STRUCTURAL AND HYPERFINE INTERACTION STUDIES IN TRANSITION METAL BORATES AND MALEATES BY MÖSSBAUER AND E.S.R. SPECTROSCOPY

A THESIS
SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

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Dedicated to:

My Parents
and
Teachers

CONTENTS

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in School of Chemistry, University of Hyderabad, Hyderabad, India, under the supervision of Dr. R. Jagannathan.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

M. VITHAL

Hyderabad
April 1985

CERTIFICATE

Certified that the work 'STRUCTURAL AND HYPERFINE INTERACTION STUDIES IN TRANSITION METAL BORATES AND MALEATES BY MÖSSBAUER AND ESR SPECTROSCOPY' has been carried out by Mr. M. Vithal under my supervision and the same has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

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PREFACE

The thesis presents structural and hyperfine inter-
action studies in iron borates or more appropriately borofer-
rites and transition metal maleates by Mössbauer Spectroscopy
and electron spin resonance (ESR) measurements. The interest
in the boroferrites stems from the fact that boron in these
materials can exist as planar BO_3^{3-} or BO_4^{5-} tetrahedra giving
rise to unusual magnetic interactions leading to ferro-
magnetism, antiferromagnetism, spin-reorientation etc.
Further the boroferrites exhibit unusual combination of
physical properties of fundamental interest such as, for
example, ferromagnetism-ferroelectricity in the boracites,
magneto-optical properties in iron borate $FeBO_3$ etc., which
make these materials worthy of detailed investigations. It
is only natural to choose Mössbauer Spectroscopy as the
technique, for the method provides a powerful probe for
investigations pertaining to iron-bearing magnetic materials.
The first part of the thesis pertains to the Mössbauer
studies of boroferrites and presented in four chapters which
include in the first chapter (i) a very brief introduction
to the effect and the hyperfine interactions followed by a
review on the boroferrites pointing out the salient features
of their structural aspects and physical properties and in

the second chapter (ii) details of experimental procedures employed and presentation of the mathematical steps involved in (a) the analysis of temperature dependence of quadrupole splitting for the $3d^6$ case (b) the analysis of hyperfine fields in substituted systems by static method due to Coey and model independent approach due to Window and line shape analysis to account for relaxation effects.

Chapter 3 deals with the Mössbauer investigations of $FeBO_3$ and the substituted borates $Fe_{0.9}M_{0.1}BO_3$ (M=Al, Ga and Cr). Ferric borate, $FeBO_3$, is of considerable interest as it is the only candidate in borates to be a transparent magnetic material with a lot of potential magneto-optic applications. The Mössbauer spectra of $FeBO_3$ as well as its solid solutions close to T_c have been looked into with a view to understand the effect of substitution on relaxation process and/or superparamagnetism. The Curie temperatures of $FeBO_3$, $Fe_{0.9}Ga_{0.1}BO_3$, $Fe_{0.9}Al_{0.1}BO_3$ and $Fe_{0.9}Cr_{0.1}BO_3$ have been determined to be 352, 319, 317 and 335 K respectively. The reduced hyperfine field vs reduced temperature follows the Brillouin behaviour for S = 5/2 for all the cases. It is shown that Coey's model is inadequate in simulating the Mössbauer spectra of solid solutions close to T_c. In the parent material viz., $FeBO_3$,

relaxation effects are found to be important only very close to T_c i.e. 1° below T_c. The model due to Blume and Tjon fairly reproduces the line profiles near T_c in this case. On the other hand, analyses of the Mössbauer spectra close to T_c of $Fe_{0.9}Al_{0.1}BO_3$ and $Fe_{0.9}Ga_{0.1}BO_3$ have been found to require the introduction of the additional order parameter η, proposed by van der Woude and Dekker. Estimates of activation energies for the spin-flip process have been found to be 9.93×10^{-13} and 5.87×10^{-13} erg/degree for $Fe_{0.9}Al_{0.1}BO_3$ and $Fe_{0.9}Ga_{0.1}BO_3$ respectively. In the solid solutions the relaxation effects dominate even 15° below T_c. These results have been interpreted to arise from dominant superparamagnetic relaxation effects due to the presence of clusters produced by substitution of magnetic by non-magnetic ions. Evidence for the cluster formation is also obtained by comparing the distribution in the hyperfine fields by the model independent approach due to Window in analysing the spectra. Simple relaxation models have been found to be inadequate in fully reproducing the experimental spectra close to T_c for $Fe_{0.9}Cr_{0.1}BO_3$ and the possible reasons are presented in the light of existing literature.

Chapter 4 gives an account of Mössbauer investigations on Fe_3BO_6 and 4% Ga^{3+} substituted Fe_3BO_6 carried out keeping

particularly in mind the spin-reorientation phenomena exhibited by the parent material at 418 K. Mössbauer measurements of hyperfine parameters close to spin-reorientation temperature (T_{SR}) have been shown to display no hysteresis effects in spite of the reorientation following a first order phase transformation. However, as is characteristic of first order change, significant change in structure is indicated by the changes in the quadrupole interactions. 4% substitution of Fe^{3+} by Ga^{3+} brings down T_{SR} from 418 to 403 K. The temperature dependence of hyperfine field for the 8d site follows closely the Brillouin function for $S = 5/2$ both for the parent as well as the substituted compound. The deviation of the 4c site from the Brillouin curve has been explained by including the biquadratic exchange interaction giving rise to $j/J = 0.015$. It is found that Ga^{3+} has no site preference. Unlike in the case of experimental spectra close to T_c it is found that the static model due to Coey can be employed for simulating the experimental spectra at temperatures far away from T_c. An exchange constant $J \sim 10$ cm^{-1} has been obtained on the basis of this model.

The second part of the thesis presents structural and hyperfine interaction studies in acid complexes formed

between maleic acid and transition metal ions. The interest
in these systems stems from the observations that (i)
organic acids give rise to a variety of structures with
transition metal ions enabling a comparative study of
complexes of same carboxylic acid with different metal ions
and of different carboxylic acids with the same metal ion,
(ii) the work has scope for a comparative study of transi-
tion metal ions with the rare-earths, (iii) in many instances
single crystals can be prepared leading to studies with
unambiguous conclusions, (iv) furthermore the decomposition
of these complexes into metallic oxides provide interest
both from the preparatory point of view of the oxides/
ferrites and also scope for solid state studies regarding
the bearing of structures on the differences in their decom-
position behaviour.

This part of the thesis is presented in five chapters.
The first chapter of this part (Chapter 5) provides a
comprehensive review of the literature on the carboxylic
acid complexes   focussing attention on these features of
interest to facilitate discussion of the results presented.
This is followed by a chapter on the methodology relevant
to the analysis of ESR spectra of single crystal studies
employing Cu^{2+} and Mn^{2+} as ESR probes giving an account of

the desired expressions for obtaining chemical information
and analysing forbidden ESR transitions, which are of
particular interest in Mn^{2+} systems.

The next chapter deals with the preparation and
temperature dependent Mössbauer measurements of iron(II)
maleate tetrahydrate. From the analysis of the temperature
dependence of quadrupole splitting and optical spectral
data, the crystal field parameters <u>viz</u>., the 10 Dq, tetra-
gonal field, rhombic field and the splitting of the e_g
levels have been derived. Results of powder X-ray diffracto-
grams establishing the isomorphism of ferrous maleate tetra-
hydrate with manganese maleate tetrahydrate have been
presented. The results of differential thermal analysis and
thermogravimetric analysis on ferrous maleate tetrahydrate
and the independent decomposition studies are submitted.

Chapter 8 presents the results of a single crystal
ESR studies of Cu^{2+} doped in zinc maleate tetrahydrate.
Copper maleate tetrahydrate and zinc maleate tetrahydrate
are not isomorphous. From the single crystal ESR measure-
ments it is concluded that Cu^{2+} in zinc maleate tetra-
hydrate occupies a substitutional position with a micro-
symmetry dictated by the parent lattice. The ground state
of Cu^{2+} in zinc maleate tetrahydrate is derived to be
$0.724|3z^2-r^2\rangle + 0.173|x^2-y^2\rangle$.

xii

In the last chapter the single crystal ESR results of Mn^{2+} doped in zinc maleate tetrahydrate are presented. The low symmetry of the Mn^{2+} ion is found to give rise to a number of forbidden transitions in addition to the allowed five sextets of 30 transitions. Further the orientation along the principal Z-axis also is achieved when a neat and simple 30 line spectrum eliminating the appearance of any forbidden transitions is obtained which is used for detailed analysis of the spectra. The line positions were analysed to obtain the hyperfine parameters viz., A, g, D, E and 'a' which are the hyperfine splitting constant, the g-factor, axial component of zero field splitting, rhombic component of zero field splitting and cubic field term respectively. The sign of D is found to be positive indicating that Mn^{2+} like Cu^{2+} goes into substitutional site and occupies axially compressed octahedron. An analysis of the forbidden transitions also is presented which leads to $Q' = 1.69$ and $Q'' = 0.304$ for the values of the axial and rhombic components respectively of the quadrupole coupling constant.

PART - A

1.1 The Mössbauer Effect

Rudolph L. Mössbauer discovered in 1957 the phenomenon of recoilfree nuclear resonance fluorescence [1]. This observation, referred to as the Mössbauer effect, has gained fundamental importance and shown unique potentiality ever since Kistner and Sunyar established the role of hyperfine interactions underlying the effect [2]. The hyperfine interactions appear as a shift in the centre of gravity of the spectrum, splitting of the lines and line broadening effects. The interactions leading to shifting and splitting of the lines have resulted in the application of the technique particularly to problems of chemical and structural interest. The applications have also been extended from static to dynamic effects, rendered possible due to sharply defined energy of the gamma radiation leading to changes in the profiles due to time dependent

effects. In this chapter a brief introduction to the hyperfine interactions in Mössbauer spectroscopy is given. Detailed discussions of fundamental aspects and applications are available in literature [3-7].

1.2. Basic features of Mössbauer spectroscopy

1.2.1. The Technique

In a classical model, a γ-ray emitter in the excited state may be treated as a damped oscillator emitting electromagnetic radiation. The energy distribution of the emitted radiation is given by

$$I(\omega) \; \alpha \; | \int_0^\infty E(t) \; e^{-i\omega t} \; dt \; |^2$$

$$I(\omega) \; \alpha \; \frac{1}{(E-E\gamma)^2 + (\Gamma_{nat}/2)^2} \qquad \ldots (1.1)$$

where E(t) is the electric field of the γ-radiation, $E = \hbar\omega$, Eγ is the nuclear transition energy, h is the Planck's constant and the natural width $\Gamma_{nat} = \frac{\hbar}{\Gamma_n}$ where Γ_n is the mean lifetime of the excited nucleus. Eq.(1.1) represents a lorentzian line centered at Eγ with full-width at half-maximum (FWHM) equal to Γ_{nat}.

A distinct feature in Mössbauer spectroscopy is the use of Doppler effect; the source is given a velocity V with respect to the absorber and the energy of the emitted radiation Eγ as seen by the absorber is given by

$$E(V) = E\gamma(1 + \frac{V}{C}) \qquad \ldots (1.2)$$

where V and C are the velocities of source and light respectively. Thus the intensity of the unabsorbed γ-radiation vs the Doppler velocity provides the spectral profile in a transmission experiment. Energy differences are expressed in terms of the Doppler velocity. The properties of interest for the case of ^{57}Fe are given in Table 1.1.

