CHAPTER 1

PROLOGUE AND SYNOPSIS
INTRODUCTION

The rare earths (RE) are chemically alike and have some common physical properties. But they have striking differences in their magnetic properties which make them a highly interesting subject for systematic magnetic study.

The rare earths are not really rare in nature. They are widely scattered in nature in low concentrations, and they occur in most common minerals e.g., monazite, bastnasite etc. Initially it was very difficult to separate them from the minerals. But nowadays pure RE elements are available in large quantities with the help of ion exchange, solvent extraction and metal reduction techniques.

The rare earths are a group of 17 elements which occur in the third column; elements 21, 39, and 57, and elements 58 through 71 which appear in the extended sixth row of the periodic table constitute the group. They all form trivalent compounds with three electrons in their valence shell, and in the metals most of them have three electrons in their conduction bands.

The difference in the magnetic properties of the various RE ions arises from the difference in the occupation of the 4f shell which otherwise have little effect on their chemical and some physical behavior. With the increase in the atomic number of lanthanides, the 4f electrons are pulled towards the interior of the atom leaving the 5s, 5p etc. shell electrons unaffected, called the lanthanide contraction [1-3]; this arises due to imperfect mutual shielding of the 4f electrons. As a result of this contraction, the neighboring atoms of a RE ion in a crystal approach closer to the RE ion leading to an effective change in the lattice parameters across the lanthanide series.

The 4f electrons have unbalanced orbital angular momenta and spin angular momenta and this leads to strong paramagnetism of lanthanide elements and extremely complex spectra. The rare
earths are prolific compound former; they enter into chemical union with metals of almost every group giving a vast range of inter-metallics; they also give a wide variety of ionic compounds with other elements and group of elements. Moreover, RE compounds accept a wide range of dopings and the RE ions also go into other compounds as dopant; in the later case when a RE ion substitutes a divalent ion, very interesting properties arise due to charge compensation. The 4f-orbits lie well inside the electronic shell and are well protected due to which they are especially valuable for the study of crystal spectra. The change in the properties of the ion in different hosts find multidirectional applications in various branches of physics. The complex spectra of RE ions make them a rich source of laser materials (e.g., neodymium aluminium borates have already been established as minilasers), television phosphors etc. RE inter-metallics possess interesting superconducting and magnetic properties at high temperatures (used in industrial permanent magnets). RE ions doped in crystalline hosts viz., LaF₃, CaWO₄ etc. are used for laser excitations. RE doped YF₃ is a very useful up-converter for infrared applications. These developments have heightened interest in the study of the behavior of RE ions in the condensed state of matter.

When a RE ion is embedded in a crystal lattice, due to interactions between the ion and its surroundings the energy level pattern of the free ion gets modified; and, thus nearly all electronic (optical, magnetic, and thermal) and some nuclear properties (e.g., NMR, Mössbauer spectra, nuclear specific heat etc.) undergo considerable change. In the earlier stages explanation of the thermal variation of the magnetic susceptibilities of the RE³⁺ ions was attempted with the Curie-Weiss law. However, it was soon discovered that the Curie-Weiss law would not account for the observed results over a wide range of temperature and it was suggested that the deviation from this law was due to the electric field acting on the central ion by the charges on the ligands surrounding
it. This was further necessitated by the fact that almost all crystals having symmetry lower than the cubic showed considerable magnetic anisotropy as revealed by the extensive magnetic measurements undertaken by Krishnan and Mookherjee [4]. The effects of coordination between the RE ion and its ligands are described and characterized by an effective static crystalline electric field model. The basic idea of a crystal field (CF) originating from the ligands is due to Becquerel [5]; he pointed out that the absorption lines of some of the RE crystals show a considerable Zeeman splitting in the magnetic field. The invention of the CF theory by Bethe [6] and the application of group theory to impurity in spectroscopy by him [7] and Kramers [8] helped a lot in the early development of the theory. The theory was further refined by Van Vleck [9], Schlapp and Penney [10], Jahn and Teller [11], Pryce [12], Stevens [13], Elliot [14] and Judd [15]. During the post war period, the paramagnetic resonance was discovered. This phenomenon gave information on the various aspects of the transition between the Zeeman components of the ground state of the paramagnetic ions with considerable accuracy. The paramagnetic resonance was studied by many workers. Among them Bleaney and his co-workers [34], Abragam and Pryce [16], Stevens [17] and Elliot and Stevens [18] contributed greatly to understanding the behavior of the paramagnetic ions belonging to different transition groups in various crystalline hosts. However, it was seen that paramagnetic resonance results by themselves are not adequate enough in fixing the crystal field but as supplementary data they help immensely in checking and refining the crystal field parameters obtained from optical or magnetic measurements. Later, other high resolution resonance techniques such as NMR, ENDOR, Mössbauer spectroscopy, quadrupole resonance etc. were developed. With development of these techniques, a deeper insight into the nuclear hyperfine behavior, which is strongly influenced by the crystal field, was obtained.
Due to the electrostatic interaction of the rare earth ion with its nearest neighbors, the different J-multiplets of the ground term split resulting in a drastic change in the optical, magnetic, thermal and nuclear hyperfine properties of the ion. The information on the energy level pattern of the different J-multiplets of the RE ion in the crystalline environment are obtained directly from the spectral study (Visible, IR, UV, FTIR) and from the neutron inelastic scattering data. As the magnetic susceptibilities and the electronic heat capacity are aggregate effects of the lowest and the excited CF energy levels, they act as sensitive indices for the crystal field. Hence a comprehensive picture of the free ion energy level splitting due to the crystal field may be obtained from the study of principal magnetic susceptibilities and their anisotropy over a wide range of temperature (preferably down to very low temperatures), and to a lesser extent from the heat capacity measurements since the latter involve only energy level structure while the former involve eigenfunctions as well.

