is shown in fig. 7.1.



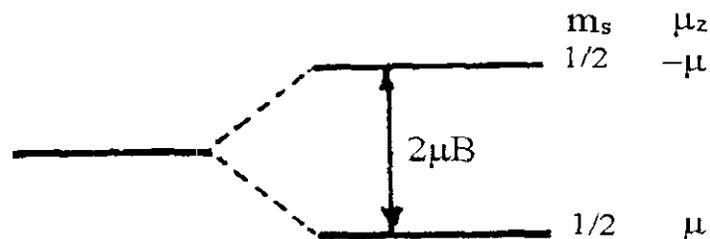


Fig. 7.1 Energy level splitting for one electron in a magnetic field  $B$  directed along the positive  $Z$  axis.

If a system has only two levels the equilibrium population are, with  $\tau \equiv k_B T$

$$\frac{N_1}{N} = \frac{\exp\left(\frac{\mu B}{\tau}\right)}{\exp\left(\frac{\mu B}{\tau}\right) + \exp\left(\frac{-\mu B}{\tau}\right)} \quad 7.5$$

$$\frac{N_2}{N} = \frac{\exp\left(\frac{-\mu B}{\tau}\right)}{\exp\left(\frac{\mu B}{\tau}\right) + \exp\left(\frac{-\mu B}{\tau}\right)} \quad 7.6$$

Here  $N_1$  and  $N_2$  are the populations of the lower and upper levels, and  $N = N_1 + N_2$  is the total number of atoms in the system.

The projection of magnetic moment of the upper state along the field direction is  $-\mu$  and of the lower state is  $\mu$ . The resultant magnetisation for  $N$  atoms per unit volume (with  $x \equiv \mu B/k_B T$ ) is

$$M = (N_1 - N_2)\mu = N\mu \frac{(e^x - e^{-x})}{(e^x + e^{-x})} \quad 7.7$$

$$= N\mu \tan hx$$

For  $x \ll 1$ ,  $\tan hx \sim x$ , and we have

$$M \cong N\mu \left( \frac{\mu B}{k_B T} \right) \quad 7.8$$

In a magnetic field an atom with angular momentum quantum number  $J$  has  $2J + 1$  equally spaced energy levels.

The magnetisation is given by

$$M = N_g J\mu_B B_J(x), \quad (x = gJ\mu_B/k_B T) \quad 7.9$$

Where the Brillouin function  $B_J$  is defined by

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh} \left( \frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \operatorname{ctnh} \left( \frac{x}{2J} \right) \quad 7.10$$

Equation (7.8) is a special case of eq (7.10) for  $J = \frac{1}{2}$ , for  $x \ll 1$ , we have

$$\operatorname{ctnh} x = 1/x + x/3 - x^3/45 + \dots \quad 7.11$$

And the susceptibility is

$$\frac{M}{B} \cong \frac{NJ(J+1)g^2\mu_B^2}{3k_B T} = \frac{N\mu_{\text{eff}}^2\mu_B^2}{3k_B T} = \frac{C}{T} \quad 7.12$$

Here  $\mu_{\text{eff}}$  is the effective number of Bohr magneton defined as

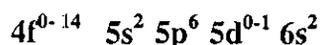
$$\mu_{\text{eff}} \equiv g[J(J+1)]^{1/2} \quad 7.13$$



The constant  $C$  is known as the Curie constant, The equation 7.12 is known as Curie law<sup>10</sup>.

#### 7.4 Magnetic properties of rare earth ions

The ions of the rare earth element have closely similar chemical properties, and their chemical separation in tolerably pure form was accomplished only long after their discovery. Their magnetic properties are fascinating. In the rare earth elements they are unique in almost all cases, in that the electrons actually responsible for the paramagnetism are to a great extent shielded from the external influence. The electronic configurations of the rare earth elements are



Almost all of these elements are trivalent in nature, losing their 6s and 5d electrons. Evidence exist that the 4f electrons are responsible for paramagnetism. Most of the rare earths are astonishingly alike chemically and that their absorption bands and magnetic susceptibilities are little affected by change of its environment, such as by the formation of a compound or of a solvent. Therefore we may assume that the Van Vleck theory is applicable. The susceptibility is given by

$$\chi_M = Ng^2 \mu_{\text{eff}}^2 J(J+1)/3k_B T$$

In this relation the multiplet separation is assumed to be very wide compared to  $k_B T$ . This relation was used by Hund<sup>11</sup>, in his calculation of the magnetic moments of the rare earths which, with some exceptions, are experimentally verified. Hund had no available spectroscopic evidence for the spectral terms of the rare earth ions. His evaluation of  $L$ ,  $S$  and  $J$  proceeds as follows.