1.2.2. Hyperfine Interactions

i) Isomer Shift

The electrostatic interaction between the Mössbauer nucleus and the surrounding electric charges give rise to isomer shift and quadrupole splitting effects of the nuclear levels. The electronic charge density at the nucleus $-e|\psi(0)|^2$ gives rise to energy shifts of the nuclear levels which depend on the nuclear radius. As the size of the nucleus changes

Table 1.1 Properties of the ^{57}Fe nucleus [12].

natural isotopic abundance	2.14 %
Gamma-ray energy	14.413 keV
natural line width (Γ_o)	0.194 mm/Sec
internal conversion coefficient (α)	8.2
maximum resonance cross section (σ_o)	3.45×10^{-19} cm^2
nuclear quadrupole moment (Q^e)	0.21×10^{-24} m^2
magnetic moment (μ_g)	+0.0903 nm
(μ_e)	-0.1547 nm.
half-life time of parent ^{57}Co nucleus ($t_{1/2}$)	270 days.
energy conversion factor	1 mm/sec = 7.7019×10^{-27} J
	= 4.8077×10^{-8} eV.

during decay, the effect results in a shift in the nuclear
transition energy given by

$$\delta E = \frac{2\pi}{3} Ze^2 \, |\psi(0)|^2 \, (\langle r_e^2 \rangle - \langle r_g^2 \rangle) \qquad \ldots (1.3)$$

where Z is the atomic number of the Mössbauer atom and $\langle r_e \rangle$
and $\langle r_g \rangle$ are the mean square radii of the nucleus in the
excited and ground states respectively, in a point charge model
[8]. If the Mössbauer atoms in the source and absorber are
different, eq. 1.3. may be rewritten as

$$\delta = \frac{2\pi}{3} Ze^2 (|\psi_a'(0)|^2 - |\psi_s(0)|^2) \, (\langle r_e^2 \rangle - \langle r_g^2 \rangle) \qquad \ldots (1.4)$$

where the subscripts a and s represent absorber and source
respectively. δ, the isomer shift is proportional to the
difference between the electronic charge densities at the
source and absorber nuclei. Isomer shift has not been completely
characterised although it is known to be influenced by (a)
the effects due to overlaps of the orbitals in bonding [9]
(b) covalency effects due to partial transfer of electrons
from the ligand to the Mössbuer atom or vice versa (c) poten-
tial distortion and (d) relativistic effects etc. [10].

ii) Quadrupole interaction

Any nucleus with a quantum number $I > 1/2$ has a non-spherical charge distribution, which when expanded in a series of multipoles contains a quadrupole term. The electrostatic interaction energy E_Q, between the quadrupole moment and the electric field gradient tensor, may be written as [5]

$$E_Q = 1/6 \sum_i \sum_j Q_{ij} V_{ij} \qquad \ldots (1.5)$$

where Q_{ij} and V_{ij} are the components of the Quadrupole moment tensor and e.f.g tensor respectively given by

$$Q_{ij} = \int^{V_N} (3x_i x_j - \delta_{ij} r^2) \, \rho(r) \, \partial \tau$$

$$\text{and} \quad V_{ij} = \frac{\partial^2 V}{\partial x_i \, \partial x_j}.$$

Here V_N is the volume of the nucleus and $\rho(r)$ is its charge density and a value of $1/6$ gets associated in the series expansion. The energy levels of E_Q can be calculated as the expectation values of the operator H_Q, that corresponds with E_Q, working on the wave function of the whole system. In the principal axes system the interaction energy can be written as

$$E_Q = 1/6 \ \sum_i V_{ii} \ Q_{ii} \qquad \qquad \cdots (1.6)$$

The corresponding Hamiltonian assumes the form,

$$H_Q = \frac{eQV_{zz}}{4I(2I-1)} [3I_z^2 - I(I+1) + \frac{\eta}{2} (I_+^2 + I_-^2)] \qquad \cdots (1.7)$$

where Q corresponds to Q_{zz}, $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$ and I_+ and I_- are the shift operators. For the ^{57}Fe case the splitting due to the quadrupole interaction reduces to

$$Q.S = \frac{1}{2}eV_{zz}Q\sqrt{1 + \frac{\eta^2}{3}} \qquad \qquad \cdots (1.8)$$

where V_{zz} is the expectation value of V_{zz}. The details of evaluation of V_{zz} for the $3d^6(Fe^{2+})$ configuration, relevant to our own studies on iron maleate, are given in the next chapter.

The experimental evaluation of quadrupole splitting in the absence of magnetic field is straight forward. The evaluation in the case when a magnetic field is present and the influence of quadrupole interaction appears through shifts in the line positions in the hyperfine split spectra are briefly discussed in the next chapter.

iii) Magnetic hyperfine interactions

The Zeeman interaction of the nuclear magnetic dipole moment with a magnetic field H_n in the Z-direction at the nucleus completely lifts the degeneracy of the nuclear states. The shifts in the energies of the nuclear substates are given by

$$E_m = - g_n \mu_N H_n m \qquad \ldots (1.9)$$

where g_n is the gyromagnetic ratio, μ_N is the nuclear magneton and m is an eigen-value of the nuclear spin operator I_z. The splitting of the levels results, for instance in ^{57}Fe, six allowed transitions as the excited state with $I_e = 3/2$ and ground state with $I_g = 1/2$ split into 4 and 2 non-degenerate levels respectively. The relaxing of selection rules due to mixing of the levels in the presence of combined magnetic dipole and electric quadrupole interactions are discussed in literature [11]. In such a case, the Hamiltonian is given by

$$H = H_o + H_M + H_Q \qquad \ldots (1.10)$$

where H_o represents the energy of the nuclear state in the absence of the last two terms. H_M and H_Q represent the magnetic dipolar and electric quadrupolar terms respectively. When both nuclear quadrupole and Zeeman interactions are present,

the Hamiltonian describing the hyperfine interaction is given
by

$$H = -g_n \mu_n \vec{H}_n \cdot \hat{\vec{I}} + \frac{eQ_n V_{zz}}{4I(2I-1)} [3\hat{I}_z^2 - \hat{I}^2 + \eta(I_+^2 + I_-^2)/2]$$

$$\dots (1.11)$$

1.2.3. Relaxation Effects in Mössbauer Spectroscopy

Figure 1.1 gives the appropriate frequency ranges of
the relaxation rates for various spin fluctuation processes
and the techniques used for their study. The effect of electron
spin on Mössbauer spectra is implied in the magnetic inter-
action H_M in eq. 1.10. In the spin-Hamiltonian formalism H_M
may be written as

$$H_M = \vec{I} \cdot \vec{\vec{A}} \cdot \vec{S}$$

where A is the hyperfine coupling tensor and S, the effective
electron spin. The effective electron spin of electrons in an
electronic state can be replaced by the expectation value in
the state <S>. When transition between different electronic
states occur, the orientation of the electron spin changes in
time and the hyperfine interaction becomes time dependent.
The simplest case is to visualise the relaxation process occur-
ing between two levels with opposed electron spin quantum
numbers, inducing a reorientation of the electron spin and the
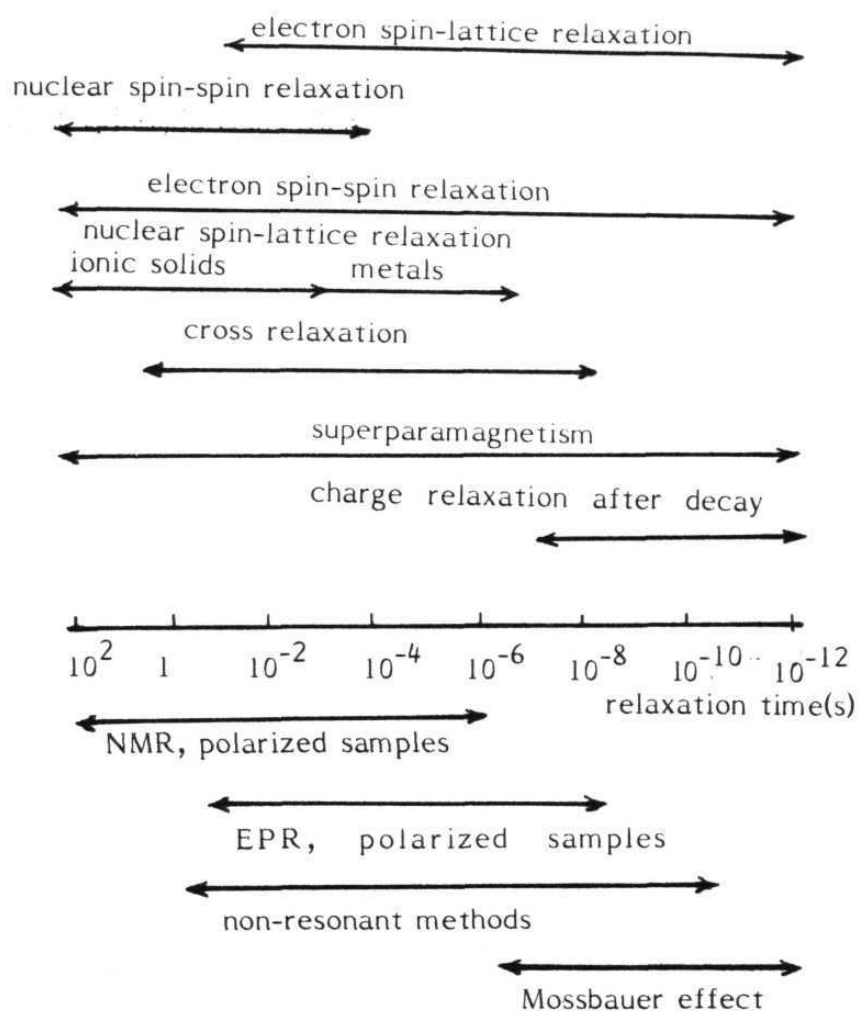
Fig.1.1 Typical ranges of relaxation times of various relaxation processes and the appropriate experimental methods.

hyperfine field. This is called the spin flip process. The shape of the Mössbauer spectra in the presence of relaxation is determined by the frequency of the spin flips, ω_{SF}, the Larmor precession frequency, ω_L, and the nuclear life-time of the excited state, Γ_N. Simple or complex spectra appear depending upon the relative values of ω_{SF}, ω_L and $1/\Gamma_N$. Among the various relaxation processes electron spin relaxation and superparamagnetic fluctuation influence most the Mössbauer spectral line shape. The two common forms of electron spin relaxation are the spin-lattice and spin-spin relaxation. Information about the relaxation process is generally obtained by studying relaxation times as a function of temperature, magnetic field or concentration. A large number of theoretical papers dealing with the influence of time dependent hyperfine interactions on the Mössbauer line shape may be found in literature [13]. The most general theories are based on stochastic or perturbation models. On the basis of a stochastic model Blume arrives at general line-shape expressions employing a formalism in which super operators (Lioville operators) are used. In a closely related treatment Dekker and van der Woude and Dekker have developed line shape expressions who have also taken into account the possible difference in the probabilities of finding the electron between two given states in magnetic materials. We have used the line shape

expressions developed by these authors to analyse the spectra of substituted borates. A brief outline of their models and final line shape expressions obtained are presented in the next chapter.

1.3. A review of work done on boroferrites

Our own Mössbauer studies pertain to hyperfine interactions in some of the boroferrites. It would be appropriate at this stage, a brief survey of the boroferrites, bringing out the salient features of their structural aspects and physical properties pointing out why we embarked on a study of these materials.

Preparation, characterization and detailed investigations of structure and physical properties of the anhydrous transition metal borates are scattered in literature. But the available studies show very many interesting and unusual properties worthy of detailed investigations in these materials. One of the attractive features in the borates is the possibility to study materials exhibiting coexistance of magneto-optic-electric properties. The simplest iron borate for example $FeBO_3$ is a magneto-optic material and the naturally occuring

mineral boracite shows the unusual combination of ferromagne-
tism and ferroelectricity [14,15]. That boron can exist as
planar BO_3^{3-} or BO_4^{5-} tetrahedra provides scope for exhibition of
strongly anisotropic magnetic interactions by the so called
boroferrites. One of the most fascinating fields of current
interest happens to be the study of amorphous materials.
Borates present a situation where attempts can be made to
prepare glassy and crystalline materials with closely related
compositions rendering interesting comparisons of physical
properties in related ordered and amorphous materials. An
extension of the studies from the transition metal to the rare
earths provide further scope as many of them show lasing
properties. With these points of view in mind a beginning is
made on the study of simple and substituted boroferrites, as
these materials are suitable for detailed investigations by
Mössbauer spectroscopy. We scan below the literature
partaining to boroferrites and related materials bringing out
features of interest.

Most of the anhydrous transition metal borates may be
comprehended to occur as $x.MO. y.M_2'O_3 .z.B_2O_3$. Interestingly
the ratio of the metal oxides to the B_2O_3 exhibit a wide range,
as illustrated by the examples given below. An extensive
study of the infrared spectra of the crystalline inorganic

borates was first reported by Weir and Schroeder [16]. Their studies show that the coordination of boron deciding whether it exists as planar BO_3^{3-} or tetrahedral BO_4^{5-} can be reliably fixed from the infrared spectra. The crystal structure and related works on the anhydrous transition metal borates of interest are discussed below.
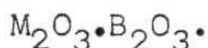
$M_2O_3 \cdot B_2O_3$.