1-2 The subject and aim of this investigation

The major part of the thesis deals with magnetic measurements on the single crystals of rare earth aluminium borates [REAl₃(BO₃)₄], rare earth bromates [RE(BrO₃)₃·9H₂O], and rare earth trifluoromethanesulfonates [RE(CF₃SO₃)₃·9H₂O] which exhibit wide variety of interesting magnetic and other thermo physical properties.
In recent times much attention has been focused on the luminescence properties of rare earth aluminium borate crystals [19]. In most laser hosts the intensity of luminescence decreases with the increase of concentration of RE ions (the so-called concentration quenching). An ineffective concentration quenching is connected with the development of single crystal minilasers [20]. Neodymium aluminium borate has already been established as a laser material [21, 22] and other RE aluminium borates are subject of intensive study for their immense potential in different optical applications. Single crystals of Tb, Eu, Gd, Dy and Sm-aluminium borate have been investigated but Ho and Er-aluminium borate are yet to be explored for these studies.

RE trifluoromethanesulfonates are very similar in structure to the extensively studied RE ethyl sulfates. The magnetic ordering [23], electron paramagnetic resonance [24], and heat capacity of a number of RE trifluoromethanesulfonates were studied by the Friedberg group. The electronic absorption spectra of neodymium trifluoromethanesulfonate were studied by Quagliano et al [25].

The rare earth bromates easily form well-crystallized precipitates and due to this they were earlier used in fractional crystallization processes aiming at the separation of individual rare earths.

The single crystals of rare earth bromates and rare earth trifluoromethanesulfonates were grown in our laboratory. The flux grown single crystals of rare earth aluminium borates were obtained from Clarendon Laboratory, Oxford, under a collaborative program.

Our magnetic measurements include:

A. Measurement of principal magnetic susceptibilities ($\chi_{||}$ or $\chi_{\perp}$, or both) in the temperature range 300 to $\sim 13$ K.

B. Measurement of magnetic anisotropy $\Delta \chi = \chi_{||} - \chi_{\perp}$ in the temperature range 300 to $\sim 80$K.
Our observed results of magnetic measurements are analyzed invoking the crystal field interaction of the rare earth ion with its immediate neighbors. In order to fix the crystal field, in addition to our magnetic data we take into consideration all available experimental results e.g., optical and inelastic neutron scattering data, g-values, very low temperature (\(< 4 \text{ K}\)) magnetic data, thermal variation of electronic and nuclear heat capacities etc.

1-3 SUMMARY OF RESULTS:

A. HOLMIUM ALUMINIUM BORATE \([\text{HoAl}_3(\text{BO}_3)_4]\)

Single crystals of holmium aluminium borate were grown using standard flux growing techniques \cite{26}. The crystals are well-defined prismatic and elongated along the crystallographic c-axis. The principal magnetic susceptibilities, \(\chi_{\parallel}\) and \(\chi_{\perp}\), parallel and perpendicular to the crystallographic symmetry axis c were measured from room temperature down to 14.5 K. As \(\chi_{\parallel}\) is greater than \(\chi_{\perp}\), we were able to measure \(\chi_{\parallel}\) and \(\chi_{\perp}\) individually by the Faraday balance. The magnetic anisotropy \(\Delta\chi (\chi_{\parallel} - \chi_{\perp})\) of this crystal was measured directly down to 80 K as a check on the absolute susceptibility measurements. The variations of \(\chi_{\parallel}\) and \(\chi_{\perp}\) with decreasing temperature are similar in nature, with \(\chi_{\parallel}\) increasing slightly faster than \(\chi_{\perp}\). The effective Bohr magneton number at room
temperature turns out to be 10.52, which is slightly lower than the free ion value. A least squares fit of the observed \( \chi = \frac{\chi_{11} + 2\chi_{\perp}}{3} \) in the range 300 - 14.5 K to the Curie-Weiss law yields the Curie constant 13.53 emu K and the paramagnetic Curie temperature \( \theta = -2.74 \) K. A theoretical analysis of the experimental results invoking the crystal field interaction of the Ho\(^{3+}\) ion with D\(_3\) site symmetry, obtained from structural data, provide a very satisfactory explanation to the observed behavior of the ion over the entire range of temperature of our study [27]; this rules out any significant exchange or dipolar effects down to 14.5 K. The computed crystal field spectra led us to locate the peaks in the electronic heat capacity (C\(_e\)); C\(_e\) has two sharp peaks at 13 and 0.7 K, and one broad peak centered about 77 K. The quadrupole splitting of the nuclear ground state of \(^{165}\)Ho caused by the EFG at the nuclear site due to the crystal field has been computed, which predicts a peak at about 5.5 mK in the hyperfine heat capacity.

**B. ERBIUM ALUMINIUM BORATE [ErAl\(_3\)(BO\(_3\))\(_4\)]**

Single crystals of ErAl\(_3\)(BO\(_3\))\(_4\) were produced by flux growing techniques [26]. The principal magnetic susceptibility perpendicular to the crystallographic symmetry axis c, i.e., \( \chi_{\perp} \), was measured from room temperature down to 14.2 K with the help of a highly sensitive electronic balance. The magnetic anisotropy \( \Delta\chi = \chi_{\parallel} - \chi_{\perp} \) of a single crystal of erbium aluminium borate was measured directly, using a quartz torsion balance, down to liquid nitrogen temperature. As \( \chi_{\perp} \) is greater than \( \chi_{\parallel} \) throughout the temperature range of our study, we were unable to measure \( \chi_{\parallel} \) directly with a freely suspended crystal in the Faraday system; we obtained \( \chi_{\parallel} \) by comparing \( \Delta\chi \) and \( \chi_{\perp} \) data. The natures of variation of \( \chi_{\perp} \) and \( \chi_{\parallel} \) with decrease of temperature are quite different,
whereas $\chi_{||}$ increases gently, almost linearly, down to 80 K, $\chi_{\perp}$ undergoes a very rapid rise from 120 K with decreasing temperature. A least squares fit of the observed $\chi$ to the Curie-Weiss law yields a Curie constant of 12.26 emu K and a paramagnetic Curie temperature $\theta = -4.96$ K. A crystal field conforming to D$_3$ site symmetry accounts very well for the observed thermal variation of the magnetic susceptibilities; this yields $g_{||} = 2.32$ and $g_{\perp} = 8.95$ [28]. Computed electronic heat capacity shows a Schottky anomaly at around 45 K. Calculated quadrupole splitting of the nuclear ground state of $^{167}$Er due to crystal field effects shows a smooth decrease with decreasing temperature. In the present case, the hyperfine heat capacity ($C_N$) is contributed mainly by the magnetic hyperfine splitting; a rounded maximum is observed at about 8 mK in the thermal variation of $C_N$.