Whenever there are several equivalent electrons, the Pauli exclusion principle severely limits the possible spectral terms. Hund assumed that the lowest energy is possessed by the spectral term of highest multiplicity. If when the multiplicity  $2S+1$  has its maximum value, there are several possible values of  $L$ . Then the least energy is assumed to be given by the greatest  $L$  consistent within this  $S$ . Other possible



states are assumed to be not normal, because they have so much more energy. Applying this in the case of praseodymium in which there are two equivalent 'f' electrons, the following terms are admitted by the Pauli exclusion principle:  $^1S$ ,  $^3S$ ,  $^1D$ ,  $^3F$ ,  $^4G$ ,  $^2H$ ,  $^1I$  and the  $^3S$ ,  $^1P$ ,  $^3D$ ,  $^1F$ ,  $^3G$ ,  $^1H$  and  $^3I$  states are excluded. Under Hund's assumptions, of the first group of terms only the  $^3H$  term is a normal state.

For calculating the susceptibilities the following equation was used by Van Vleck<sup>12</sup>

$$\chi_M = \frac{N\mu_{eff}^2}{3k_B T} [4S(S+1) + L(L+1)] \quad (a)$$

$$\chi_M = \frac{Ng^2\mu_{eff}^2 J(J+1)}{3k_B T} + N\alpha \quad (b)$$

or

$$\chi_M = N \frac{\sum_{J=L-S}^{2S} \left\{ \frac{g_J^2 \mu_{eff}^2 J(J+1)}{3k_B T} + \alpha_J \right\} (2J+1) e^{\frac{-W_J^0}{k_B T}}}{\sum (2J+1) e^{\frac{-W_J^0}{k_B T}}} \quad (c)$$

This is done by supposing that the normal state is the one whose component has a minimum or maximum J, depending on whether the multiplet is regular or inverted. For less than seven 4f electrons, the multiplet is 'regular'; for more inverted. The trivalent ion of gadolinium, with seven 4f electrons is in an S state. For europium, samarium and to a slight degree neodymium, the general equation (c) must be used as described below.

A convenient comparison of theoretical with observed susceptibilities is done by the aid of "effective Bohr magneton numbers ( $\mu_{eff}$ )" instead of susceptibilities and are described in literature<sup>9</sup>.

These are defined as



$$\mu_{eff} = \sqrt{\frac{3k_B \chi_M T}{N \mu_{eff}^2}} = 2.84 \sqrt{C}$$

and is a function of temperature.

Theoretical effective Bohr magneton numbers calculated from the appropriate equation of Van Vleck are in good agreement with observed values. In fig. 7.2 the averages of experimental value at room temperature have been shown and compared with Van Vleck's results.

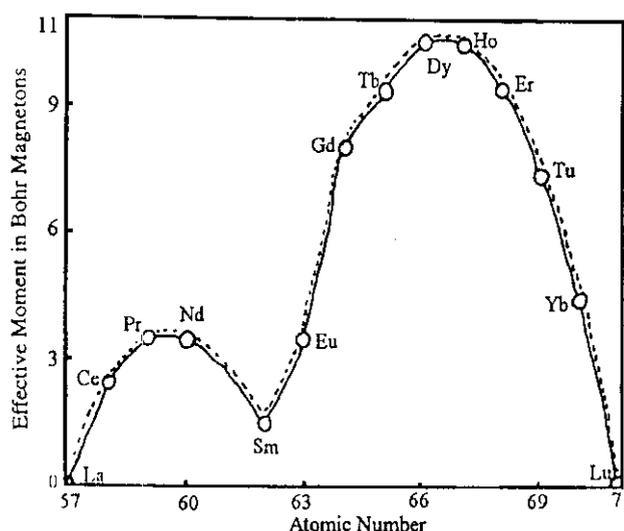


Fig. 7. 2 Effective Bohr magneton numbers for the trivalent rare earth ions at room temperature. The dotted line shows theoretical numbers calculated from the appropriate equation of Van Vleck

Some remarks may be made concerning the experimentally determined susceptibilities of the trivalent rare earth ions. The crystallisation process and the purity of the crystals are highly dependant on the magneton number. Influence of the presence of electronic environment of other electrons. Which means that during the growth process rare earth element combined with diamagnetic materials. The diamagnetic contribution of the moment also needs to take in account.