One of the early candidates to be prepared in this series is $Fe_2O_3 \cdot B_2O_3$ or more simply $FeBO_3$. Bernal synthesised this monoborate and showed it to have the calcite structure [17]. Kurtzig et al established this material to be a green, room temperature ferromagnet [14]. Muller established a simpler synthetic technique for preparing this monoborate and the isomorphous $CrBO_3$ and $InBO_3$ and their solid solutions [18]. He also reported detailed susceptibility studies of these borates. An early account of Mössbauer studies on the pure iron borate was reported by Eibschutz and Lines [19].

It is interesting to note that in this system partial substitution of Fe_2O_3 by 0.25 La_2O_3 and 0.5 La_2O_3 (La=Y,Gd,Sm, Dy) leads to totally different crystal structures from the parent compound. The former gives rise to huntite and the latter to the dolamite structure [20,21].
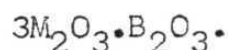
$3M_2O_3 \cdot B_2O_3$.

$3Fe_2O_3 \cdot B_2O_3$ happens to be the only known member of this composition. White et al determined its crystal structure [22]. Unlike in $FeBO_3$, boron has a tetrahedral configuration in this case and the material is magnetic. The phase transformation in the magnetic state has been studied by susceptibility and Mössbauer techniques [23-25]. These reports however do not agree on the order of the phase transformation.

$MO \cdot B_2O_3$.
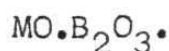
Monoborates of this class, referred to as the metaborates, are well characterised where M = Zn^{2+}, Cu^{2+}. In both cases boron has tetrahedral symmetry. However Zn^{2+} occurs in one type of site with tetrahedral symmetry whereas Cu^{2+} occurs in two types of sites, one of which is octahedral and the other square planar [26,27].

$2MO \cdot B_2O_3$.
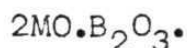
Monoborates of this class, referred to as the pyroborates commonly occur with divalent ions such as Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+}. Boron in these isomorphous borates have

planar geometry. The metal ions are situated in more than one type of sites with octahedral symmetry [28].

$3MO.B_2O_3$.
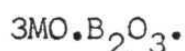
Monoborates of this type referred to as the orthoborates also occur with divalent ions of Co^{2+}, Mg^{2+} and Mn^{2+}. These are highly coloured transparent materials but their optical properties in the visible have not been characterised. These orthoborates are isomorphous unlike their zinc analogue. In these cases M^{2+} occupies two inequivalent octahedral sites in orthorhombic unit cell [29-31]. In the case of zinc compound, Zn^{2+} occupies three inequivalent sites with tetrahedral symmetry in a monoclinic unit cell [32]. Mitchell has characterised the infrared spectra of some of these orthoborates in detail [33].

$MO.2B_2O_3$.
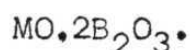
Diborates of this class contain $[B_4O_7]^{2-}$ anions with the boron atoms occurring both in tetrahedral as well as in planar geometry, and differ in this from all other systems discussed in literature. The metal ions in these cases occupy distorted tetrahedral symmetry [34].

$M_2O_3.4M'O.B_2O_3$ and $M_2O_3.2M'O.B_2O_3$.
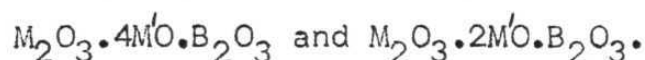
Borates of these general formulae occur naturally with $M = Mn^{3+}$, Fe^{3+} and $M' = Mg^{2+}$, Fe^{2+}, Mn^{2+}. The crystal structures of these minerals viz., ludwigite and pinakiolite were first characterised in detail by Takeuchi et al and Bertaut [35,36]. Compounds with analogous structures containing other transition metal ions, $M' = Co^{2+}$, Cu^{2+} and Ni^{2+} have also been synthesised [36]. Relatively recently the magnetic properties of ludwigite have been looked into by Apostolov et al and Weidenmann and Burlet [37,38]. It is shown that partial substitution of Mg^{2+} by transition metal ions leads to the observation of more than one antiferromagnetic transition, the one taking place at the higher temperature arising due to one dimensional M-M interaction and the other at the lower temperature resulting due to three dimensional M-M interaction [37]. The latter authors have suggested spin-glass behaviour in these systems on the basis of susceptibility, Mössbauer, neutron diffraction and specific heat data. Although the absence of three dimensional ordering has been claimed by Apostolov et al on the basis of Mössbauer data, no details are presented [37]. Abe et al studied more extensively by susceptibility and Mössbauer spectral measurements the borates of the formula $Fe_2O_3.B_2O_3.4NiO$ and $Fe_2O_3.B_2O_3.2Nio$ [39].

These authors observed that the bulk susceptibility measure-
ments in these cases gave significantly lower T_N values than
the values derived from Mössbauer measurements and attributed
to relaxation phenomena in these low dimensional magnetic
materials [39]. Weidenmann and Burlet suggested that inversion
of Fe^{3+} and Mg^{2+} in these structures lead to spin-glass
behaviour. Abe et al found no evidence for any significant
inversion from their Mössbauer study [39].

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CHAPTER 2

EXPERIMENTAL METHODS AND METHODOLOGY

Abstract

The experimental details pertaining to the Mössbauer
spectrometer used and variable temperature measurements made
from 77 to 900 K and powder X-ray diffractogram measurements
are presented. Some of the details of (a) calculation of
temperature dependence of quadrupole splitting for $3d^6$ case
in different crystal fields (b) the line shape expressions
based on the relaxation models due to (i) Blume and Tjon and
(ii) van der Woude and Dekker, (c) the static model of
Coey and (d) the model independent approach due to Window
in the analysis of hyperfine field distribution are pre-
sented.

2.1. Experimental Techniques

2.1.1. Mössabuer measurements

In recording the Mössbauer spectra the source is moved with respect to the absorber or _vice versa_ to achieve the Doppler shift and the intensity transmitted through the absorber is measured as a function of velocity. The spectra reported here were measured using a constant acceleration spectrometer (Elscint), a block diagram of which is given in Figure 2.1. The spectrometer consists of (i) the drive assembly consisting of two coupled loudspeakers (model MVT-3) one having the driving coil and the other having the sensing coil giving rise to a feed-back signal, wound around the same rod freely suspended with two phosphor-bronze leafsprings. The velocity of the rod is proportional to a reference voltage delivered by the driving unit (MD-3). A function generator (MFG-3) produces the desired wave-forms and the necessary timing signals, (ii) a multi-channel analyser (Promeda) which receives the timing signals for opening the 512 channels of the MCA periodically and the desired γ-ray pulses. In this system the motion of the source is independent of the MCA and during data accumulation synchronisation between velocity and channel number is established over every period of the drive signal, (iii) the detection system consisting of a 'Cento' xenon proportional

VELOCITY TRANSDUCER

drive magnet pick up magnet source absorber

γ-ray detection

crostat

feedback amplifier

reference signal

6.1 ms 512 ms 512 ms
256x 0.4ms 256x 0.4ms

channel advance

start

SYNCHRONIZER

channel advance start

input
γ-count
channel 1-512

MULTI-CHANNEL-ANALYSER
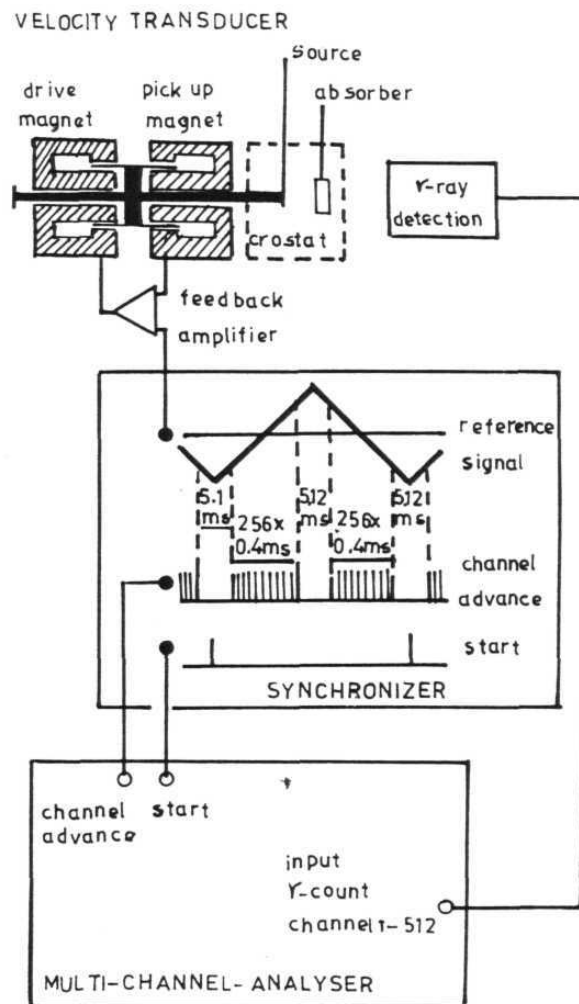
Fig.2.1   Schematic diagram of the Mössbauer spectrometer.

counter. The amplitude of the pulses produced in the counter
is proportional to the energy of the photons. The pulses are
amplified and fed into a single channel analyser (SCA-N-3)
which selects the 14.4 keV peak for the ^{57}Co isotope and
transforms into standard pulses which are received and counted
by the MCA (Promeda). The recording of the spectra could be
carried out without interference due to external disturbances.
A hard copy of the data was obtained as a print out using a
Teletype typewriter.

A source of ^{57}Co in rhodium matrix with a strength of
25 mCi is employed. The absorbers were prepared by sandwiching
thoroughly ground powder material into a perspecx absorber
holder of 2 cm dia. For high temperature measurements, copper
ring holders with thin aluminium windows were employed. In
all the absorbers the iron content was kept at ∿10 mg/cm^2.

The spectrometer was standardised recording spectra of
samples of α-Fe$_2$O$_3$, iron-foil, K$_4$Fe(CN)$_6$ and sodium nitro-
prusside dihydrate and comparing the peak positions with values
reported in literature [1,2]. A standard spectrum of the iron
foil is recorded for each measurement. The per-channel
velocity is obtained by taking the splittings of the outer
most lines in terms of mm/sec and equating with peak positions

obtained in terms of channel numbers for the measured standard spectra using a least square fit programme [3]. The errors quoted in line positions correspond to the standard deviation obtained by an error analysis, details of which are discussed in literature [4]. Some of the standard spectra are shown in Figure 2.2.