C. NEODYMIUM TRIFLUOROMETHANESULFONATE [Nd(CF$_3$SO$_3$)$_3$ · 9H$_2$O]

Neodymium trifluoromethanesulfonate nonahydrate (NdTFMS) crystals were grown in our laboratory. At room temperature, $\chi_{||} > \chi_{\perp}$, as found in the structurally similar Nd-ethyl sulfate. The principal magnetic susceptibilities, $\chi_{||}$ and $\chi_{\perp}$, parallel and perpendicular to the crystallographic symmetry axis c, respectively, were measured from 300 K down to 12.5 K. $\chi_{||}$ is observed to be greater than $\chi_{\perp}$ at all temperatures. Although the magnetic anisotropy at room temperature is small, with lowering of temperature $\chi_{||}$ increases more rapidly than $\chi_{\perp}$ giving rise to a very high anisotropy at low temperatures [29]. A least squares fit of the observed $\chi$ to the Curie-Weiss law was tried; it is seen that a single set of Curie constant and paramagnetic Curie temperature
could not fit the observed $\chi$ over the entire range of temperature of our study; this is definitely
different from our experience with other RE compounds that we have studied but it should not be
construed as very unexpected. The crystal structure of NdTFMS is very similar to that of the
hydrated rare-earth ethylsulfates with the Nd$^{3+}$ ion occupying a site of $C_{3h}$ symmetry. A very good
description of the observed results was obtained using one-electron crystal field theory with the
spectroscopic CF parameters of Quagliano et al. [25]. The g-values obtained from the crystal field
analysis are, $g_{||} = 3.81$ and $g_{\perp} = 2.02$. The computed electronic specific heat at different
temperatures shows a broad Schottky anomaly around 100 K. The nuclear quadrupole splitting and
nuclear heat capacities were also computed for the two isotopes of neodymium which brings out
much commonness with Nd- ethylsulfate.

D. THULIUM BROMATE [ Tm(BrO$_3$)$_3 \cdot$9H$_2$O ]

Single crystals of thulium bromate enneahydrate were grown in our laboratory. The crystals grow
in a needle shaped prismatic form with a purple tinge. Unlike bromates of other non-Kramers ions,
viz. Pr and Ho, $\chi_{\perp} > \chi_{||}$ at room temperature in the present case. This prevented us from
measuring $\chi_{||}$ directly by the Faraday balance where the crystal is suspended freely with a thin
fibre. The magnetic susceptibility $\chi_{\perp}$ and the magnetic anisotropy $\Delta \chi$ ($\chi_{||} - \chi_{\perp}$) were measured in
the range 300 – 14K and 300 – 80K, respectively. $\chi_{||}$ and $\chi_{\perp}$ show widely divergent thermal
variation; the $\chi_{||}$ versus T plot is nearly flat compared to that of $\chi_{\perp}$. $\chi_{\perp}$ displays more or less a
Curie type variation over nearly the entire range of temperature, viz. 300 – 20 K [30]. A least-
squares fit of the observed $\chi$ values to the Curie-Weiss law down to 80 K yields Curie constant 7.156 cm$^3$ K/mole and the paramagnetic Curie temperature – 17.6 K. A crystal field conforming to $D_{3h}$ site symmetry accounts very well for our observed data and that of Simizu et al [31] below 4 K. Very brief comment on the behavior of $\chi_{\parallel}$ below 4K by Simizu et al. is borne out qualitatively by our theory, but their absolute value seems abnormally high, which makes it suspect. The computed crystal field spectra led us to locate the peaks in the electronic heat capacity and to find the quadrupole splitting of the 8.42 keV nuclear excited state of $^{169}$Tm; high magnetic field enhancement at the nucleus suggests complex Mössbauer spectra in the presence of a magnetic field perpendicular to the symmetry axis.

E. NEODYMIUM BROMATE [Nd(BrO$_3$)$_3$.9H$_2$O ]

When freely suspended, the hexagonal crystal sets with its symmetry axis, c, along the applied magnetic field, indicating $\chi_{\parallel} > \chi_{\perp}$ at room temperature. The principal magnetic susceptibility perpendicular to the symmetry axis c of the hexagonal crystal has been measured in the temperature range 300 to 13 K. The magnetic anisotropy $\Delta\chi ( = \chi_{\parallel} - \chi_{\perp})$ was measured from room temperature down to 90 K. But $\Delta\chi$, which is relatively small, decreases with temperature and suffers a reversal at $\sim$ 155 K. The principal magnetic susceptibility parallel to the symmetry axis ($\chi_{\parallel}$) was determined using $\chi_{\perp}$ and $\Delta\chi$ values. The effective magnetic moment $P_{eff}$ calculated at room temperature turns out to be 3.61, which is almost same as the free ion value. A theoretical analysis of the experimental results invoking crystal field conforming to $D_{3h}$ site symmetry of Nd$^{3+}$ in this crystal matrix provide an excellent explanation to the observed variation of $\chi_{\perp}$ and $\chi_{\parallel}$.
over the entire temperature range of our study including the crossover of $\Delta \chi$, the overall crystalline Stark splitting of the ground J manifold observed by Satten [32] and the reported $g$-values [33]. The electronic heat capacity is computed; it shows a Schottky anomaly at around 100 K. The nuclear quadrupole splitting, and the nuclear heat capacity were also worked out.
REFERENCES


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