In the lanthanide family, lanthanum and lutetium are diamagnetic. The susceptibilities of compounds containing the other rare earth trivalent ions like  $Dy_2O_3$  and  $Ho_2O_3$  are the most powerfully paramagnetic substance known.

In addition to Van Vleck a good number of investigators have reported work on rare earth elements<sup>13,14</sup>. Decker<sup>15</sup> has measured the susceptibilities of neodymium nitrate solutions in a range of concentration. He observed that the susceptibility increases with concentration.

Following sections give the details of the magnetic measurements.

### 7.5 Magnetic measurements

There are several methods available for magnetic measurements and these are divided broadly into two categories depending on the measurement of changes in various properties of the materials caused by the presence of magnetic field. The measurements of the magnetisation are either force measurements such as in the torque magnetometer or gradiometer measurements which measure the difference in magnetic induction with and without the sample present.

Measurement of magnetic moments or magnetic properties of the materials can be divided into two broad categories, viz. 1. Induction method and 2. Methods depending on changes in material properties.

The induction methods of measuring magnetic flux depend on Faraday's laws of electromagnetic induction. This states that the e.m.f (V) induced in a circuit is equal to the rate of change of flux linking the circuit.

$$V = -N \frac{d\phi}{dt}$$

If  $A$  is the cross-sectional area of the coil and  $N$  is the number of turns, the magnetic induction is then  $B = \phi/A$

$$V = -NA \frac{dB}{dt}$$



The coil methods measure the magnetic flux  $\phi$  passing through the coil and from the knowledge of the cross sectional area  $A$  the magnetic induction  $B$  can be found. The induced voltage is increased if  $B$  is increased while  $H$  is maintained constant by inserting a high permeability core into the coil. In free space  $B = \mu_0 H$

and 
$$V = -\mu_0 N A \frac{dH}{dt}$$

### 7.5.1 Stationary coil method

Stationary coil method can only measure the rate of change of magnetic induction by measuring the induced voltage. Such devices do have applications but if magnetic induction measurements are required it is necessary to include some form of time integration<sup>16</sup>.

The magnetic induction is

$$-\frac{1}{NA} \int V dt$$

The instruments making use of this formula are used extensively in hysteresis graphs for the measurement of the magnetic properties of soft magnetic materials<sup>17</sup>. The use of instruments needs much care. There are several problems associated with high-sensitivity measurement when the magnetic flux needs to be measured to better than about  $10^{-10}$  weber (0.01 maxwell)

### 7.5.2 Moving-coil (extraction) method

From the Faraday law of electromagnetic induction the induced e.m.f in a coil resulting from a change in flux linking the coil is given by

$$V = -NA \frac{dB}{dt}$$

Integrating this gives

$$\int V dt = -NA(B_f - B_i)$$



Where  $B_i$  is the initial magnetic induction and  $B_f$  is the final magnetic induction. Measurement up to 1% accuracy is possible for the method.

### 7.5.3 Rotating- coil method

For measuring the magnetic induction, it is also possible to use various moving coils which rotate at a fixed angular velocity ' $\omega$ '. Under these conditions the flux linking the coil is

$$B(t) = B \cos \omega t$$

and the voltage generated is

$$\begin{aligned} V &= -NA \, dB/dt \\ &= -\mu_0 NA \, dH/dt \\ &= -\mu_0 NA \omega H \sin \omega t \end{aligned}$$

Therefore the amplitude of the voltage generated by the rotating coil is proportional to the magnetic induction and therefore the amplitude can be used to measure B or H in free space. The signal can be read directly as an a.c voltage or converted to a d.c voltage which is proportional to the amplitude. Typical induction for this instrument range from 10 tesla down to  $10^{-7}$  tesla. The electrical connection to the rotating coil includes slip rings, which are a source of error in dealing with small voltages. The precision is of the order of one part in  $10^4$ .