2.1.2. Cryostat

A simple cryostat constructed in our laboratory for Mössbauer measurements at liquid-nitrogen temperature (-196°C) is shown in Figure 2.3. The copper vessel of 10 cm diameter and 21 cm height is sorrounded by a thermocole and inserted into a wooden box. A copper block of 5 x 4 x 2 cm is welded to the bottom of the copper vessel through a cold finger (1 cm dia and 3.5 cm long). In this block a provision is made for the absorber which could be firmly fixed by a screwable cylindrical ring. The thermocouple junction is kept in a thin hole inside the copper block close to the absorber. The thermocouple reading was measured with a digital multimeter (Keithley 174). The temperature remained stable to ±0.5 °C during the measurements. The liquid nitrogen consumption was about 0.5 litre per hour.
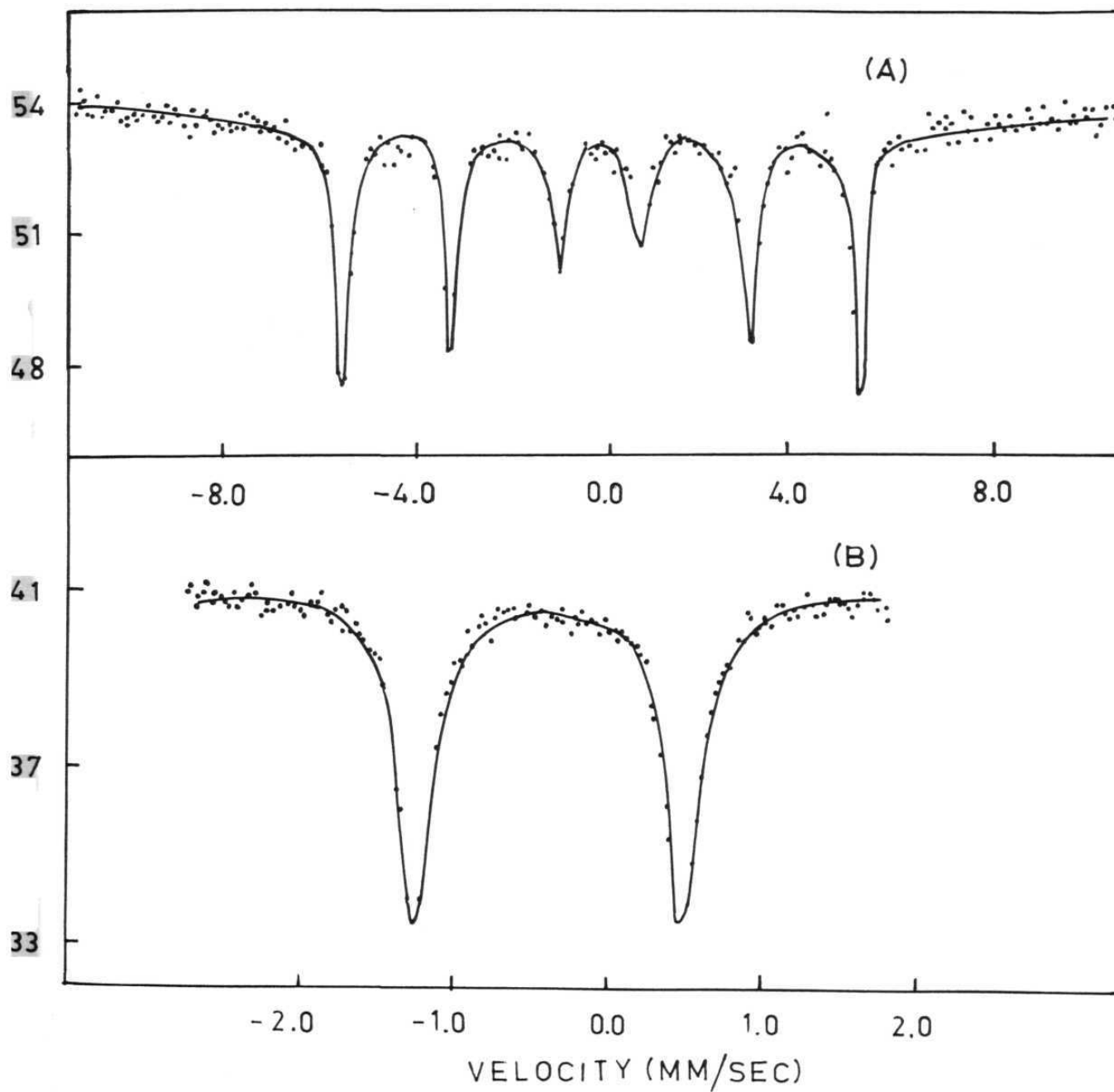
Fig.2.2 Mössbauer spectra of (a) Iron foil and (b) sodium nitro prusside dihydrate.

THERMOCOUPLE

WOODEN BOX

STYROFOAM INSULATION

COPPER LINER

LIQUID NITROGEN

DRIVE

SOURCE

SENSE

DETECTOR
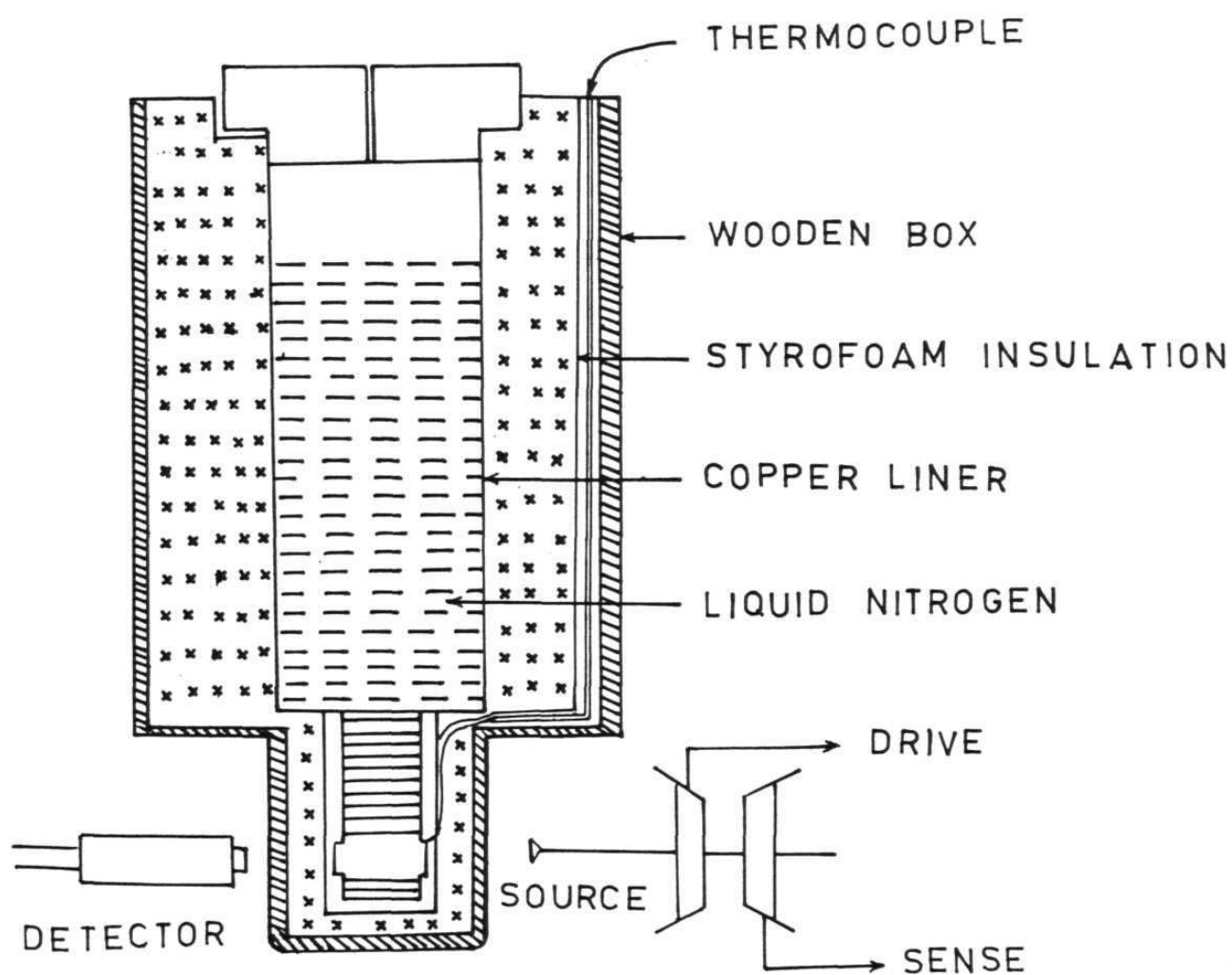
Fig.2.3 A cryostat assembly for low temperature Mössbauer measurements

2.1.3. Furnace

For measurements at temperatures above 300 K a stain-
less Ricor vacuum furnace (MF-2A) is used. It has two thin
windows for allowing the 14.4 keV γ-rays without attenuation.
Thermal shielding is obtained with thin aluminised keptone.
The sample was heated in vacuum with a low resistance heating
element. A chromel-alumel thermocouple is used for monitering
the temperature. The temperature is controlled manually ($\pm 0.5^\circ$)
by adjusting the input voltage to the heating element.

2.1.4. X-ray measurements.

The powder X-ray diffraction patterns were obtained
using the Philips X-ray diffraction unit consisting of PW 1010
generator, PW 1055/25 wide angle goniometer and PW 1051
diffractometer. A Geiger-Müller counter and nickel-filtered
Cu-Kα radiation were employed.

2.1.5. Optical spectra

The photoacoustic spectra (PAS) were recorded on a
Princeton Applied Research model 6001 instrument. The spectra
are corrected for black absorption and normalized using carbon

black as reference. The normalization corrects the observed spectrum for the power variation in the source over the spectral region of interest.

Optical spectra for solutions were recorded in a Cary-17 model spectrometer employing a quartz cell of one centimeter path length.

2.2. Methodology used for the analysis of spectra.

2.2.1. Temperature dependence of quadrupole splitting

A computer programme is written on the basis of the formalism discussed in literature to obtain the crystal field terms from a measurement of quadrupole splitting as a function of temperature. This is required for the purpose of analysing the results of our measurements on ferrous maleate tetrahydrate presented in chapter 7. A brief description of the formalism and the steps involved in writing the programme are given below.

The energy level scheme for high spin $Fe^{2+}(3d^6)$ case is given in Figure 2.4. The expression given for the quadrupole splitting in eq. 1.8 may be rewritten as

$$Q.S. = \frac{1}{2} e^2 Q (1-R_{3d}) \, V_{zz}(T) \sqrt{1 + \frac{\eta^2(T)}{3}} \qquad \ldots (2.1)$$
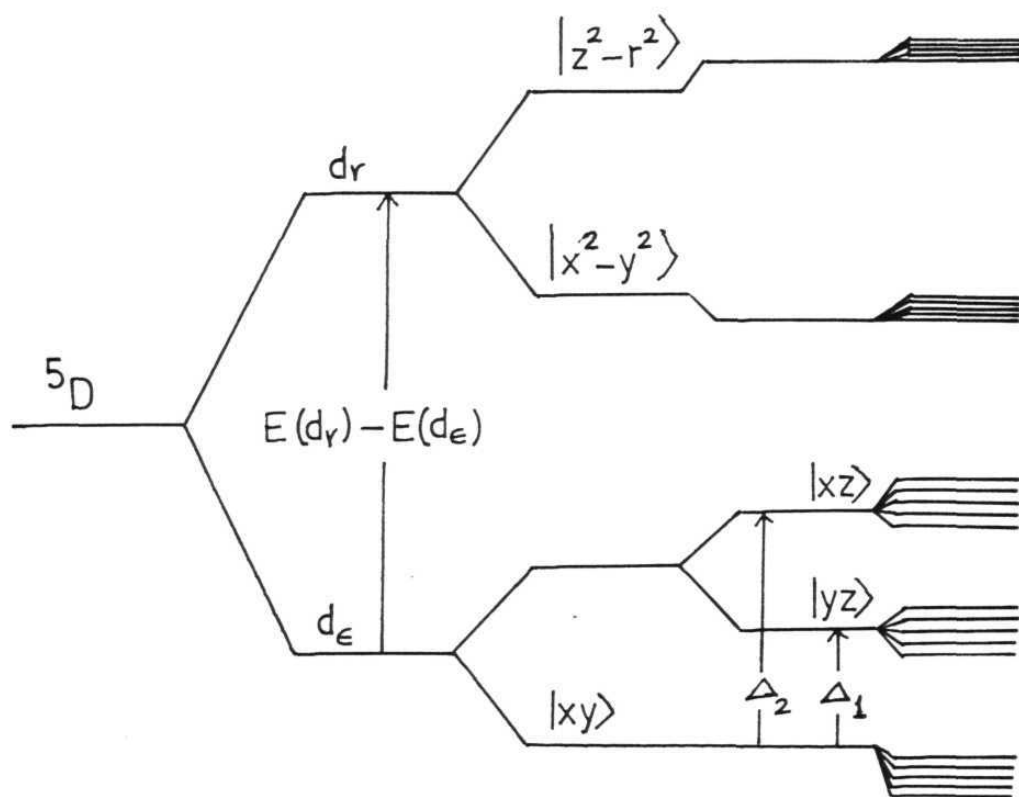
Free ion + Cubic field + Axial field + Rhombic + Spin-Orbit
                                     field   coupling

Fig.2.4 Energy level scheme for Fe^{2+} ion

A factor of $(1-R_{3d})$ arises due to polarization of inner closed shells and the lattice charges, referred to as the Sternheimer effect [5]. Thus to evaluate (2.1) it is required to obtain V_{xx}, V_{yy} and V_{zz} as $\eta = \dfrac{|V_{xx}| - |V_{yy}|}{|V_{zz}|}$. The electronic contributions to the e.f.g may be denoted by

$$V_{ii}(el) = \langle \psi | \sum_k V_{ii}(\vec{r_k}) | \psi' \rangle \qquad \cdots (2.2)$$

where the wave function ψ describes the distribution of all electrons considered and for the present case can be written as

$$V_{ii}(el) = \sum_u N_u \langle \phi_u(\vec{r}) | V_{ii}(el) | \phi_u(\vec{r}) \rangle \qquad \cdots (2.3)$$

where $V_{ii}(el) = \dfrac{e}{4\pi\varepsilon_o} \left(\dfrac{3(x_i)^2 - |r|^2}{|r|^5} \right)$, N_u is the number of electrons in the u-th molecular orbital and ϕ_u in the LCAO-MO approximation is given by $\phi_u = \sum_p C_{pu} \phi_p$, the sum being taken over all atomic orbitals of all nuclei considered but the calculations are usually restricted to the atoms to which the orbitals are localized. Expression (2.3) may be written as

$$V_{ii} = -\sum_a N(a) V_{ii}^{aa} - 2 \sum \sum n(a,a') V_{ii}^{aa'} +$$

$$\dfrac{1}{4\pi\varepsilon_o} \sum_B \left(q_B \dfrac{3(x_i)_B^2 - R_B^2}{R_B^5} \right) \qquad \cdots (2.4)$$

where $n(a,a') = \sum_u N_u C_{au} C_{a'u}$. The first term represents the valence contribution to the e.f.g tensor at the site of the nucleus and the second term denotes the so called lattice contribution.

For the high spin $Fe^{2+}(3d^6)$ case under crystal field approximation eq(2.4) can be written as [6]

$$V_{ii} = -(1-R_{3d}) \sum_a n(3d_a) V_{ii}^{aa} - (1-R_{3d}) \sum_a \sum_{a'} n(3d_a, 3d_{a'}) V_{ii}^{aa'}$$

$$\ldots (2.5)$$

where V_{ii}^{aa} and $V_{ii}^{aa'}$ are the diagonal and non-diagonal terms. The diagonal terms are given by

$$V_{ii}^{aa} = -\frac{e}{4\pi\varepsilon_o} \langle R(\vec{r})|\frac{1}{r^3} R(\vec{r})\rangle \langle Y_{1m}(\theta,\phi)|3 \cos^2\theta - 1|Y_{1m}(\theta,\phi)\rangle$$

$$\ldots (2.6)$$

where $Y_{1m}(\theta,\phi)$ are the spherical harmonics. The non-diagonal terms are given by

$$\langle d_z2|3 \cos_x^2 \theta - 1|d_x2_{-y}2\rangle - \langle d_z2|3 \cos^2\theta - 1|d_x2_{-y}2\rangle = \frac{8}{7}\sqrt{3}$$

$$\ldots (2.7)$$

Evaluating the matrix elements eqs. (2.6) and (2.7) are rewritten as follows

$$(V_{zz})_{3d} = -4/7 \frac{e}{4\pi\varepsilon_o} \langle r^{-3}\rangle_{3d}(1-R_{3d}) \, X$$

$$[n(3d_z2)-n(3d_x2_{-y}2)-n(3d_{xy}) + \frac{1}{2} n(3d_{xz}) + \frac{1}{2} n(3d_{yz})]$$

$$\ldots (2.8)$$

$$(V_{xx} - V_{yy})_{3d} = \frac{2}{7} \frac{e}{4\pi\varepsilon_o} \langle r^{-3} \rangle_{3d} (1-R_{3d}) \text{ X}$$

$$[3n(3d_{yz}) - 3n(3d_{xz}) + 4\sqrt{3n(3d_z2, \ 3d_x2_{-y}2)}] \quad \dots \quad (2.9)$$

The required matrix elements for computing the electronic population in the 15 levels and evaluating the above components is done by considering the Hamiltonian [7]

$$H = H_{axial} + H_{rhombic} + H_{s.o.}$$

$$= -|\lambda| L_z S_z - \frac{|\lambda|}{2} (L_+ S_- + L_- S_+) + \partial L_z^2 - \frac{\varepsilon}{4} (L_+^2 + L_-^2)$$

$$\dots \quad (2.10)$$

where λ is the spin-orbit coupling constant and ∂ and ε represent axial and rhombic splitting of the $^5T_{2g}$ levels (Figure 2.4) for the ^5D term. There will be $(2L+1)(2S+1) = 25$ energy levels, but only contributions from the 15 levels arising from $^5T_{2g}$ term in a distorted octahedral field are considered. The 15 x 15 matrix is set up in terms of λ, ∂ and ε which are the input parameters. The atomic orbital net population for the different orbitals are calculated using the appropriate transformations in the basis set and the relationships,

$$n_i(3d_{xy}) = \sum_{m_s} C_{xy}^2, m_s$$

$$n_i(3d_{xz}) = \sum_{m_s} C_{xz}^2, m_s$$

$$n_i(3d_{yz}) = \sum_{m_s} C^2_{yz,m_s} \quad \text{and}$$

$$n_i(3d_z2) = n_i(3d_x2{-}y2) = n_i(3d_z2, 3d_x2{-}y2) = 0 \qquad \dots (2.11)$$

where the coefficients are obtained from the eigen-vectors after the diagonalization. For the 15 energy levels ϕ_i, the e.f.g tensor contributions are calculated using the relationships (2.8), (2.9) and (2.11). The temperature dependence is introduced by assuming a Boltzmann distribution for the population and obtaining the contributions to the e.f.g. which take the form

$$V_{zz}(T) = \frac{\sum_{i=0}^{14} (V_{zz})_i \; e^{-(E_i - E_o)/kT}}{\sum_i e^{-(E_i - E_o)/kT}}$$

$$(V_{xx} - V_{yy})(T) = \frac{\sum_{i=0}^{14} (V_{xx}-V_{yy})_i \; e^{-(E_i - E_o)/kT}}{\sum_i e^{-(E_i - E_o)/kT}} \qquad \dots (2.12)$$

Substitution of these values in eq.(2.1) thus leads to the temperature dependence of quadrupole splitting. In our calculations we used $r^{-3} = 32.5$ A^{-3} [8], Q = 0.21b [9], $(1{-}R_{3d}) = 0.68$ [10]. The data were fitted to get the best fit with measured q.s. values at different temperatures by varying δ and ε. Computation and curve fitting were achieved using a computer programme written for this purpose in this laboratory [11].

where N is the coordination number. The magnetisation of
ions in different environments may be calculated using a
local molecular field theory. Introducing the reduced para-
meters $\sigma(Z) = \bar{S}_Z/Z$, $\langle\sigma\rangle_{av} = \langle\bar{S}_Z\rangle/S$, $\hat{T} = T/T_c = \dfrac{3kT}{2S(S+1)J\langle Z\rangle_{av}}$,
the magnetization can be expressed as

$$\sigma(Z) = \beta_S \frac{3S\langle\sigma\rangle_{av}Z}{(S+1)\,\hat{T}\,\langle Z\rangle_{av}} \qquad \ldots (2.14)$$

where β_S represents the Brillouin function. $\bar{S}_Z$ in (2.14) is
the time average of the spin of an iron ion along the magnetic
axis and $\langle\ldots\rangle$ denotes an average over all the iron sites in
the bulk, S is the spin of the magnetic ion i.e. 5/2 for Fe^{3+}
case and J is the exchange constant. Using the above equation
the magnetic fields for various near neighbours were calcu-
lated self-consistently. It is then assumed that each near
neighbour gives rise to a six line pattern with the corres-
ponding hyperfine field and the composite spectrum is result
of these sub-spectra. After introducing the line broadening
effects caused on account of the range of values about H(Z)
given by

$$\beta = \frac{6\gamma S}{(S+1)\langle Z\rangle_{av}\hat{T}} \frac{d\beta_S}{dy} \sqrt{Z\sum_{i=1}^{6} P_6^i(Z)[\sigma(Z) - \langle\sigma\rangle_{av}]^2} \qquad \ldots (2.15)$$

where $P_6'(Z) = P_6(Z)/(1-P_6(O))$ and $\gamma = 1$ for lines 1 and 6, 0.579 for 2 and 5 and 0.157 for 3 and 4. The composite spectra were calculated and compared with the experimental spectra. The value of Γ is altered to get a good fit with experimental points. Expression (2.14) gives the hyperfine field due to each coordination. The value of $\hat{\Gamma}$ leads to the average value of exchange constant J. An attempt is made to analyse the spectra of substituted $FeBO_3$ and Fe_3BO_6 in the range of concentration and temperature under investigation using this model and the validity of the model pointed out. A computer programme based on this formalism written for the purpose of analysis of the Mössbauer data is used [11].

2.2.3. Mössbauer spectra in fluctuating environments.

As discussed in the earlier chapter the stochastic model of ionic spin relaxation has been used for analying 'anomalous' lineshapes in Mössbauer spectroscopy. In this formalism the case when the time dependent hyperfine Hamiltonian at different instances commute with each other has been found to be simple and widely employed for explaining relaxation spectra. Such a case referred to as the adiabatic or secular case has been treated by several authors at different levels of approximations [14-27]. These authors considered a Hamiltonian $\hat{H}_o$

containing all the time-dependent interactions of the nucleus
and the sorrounding electrons and a time dependent Hamiltonian
which gives rise to transitions among the eigen states of $\widehat{H}_o$
at random instants of time. The result of the calculations
is formally expressed by [24]

$$I(\omega) = \langle A^+ (\tfrac{1}{2} \overline{T}_{nat} - i\omega - \widehat{W} - i\widehat{H}_o^x)^{-1}A\rangle \quad \ldots (2.16)$$

where $\widehat{W}$ is an operator describing the relaxation among the
eigen states of the system, H_o^x is called the Liouville operator
corresponding to the Hamiltonian $\widehat{H}_o$, and $\widehat{A}$ is an operator
describing the interaction of the system with the electro-
magnetic field. Equation (2.16) may also be expressed in terms
of matrix elements of the form

$$I(\omega) = \sum_{\substack{\mu,\nu \\ \mu',\nu'}} P(\nu) \langle \nu| \widehat{A}^+ |\mu\rangle [\mu\nu|(\tfrac{1}{2} \overline{T}_{nat} - i\omega - $$
$$\widehat{W} - i\widehat{H}_o^+)^{-1}|\mu'\nu'] \times \langle\mu'|A^+|\nu'\rangle \quad \ldots (2.17)$$

where $P(\nu)$ is the probability that the system initially is in
the state $|\nu\rangle$. In principle the matrix elements corresponding
to the second term has a dimension of $(2S+1)^2 (2I_e+1) (2I_g+1)$. In
practice only approximate methods are used. The calculation
is simplified assuming that the magnetic field fluctuates only
along the Z-direction and the e.f.g. is axially symmetric with

symmetry axis lying parallel to $Z[14]$. Under these circum-
stances $\widehat{H}_h$ given in (1.11) is modified as

$$\widehat{H}_h = Q'[3I_Z^2 - I(I+1) - g_n\mu_N\widehat{I}_Z H_n(t)] \qquad \ldots (2.18)$$

where $Q' = \dfrac{eQV_{zz}}{4I(2I-1)}$ and the magnetic field at the nucleus,
$H_n(t)$ is a random function of time. H_n may be written in the
form

$$H_n = a_0 M + H \qquad \ldots (2.19)$$

where n corresponds to the number of spin states and M assumes
values corresponding to each spin. The spectral component
corresponding to a specific nuclear transition $m_g \longrightarrow m_e$ may
then be calculated using a modified expression of (2.17) given
by [14, 17, 28-32].

$$I(\omega) = \text{Re} \left[{}_M\Sigma_{M'} \ P(M) \ A_{MM'}^{-1}(\omega) \right] \qquad \ldots (2.20)$$

where $P(M)$ is the thermal population of the electronic state
$|M\rangle$, and the matrix elements $A_{MM'}$ are given by

$$A_{MM'} = [i(\omega_M - \omega) + \tfrac{1}{2} \Gamma_{nat}] \delta_{M,M'} - \Omega_{MM'} \qquad \ldots (2.21)$$

where $\hbar\omega_M$ is the nuclear transition energy when the ion is in

the state M, and $\Omega_{MM'}$ is the transition probability rate for the ionic spin transition $|M\rangle \longrightarrow |M'\rangle$. This line shape expression has been shown to reduce to the form [26]

$$I(P) = \text{Re } \sum_{M_1 M_0} \langle M_1|A^+|M_0\rangle^2 \left[p + i\alpha + \frac{\beta^2}{(p+i\alpha+2\lambda)}\right]^{-1} \quad \ldots (2.22)$$

where M_1 and M_0 are the angular momentum quantum numbers in the excited and ground states of the nucleus respectively and λ is the relaxation rate,

$$p = -i\omega + \Gamma/2$$

$$\alpha(M_1) = Q(3M_1^2 - I(I+1))$$

$$\beta(M_0,M_1) = \mu(g_0 M_0 - g_1 M_1)h$$

and the matrix elements $\langle M_1|A^+|M_0\rangle$ are the Clebsch-Gordon coefficients. g_0 and g_1 are the nuclear g-factors for ground and excited states respectively. It is assumed that the spin jumps at random between the values of $+h$ and $-h$. The above expression may be written in a more explicit form as

$$F(\omega) = \sum_{i=1}^{6} \frac{(\frac{\Gamma}{2} + 2\lambda)[\frac{\Gamma^2}{4} + \lambda\Gamma| - (\alpha-\omega)^2 + \beta^2] + (\alpha-\omega)^2(\Gamma + 2\lambda)}{(\frac{\Gamma^2}{4} + \Gamma\lambda - (\alpha-\omega)^2 + \beta^2)^2 + (\alpha-\omega)^2(2\lambda + \Gamma)^2}$$

$$\ldots (2.23)$$

Expressing all the quantities in units of Γ, a computer programme written using the above expression for simulation of the relaxation spectra is given in Appendix I. Figure 2.5 shows representative relaxation spectra simulated using the above expression for different values of λ .