### 7.5.4 Vibrating coil magnetometer

The vibrating coil magnetometer<sup>18,19</sup> is based on the same principle as above, but is used primarily as a method of determining the magnetisation M. The coil vibrates between the sample and a region of free space and thereby acts as a gradiometer by measuring the difference in induction in the two positions. Surrounding the sample the magnetic induction is

$$B_m = \mu_0 (H + M)$$

The induction linking the coil when it has moved away from the sample is



$$B_0 = \mu_0 H$$

The change in induction is then simply

$$\Delta B = \mu_0 M$$

This method depends on the flux change caused when the coil is removed from the specimen.

$$\int V dt = -NA\mu_0 M$$

Consequently the output of the vibrating coil magnetometer is independent of H, but is dependent on M.

#### 7.5.5 Vibrating sample magnetometer (VSM)

The vibrating sample magnetometer (VSM) is identical in principle to the vibrating coil magnetometer except that the sample is moved instead of the coil. The VSM was first described by Foner<sup>20</sup> and has now widely used. In this work VSM has been utilised for studying the magnetic properties of grown crystals.

A VSM is really a gradiometer measuring the difference in magnetic induction between a region of space with and without the specimen. It therefore gives a direct measure of the magnetisation M.

A schematic diagram of VSM is shown in fig. 7.3. The specimen in general has to be rather short to be accommodated between poles of the electromagnet. The method is therefore in most cases not well suited for the determination of the magnetisation curve or hysteresis loop because of the demagnetising effects associated with the short specimen. But it is enough for the determination of saturation magnetisation  $M_s$ .

The detected signal is an a.c signal of fixed frequency and is measured using a lock in amplifier. A reference signal is provided for the lock in amplifier as shown in



fig.7.3, by using a permanent magnet and a reference pick-up coil. The magnetic moment as small as  $5 \times 10^4 \text{ Am}^2$  ( $5 \times 10^5 \text{ emu}$ ) are measurable with a VSM. Its accuracy is better than 2%.