A modified form of the line shape expression (2.20) has been derived for simulation of line profiles in magnetically ordered material within the molecular field model by Dekker, and van der Woude and Dekker, incorporating the concept of partial order [19,28]. For the simple case of $S_Z = 1/2$ the order parameter η, may be introduced such that the probabilities for S_Z to be $+ 1/2$ or $-1/2$ are $(1+\eta)/2$ and $(1-\eta)/2$ respectively with $0 < \eta < 1$. The A matrix in expression (2.20) for this case may be written as

$$\overrightarrow{A}^{-1} = \begin{bmatrix} i(\omega_2 - \omega) - \Omega_f & \Omega_s \\ -\Omega_f & i(\omega_1 - \omega) - \Omega_s \end{bmatrix} \Bigg/ det\,\overrightarrow{A} \qquad \ldots (2.24)$$

where ω_1 and ω_2 correspond to the frequencies emitted by the nucleus due to fluctuations in the spin state, Ω_f and Ω_s give the probability for the frequencies to have the values ω_1 and ω_2 respectively. Introducing a convenient frequency scale using the relationship
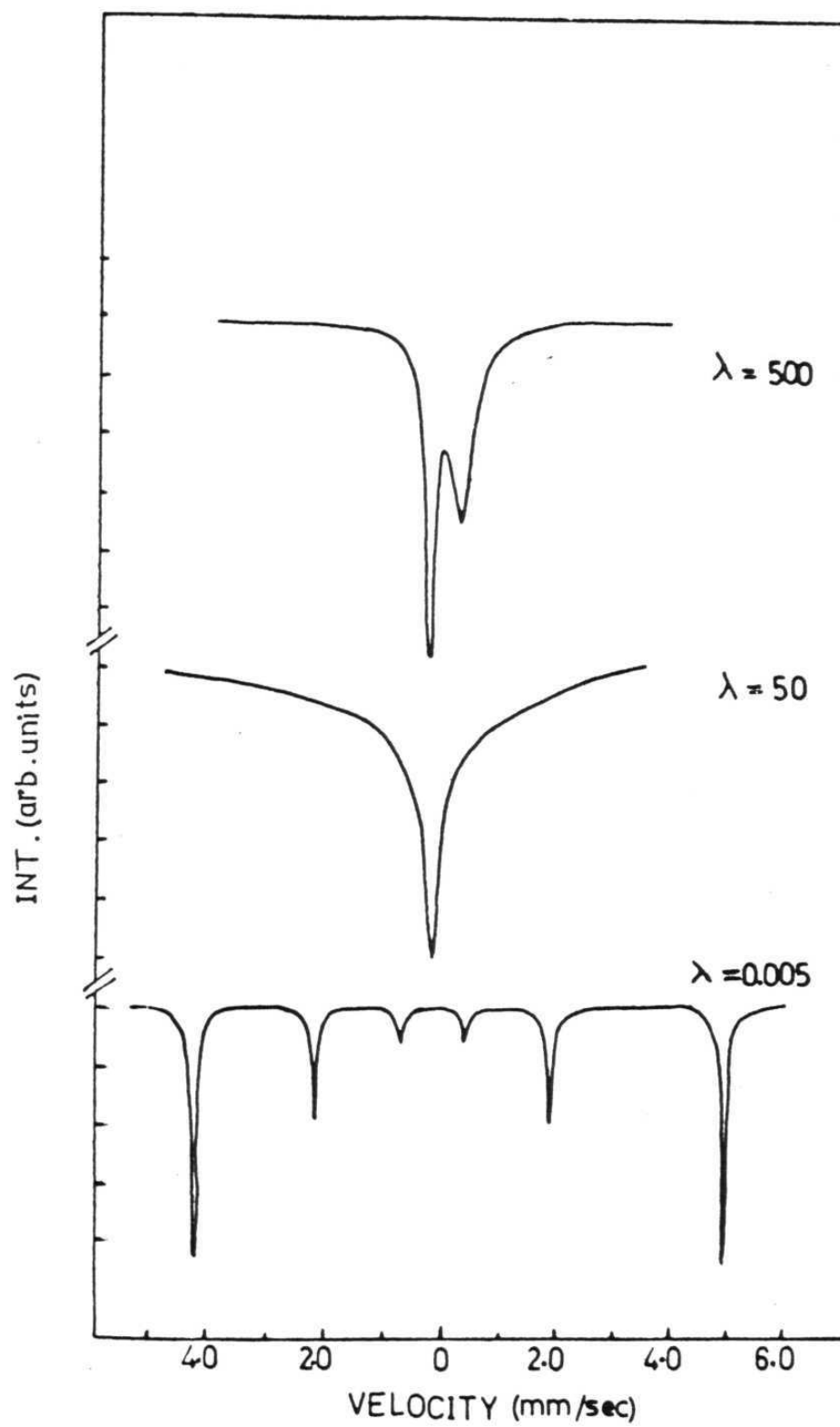
Fig.2.5 Representative spectra for different values of λ, the relaxation rate, in Eq.2.23.

$$\delta = (\omega_2 - \omega_1)/2$$

and $\omega = 0$ at $(\omega_1 + \omega_2)/2$, the line shape expression can be written as

$$I(\omega) = \frac{2\Omega_s}{(1-\eta)} \quad \times \quad \frac{\delta^2(\eta^2-1)}{(\omega^2-\delta^2)^2 + \frac{4\Omega^2_s}{(1-\eta)^2}(\omega+\eta\delta)^2} \qquad \dots (2.25)$$

In the above expression the natural line width Γ which has been neglected, when taken into account, the line shape expression becomes

$$I(\omega) = \sum_{i=1}^{6} \frac{\frac{2\Omega_s}{(1-\eta)}\delta_i^2(\eta^2-1) - \Gamma[\delta_i^2 + \omega^2 + \frac{4\Omega^2_s}{(1-\eta)^2} - 2\omega\delta_i\eta]}{(\delta_i^2-\omega^2)^2 + \frac{4\Omega^2_s}{(1-\eta)^2}(\omega+\eta\delta_i)^2 + \frac{4\Omega_s\Gamma}{(1-\eta)}(\omega^2+\delta_i^2 + 2\omega\delta_i\eta)}$$

$$\dots (2.26)$$

A computer programme written using the above expression to simulate the experimental spectra is given in Appendix II. Representative spectra simulated using the above expression are shown in Figure 2.6. The relative intensities of the different lines in the hyperfine spectra are assumed to be that of the low temperature Zeeman spectra far away from T_c where the relaxation effects are insignificant. The effect of quadrupole interaction is not taken into account in the derivation of eq.(2.26).
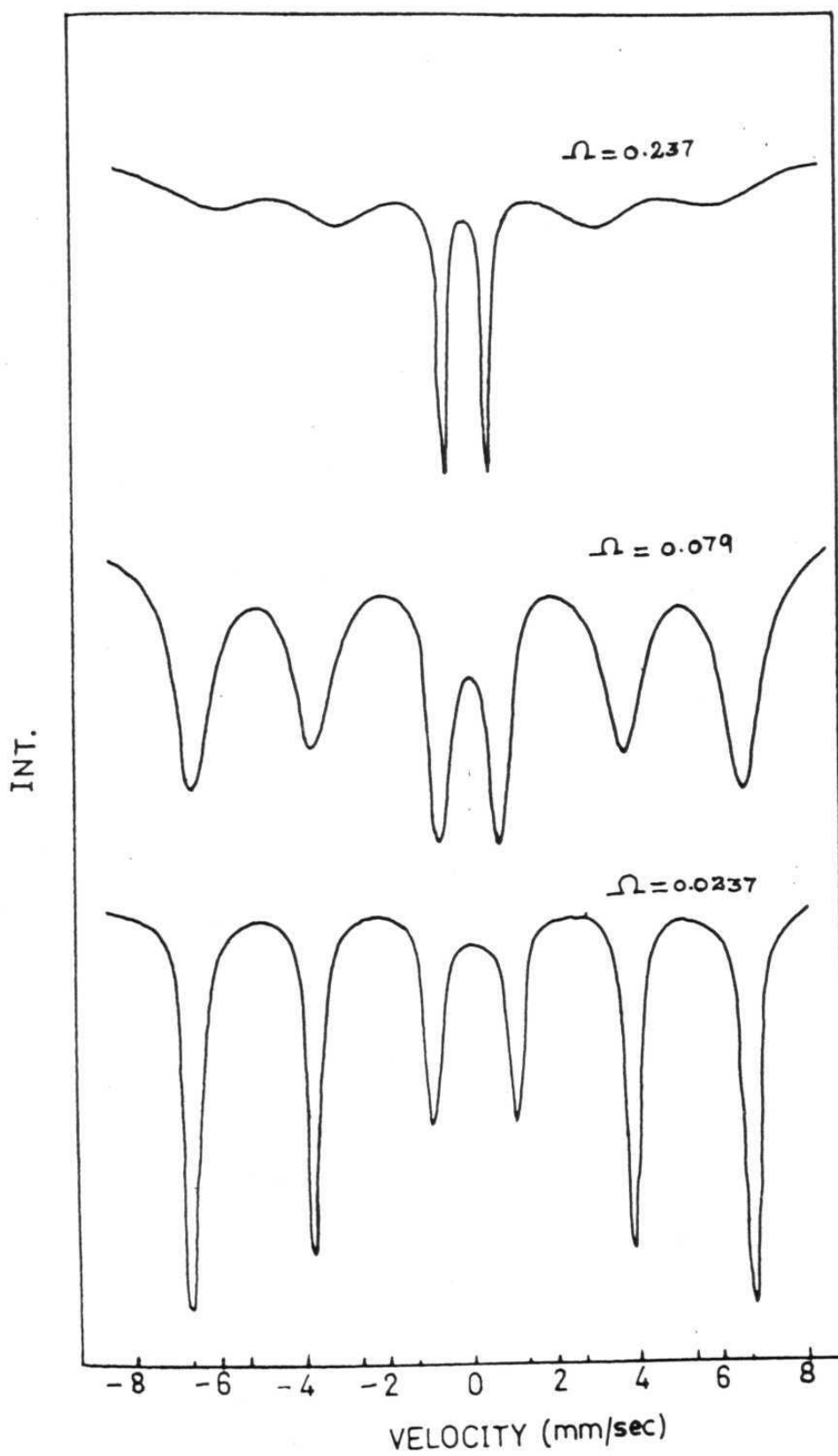
Fig.2.6 Representative spectra for different values of spin-flip frequency, Ω, in Eq.2.26.

2.2.4. Field distribution in model independent method [34].

In a substituted system such as $Fe_{.9}M_{.1}BO_3$ reported in the present work a change in the local neighbourhood of iron atoms takes place. This results in a corresponding change in the hyperfine field and results in a distribution of the field. Instances where the models such as those due to Coey and others [12,13,33] do not explain the experimental observation imply that a model dependent approach is unsatisfactory. At the same time it is possible to directly obtain the field distribution by methods such as those due to Window where no assumptions are made with regard to distribution of the hyperfine field and only experimental data are relied upon [34,35]. The technique is based on a series expansion of the probability curve P(H) using trigonometric terms satisfying certain boundary conditions. In a magnetic material it is reasonable to assume that the probabilities of zero field and that of the fields higher than the experimentally observed field are zero, i.e.

$$(\frac{dP}{dH})_{H=0} = 0 \quad \text{and} \quad (\frac{dP}{dH})_{H=H_{max}} = 0$$

The distribution of the observed field may then be taken to be

$$f_n(H) = \text{Cos} (n \pi H/H_{max}) - (-1)^n \qquad \qquad \text{... (2.27)}$$

where $n = 1 \ldots\ldots N$. The coefficients in the series then satisfy

$$P(H) = \sum_{n=1}^{H} a_n W_i(H) \qquad \ldots (2.28)$$

where the W_i are 'elementary' functions of hyperfine field distributions between $H = O$ and $H = H_{max}$. The distribution W_i may then be correlated with the spectral data in the form

$$S_i(v) = \int_{o}^{H_{max}} W_i(H) \, L_6(H,v) \, dH \qquad \ldots (2.29)$$

The above expression can be written as follows to give the complete spectrum

$$S(v) = \sum_{i=1}^{m} a_i S_i(v) \qquad \ldots (2.30)$$

The unknown coefficients a_i are then evaluated directly using the least square condition

$$\Sigma \left[S(v) - S_m(v) \right]^2 = minimum \qquad \ldots (2.31)$$

The smoothness of the desired solution in this procedure depends on 'm' the number of 'elementary' hyperfine field distributions $W_i(H)$ used in the calculation.

We have adopted this procedure in the next chapter to get insight into the distribution of the hyperfine field. In the method quadrupolar interaction is assumed to be negligible. The intensity ratio is not necessarily equal to 3:2:1:1:2:3 but modified to have a closer value to the intensity ratio obtained from the least square fit data to give a theoretically composed spectrum to fit well with the experimental data and X^2 a minimum possible value.

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CHAPTER 3

MÖSSBAUER STUDIES OF
$Fe_{1-x}M_xBO_3(x=0, 0.1; M=Al, Ga$ and $Cr)$
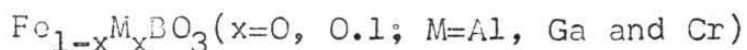
Abstract

The results of a Mössbauer study of the effect of
substitution of Al^{3+}, Ga^{3+} and Cr^{3+} in ferromagnetic
$FeBO_3$ close to T_c are presented. The Curie temperatures
of $FeBO_3$, $Fe_{0.9}Al_{0.1}BO_3$, $Fe_{0.9}Ga_{0.1}BO_3$ and $Fe_{0.9}Cr_{0.1}BO_3$
have been determined to be 352, 317, 319 and 335 K
respectively. The 'anomalous' spectra have been found to
appear just 1° below T_c for $FeBO_3$, but even 15° below T_c
for substituted borates. These spectra have been simulated
using relaxation models and estimates of activation energy
obtained for spin-flip processes. The results have been
attributed to dominant superparamagnetic relaxation effects
due to the presence of clusters. Evidence for the cluster
formation in subtituted borates is obtained by an analysis
of hyperfine field distribution. The inadequacy of static
models in explaining these spectra has been pointed out.
The difference in the results of Cr^{3+} substituted borate from
the rest of the solid solutions is brought out and the
possible reasons stated.

3.1. Introduction

Room temperature ferromagnets, transparent in the visible or infrared are not common. Dillon has reviewed the potential applications of such materials in magneto-optic devices [1]. FeF_3 and $FeBO_3$ are two such instances. For this reason attempts have been made to characterise well $FeBO_3$. The crystal structure has been studied by Bernal et al [2]. Joubert et al studied the intrinsic magnetic properties [3]. A magneto optical study on the flux grown single crystals of $FeBO_3$ showed that it has a spontaneous magnetization $4\pi M$ of 115 gauss at room temperature, Curie temperature (T_c) of 348 K, a prominent absorption window in the green (5250 Å) region with $\alpha = 39$ cm^{-1} and a large Faraday rotation of 2300° per centimeter at 5250 Å [4-6]. Other investigations on pure $FeBO_3$ include crystal structure refinement by Diehl [7], neutron diffraction studies by Pernet et al [8] and investigations of hyperfine interactions by NMR and Mössbauer techniques [9-12]. Muller succeeded in developing easy methods of preparation of $FeBO_3$ and its solid solutions and also reported susceptibility studies of the solid solutions [13]. In the course of our work a related study on $Fe_{1-x}Cr_xBO_3$ (x = 0.11, 0.5) has been reported by Ruckman et al [14]. In this chapter we present the results of our Mössbauer studies on $FeBO_3$ and the solid

solutions $Fe_{0.9} M_{0.1} BO_3$ (M = Al, Ga and Cr) close to their Curie temperatures. An attempt is made to computer simulate the spectra employing (i) the static model of Coey [15,16] and (ii) relaxation models due to Blume and Tjon, Dattagupta and van der Woude and Dekker [17-19]. It is shown that the Coey's model is not satisfactory in accounting for the experimentally observed results. On the other hand, the relaxation models are shown to account well for the experimental observations. The results of the parent compound were compared with those of the solid solutions. The supporting evidences for electronic and/or superparamagnetic relaxations have been looked into. By way of looking at the possibility of the latter mechanism it is considered worthwhile to look at the hyperfine field distribution by a model independent approach assuming that the presence of clusters should be revealed by the nature of the distribution in the parent and the solid solutions. The method due to Window is employed for the purpose and the results presented [20, 21].

3.2. Experimental

FeBO$_3$ as well as the solid solutions, $Fe_{.9} M_{.1} BO_3$ (M = Al, Ga and Cr) were prepared according to the method of Muller et al [13]. Stoichiometric amounts of metal nitrates were

dissolved with a 400% excess H_3BO_3 in hot deionised water. A
small amount of $LiNO_3$, preferably 5 moles for every 50 moles
of ferric nitrate, has been added to this solution. The
solution was slowly evaporated to dryness. The resultant
material was mixed throughly under acetone and heated in a
platinum crucible at $500^{\circ}C$ for 4 hours and at $810^{\circ}C$ for 2 days.
After cooling to room temperature the material was dissolved
in de-ionised water to remove excess B_2O_3. The material was
seperated and dried under vacuum.

X-ray powder diffractograms of $FeBO_3$ and its solid solu-
tions confirmed the formation of these compounds and absence of
starting materials as impurities [3]. The infrared and optical
spectra of these samples were found to agree quite well with
those reported [3,4]. Mössbauer spectra showed the absence of
Fe_2O_3, Fe_3BO_6 or any other iron bearing materials.

The Mössbauer measurements were carried out as described
in section 2.1.1.

3.3. Results and Discussion

i) $FeBO_3$

The Mössbauer spectra of $FeBO_3$ close to T_c (352K) in the range $348 < T < 352$ are given in Figures 3.1 and 3.2. The well resolved room temperature spectrum of the specimen is given in Figure 3.3 for comparison. The latter is found to be similar to the reported spectrum [22]. The powder spectrum gave relative intensities in the ratio 3:3:1:1:3:3 indicating strong anisotropy. At low temperatures the lines were sharp with linewidths of ~ 0.30 mm/sec. By way of characterising the sample the optical spectrum which could be measured conveniently with the photoacoustic spectral technique is reproduced along with those of solid solutions in Figure 3.4. These spectra were identical to that of Kurtzig et al reported for $FeBO_3$ [4]. Mössbauer spectra close to T_c exhibited significant differences in their profiles. For instance at 351 K a four finger pattern and at 351.5 K a spectrum with a doublet structure of unequal intensity superimposed on a broad background absorption characteristic of magnetic interaction were observed (Fig. 3.2). At 352 K a narrow doublet with line width typical of paramagnetic spectra was observed. This characteristic did not change even when the measurement was made even at