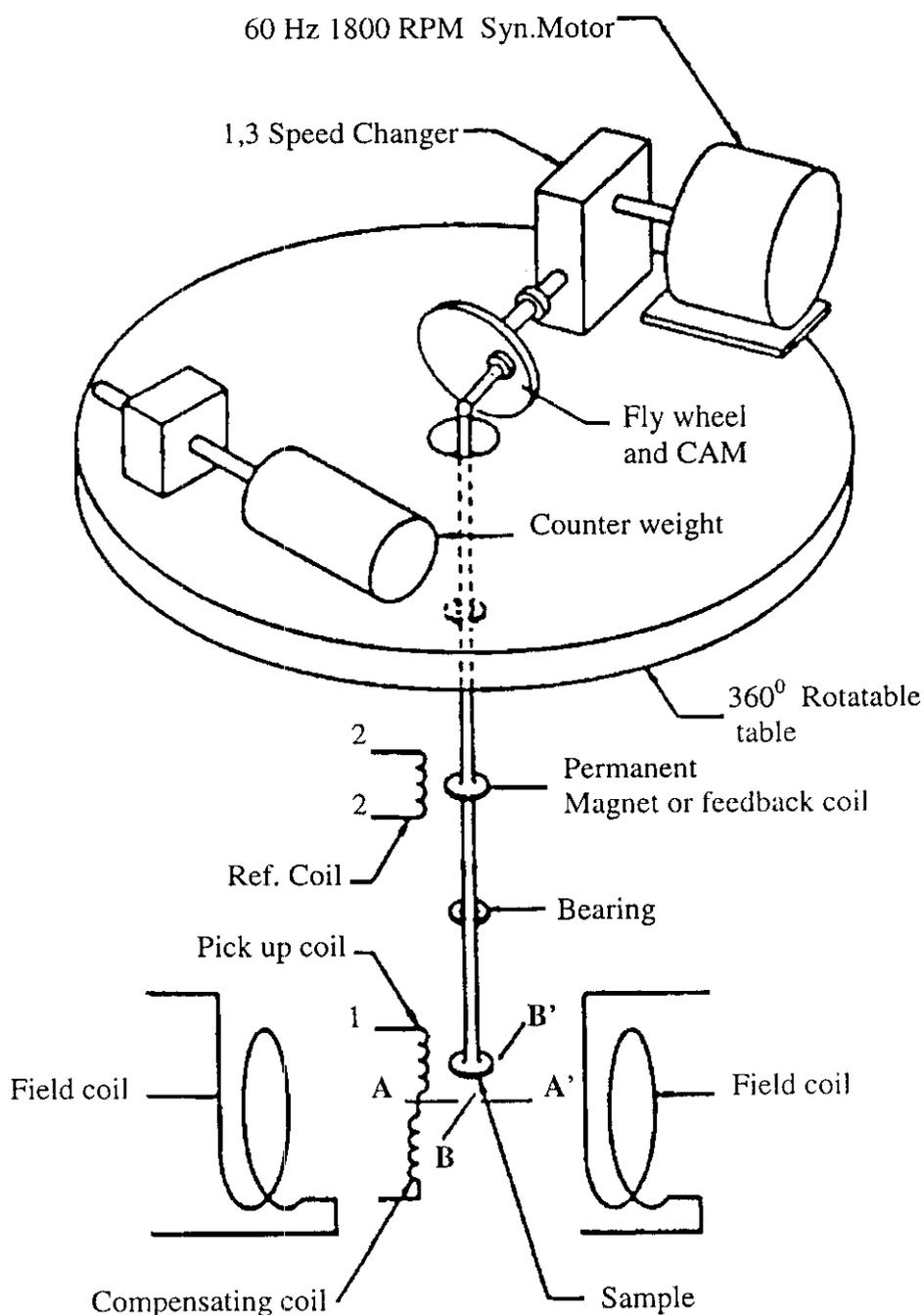


Fig. 7.3 The schematic diagram of VSM

## 7.6 Results and discussion

The magnetic properties of the crystals were studied by using a Vibrating sample magnetometer (VSM) by applying different magnetic fields. The susceptibilities of the crystals are calculated from the measured magnetic moment.

The presence of the rare earth ions in the grown crystals is verified by optical absorption studies. It is observed that the percentages of incorporation of different rare earth ions in the doubly mixed crystals are proportional to the stoichiometric ratio of the interacting ions in the upper electrolyte. The TG-DTA studies of the crystals agree with the proposed formula. The magnetic moments of the grown crystals were determined for different external fields and the gram susceptibility was calculated. The summary is given in tables 7.2 -7.5.

**Table 7.2 The magnetic data of mono (single) hydrogen selenite crystals**

Field (T)	Crystal (PHS)		Crystal (NHS)		Crystal (SHS)	
	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$
0.2	0.090	0.1219	0.080	0.1580	0.020	0.0131
0.4	0.166	0.1124	0.125	0.1235	0.036	0.0118
0.6	0.262	0.1183	0.204	0.1343	0.054	0.0118
0.8	0.359	0.1216	0.285	0.1408	0.081	0.0133
1.0	0.443	0.1200	0.345	0.1363	0.101	0.0132

**Table 7.3 The magnetic data of praseodymium neodymium hydrogen selenite.**

Field (T)	PNHS(P=25% N=75%)		PNHS(P=50% N=50%)		PNHS(P=75% N=25%)	
	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$
0.2	0.084	0.1312	0.105	0.1416	0.088	0.1491
0.4	0.154	0.1203	0.163	0.1350	0.146	0.1237
0.6	0.216	0.1125	0.251	0.1394	0.237	0.1339
0.8	0.312	0.1218	0.333	0.1387	0.316	0.1338
1.0	0.410	0.1281	0.408	0.1360	0.401	0.1359

**Table 7.4** The magnetic data of praseodymium samarium hydrogen selenite

Field (T)	PSHS(P=25% S=75%)		PSHS(P=50% S=50%)		PSHS(P=75% S=25%)	
	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$
0.2	0.040	0.03322	0.042	0.06154	0.058	0.08380
0.4	0.088	0.03650	0.076	0.05846	0.097	0.07001
0.6	0.140	0.03875	0.110	0.05641	0.158	0.07611
0.8	0.190	0.03945	0.160	0.06154	0.214	0.07730
1.0	0.232	0.03853	0.175	0.05661	0.262	0.07572

**Table 7.5** Magnetic data of neodymium samarium hydrogen selenite

Field (T)	NSHS(N=25% S=75%)		NSHS(N=50% S=50%)		NSHS(N=75% S=25%)	
	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$	Moment $\times 10^{-5} \text{JT}^{-1}$	$\chi_g \text{JT}^{-2} \text{kg}^{-1}$
0.2	0.025	0.03307	0.045	0.06132	0.062	0.09281
0.4	0.041	0.02712	0.083	0.05650	0.106	0.07931
0.6	0.070	0.03086	0.142	0.06450	0.183	0.09130
0.8	0.102	0.03306	0.190	0.06470	0.250	0.09350
1.0	0.125	0.03156	0.227	0.06181	0.302	0.90402

The variation of the effective magnetic moment for the different stoichiometric ratio of the doubly mixed rare earth crystals have been depicted in fig.7.4-7.6. The magnetic moment of the mixed crystals reflect the magnetic moment of the major constituent rare earth ions.

The molar susceptibility of the crystals were calculated by the equation

$$\chi_M = \frac{\chi_g M}{n} \quad 7.14$$

M is the molecular weight of the sample 'n' is the number of rare earth ions per molecule,  $\chi_g$  is the gram susceptibility,  $\chi_m$  is the molar susceptibility<sup>6</sup>. The effective magnetic moment of the crystals were calculated using the equation

$$\mu_{\text{eff}} = 0.8942 [(\chi_m)_{\text{corr}} T]^{1/2} \quad 7.15$$

where T is the absolute temperature.



The molar susceptibility values were corrected ( $\chi_m$ )<sub>corr</sub> for diamagnetism<sup>9</sup>. The theoretical values of the effective moment of a tripositive rare earth ion is given by the relation

$$\mu_{\text{eff}} = g[J(J+1)]^{1/2} \quad 7.16$$

and the average value for the rare earth ions incorporated in the crystals are calculated. Tables 7.6-7.8 shows the corrected values of the molar susceptibility and the experimental and theoretical values of the effective magnetic moments of the double rare earth hydrogen selenite crystals. Fig. 7.4-7.6 shows the stoichiometric variation in effective magnetic moment of the mixed crystals.

**Table 7.6 Molar susceptibility and effective magnetic moments of the PNHS crystals**

% of P and N		Corrected molar susceptibility (JT <sup>-2</sup> mole <sup>-1</sup> )	Effective magnetic moment (Bohr magneton)	
P	N		Experimental	Theoretical
0	100	0.06188	3.799	3.62
25	75	0.05325	3.5736	3.61
50	50	0.05944	3.7734	3.60
75	25	0.05843	3.7437	3.59
100	0	0.05124	3.5058	3.58

**Table 7.7 Molar susceptibility and effective magnetic moments of the PSHS crystals**

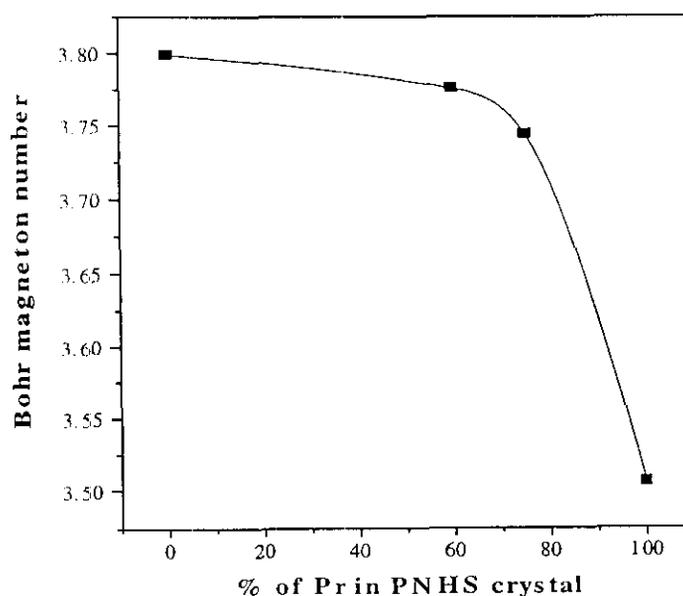
% of P and S		Corrected molar susceptibility (JT <sup>-2</sup> mole <sup>-1</sup> )	Effective magnetic moment (Bohr magneton)	
P	S		Experimental	Theoretical
0	100	0.00508	1.1495	0.85
25	75	0.01628	1.9760	1.5325
50	50	0.06018	2.5102	2.215
75	25	0.03325	2.8068	2.8975
100	0	0.05124	3.5058	3.58



**Table 7.8** Molar susceptibility and effective magnetic moments of the NSHS crystals

% of N and S		Corrected molar susceptibility ( $JT^{-2} \text{ mole}^{-1}$ )	Effective magnetic moment (Bohr magneton)	
N	S		Experimental	Theoretical
0	100	0.00508	1.1495	0.85
25	75	0.01388	1.8193	1.5425
50	50	0.02698	2.5439	2.235
75	25	0.03818	3.0554	2.92
100	0	0.06188	3.799	3.62

The observed and calculated effective magnetic moments of the doubly mixed rare earth hydrogen selenite crystals are agree with each other. It reveals that the diamagnetic nature of the free rare earth ion bound to the hydrogen selenite part of the crystal makes only negligible contribution to the actual magnetic moment of the PNHS, PSHS, NSHS crystals. It is found that in all the above doubly mixed hydrogen selenite crystals, the rare earth ions have only slight difference in electronic configuration as in pure metals and its magnetic properties are also affected negligibly by the  $HSeO_3$ ,  $SeO_3$  bonding.



**Fig. 7.4** The variation of Bohr magneton number with percentage of  $Pr^{3+}$  in praseodymium neodymium hydrogen selenite crystals

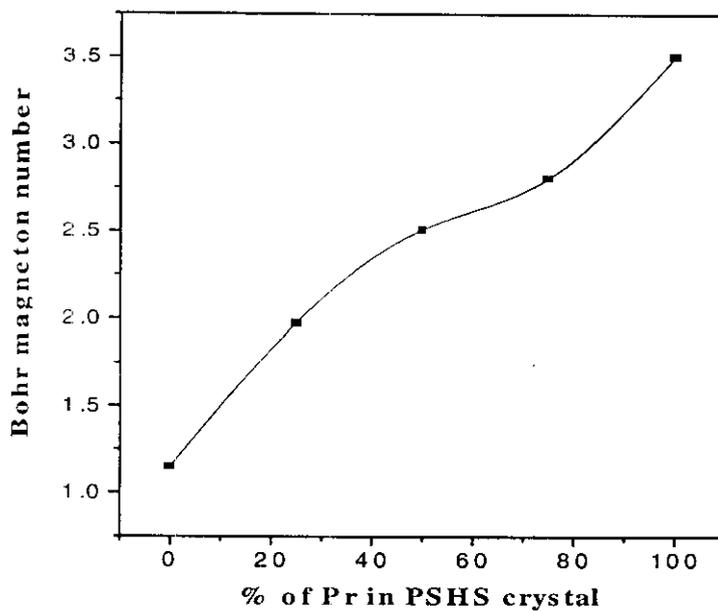


Fig 7.5 The variation of Bohr magneton number with the percentage of  $\text{Pr}^{3+}$  in praseodymium samarium hydrogen selenite crystal.

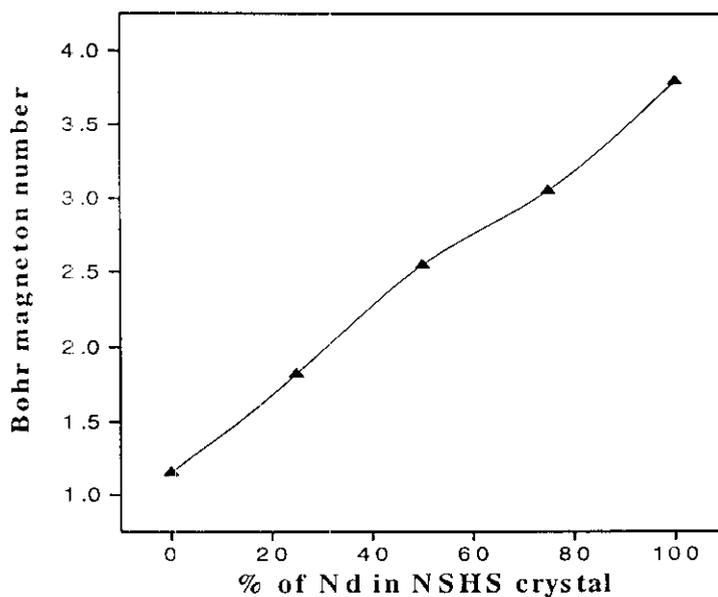


Fig 7.6. The variation of Bohr magneton number with the percentage of  $\text{Nd}^{3+}$  in neodymium samarium hydrogen selenite crystal.

## 7.7 Conclusion

Mono and doubly mixed rare earth hydrogen selenite crystals are obtained by the controlled diffusion of the reactant through the gel medium and is characterised by different techniques. The magnetic susceptibility and effective magnetic moment of the stoichiometrically different doubly mixed crystals were calculated by recording the variation of the magnetic moment with external field. The observed effective magnetic moments agree well with the theoretically calculated values. This suggests that the rare earth ions are weakly perturbed by the crystalline lattice and that the atomic properties of the rare earth ions are retained in the mixed states.

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