Fig.3.1 Mössbauer spectra of FeBO$_3$ close to T$_C$ from 348 to 350 K

FeBO$_3$

350 K
T/Tc = 0.9943

349 K
T/Tc = 0.9915

348.5 K
T/Tc = 0.99

348 K
T/Tc = 0.9886

COUNTS X 10^3

Velocity (mm/sec)
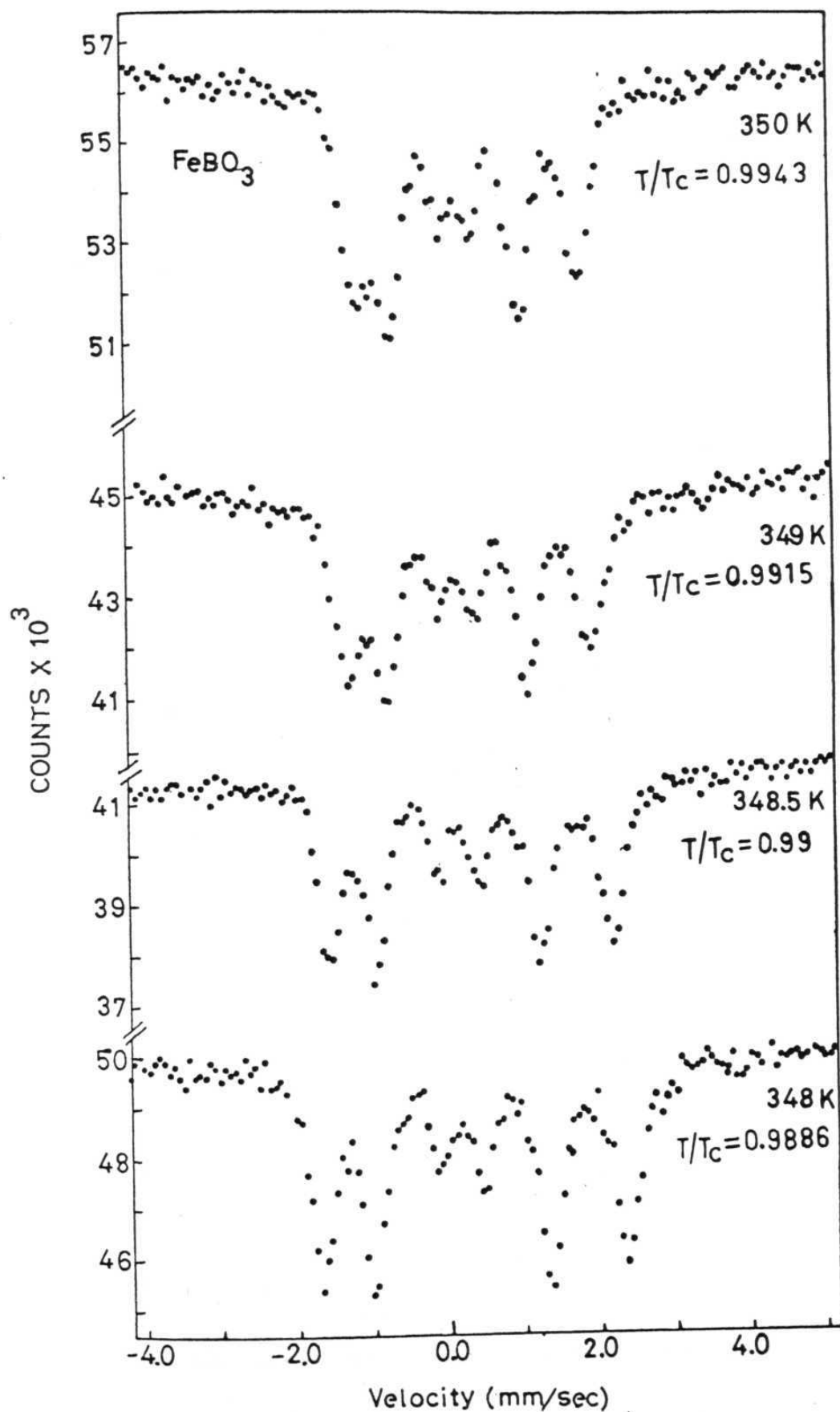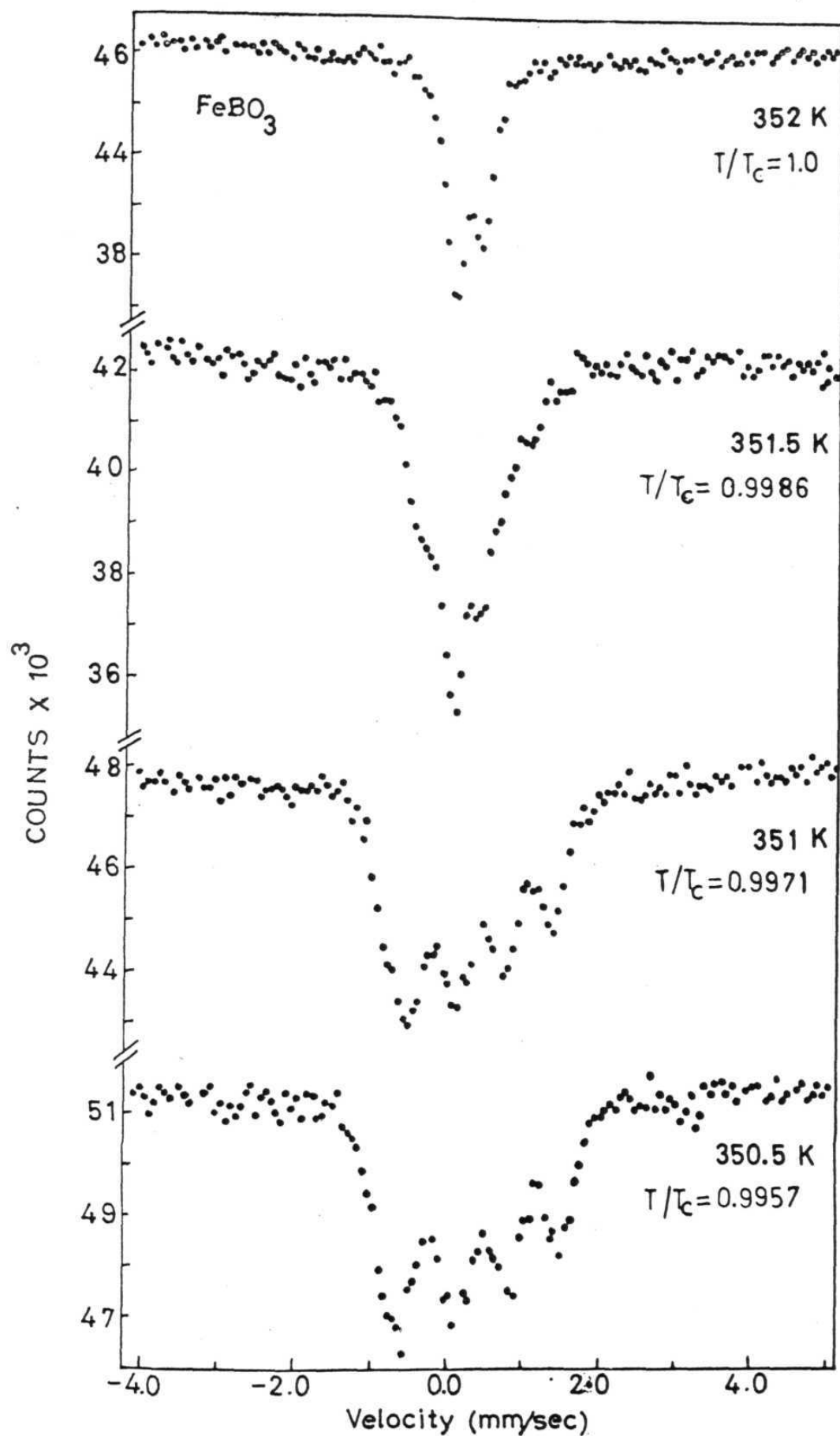
Fig.3.2 Mössbauer spectra of FeBO$_3$ close to T$_c$ from 350.5 to 352 K.
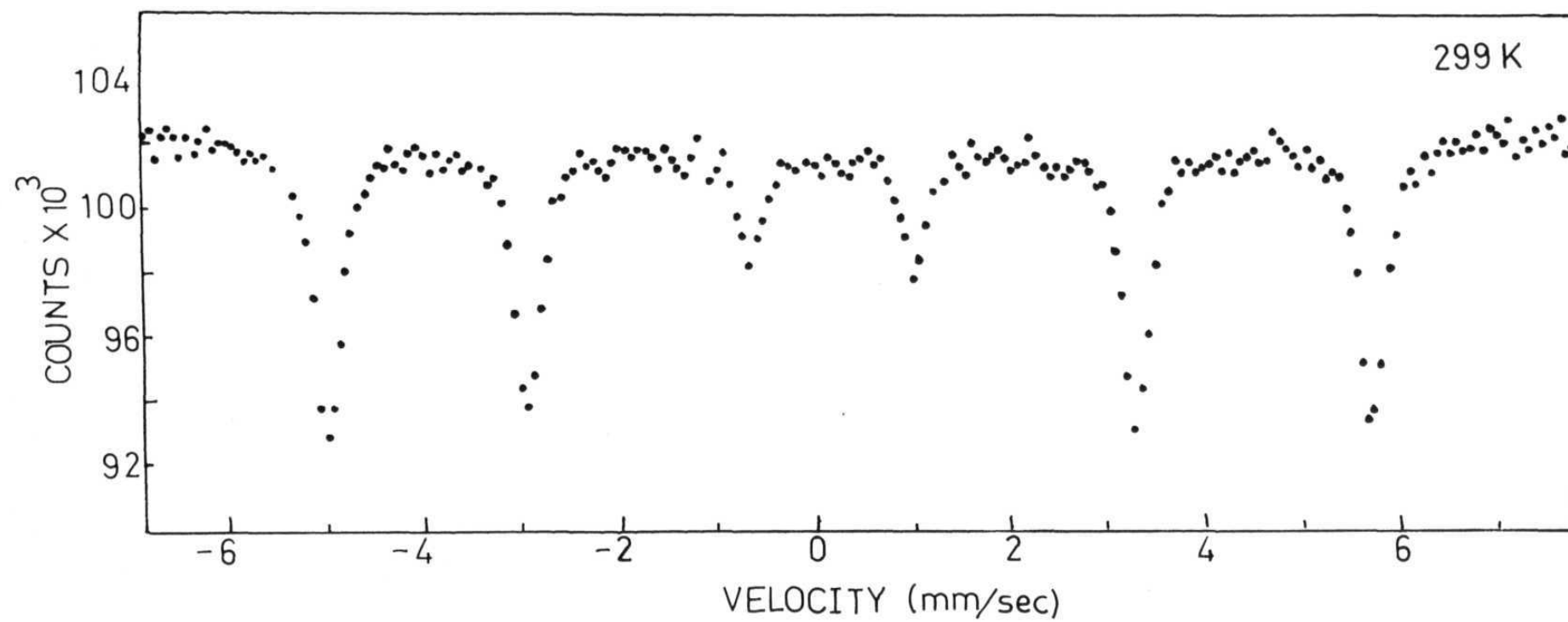
Fig.3.3 Room temperature Mössbauer spectrum of FeBO₃

RELATIVE PAS SIGNAL
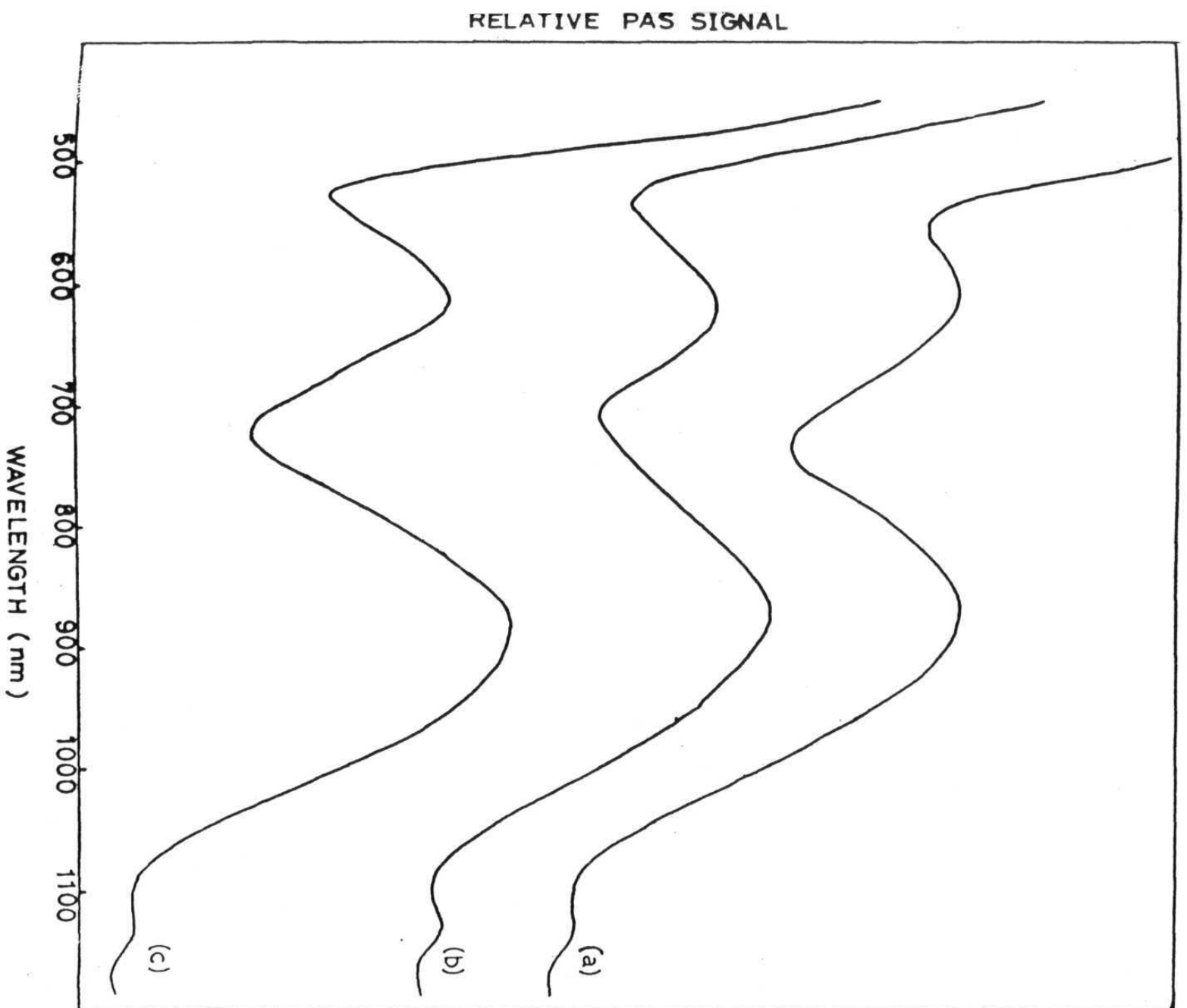
Fig. 3.4 Photoacoustic spectra of (a) $Fe_{0.9}Cr_{0.1}BO_3$ (b) $FeBO_3$ and (c) $Fe_{0.9}Ga_{0.1}BO_3$ at room temperature

much higher temperatures. An attempt is made to least square
fit the profiles of spectra close to T_c assuming a static
magnetic field and relative intensities observed for the room
temperature spectrum. The results of such a fit of Mössbauer
spectra measured at 348.5 K and 351 K are reproduced in Figure
3.5. Further as relaxation effects are also known to lead to
anomalous line shapes with an intense doublet superimposed on
broad outer lines, the spectra were also analysed using Blume's
relaxation model employing the equation 2.22 discussed in
Chapter 2. The theoretical spectra thus obtained are compared
with experimental spectra in Figure 3.6.

ii) $Fe_{0.9}Al_{0.1}BO_3$

The Mössbauer spectra of 10% Al^{3+} substituted $FeBO_3$
recorded close to T_c are reproduced in Figure 3.7. The low
temperature spectra showed no anomalous features. However the
spectra measured from 305.5 to 317 K clearly exhibited profiles
typical of time dependent hyperfine field.

Unlike in the case of $FeBO_3$, the resultant spectra in the
diamagnetically substituted system, as in the present case can
also be accounted for, in the light of Coey's model which
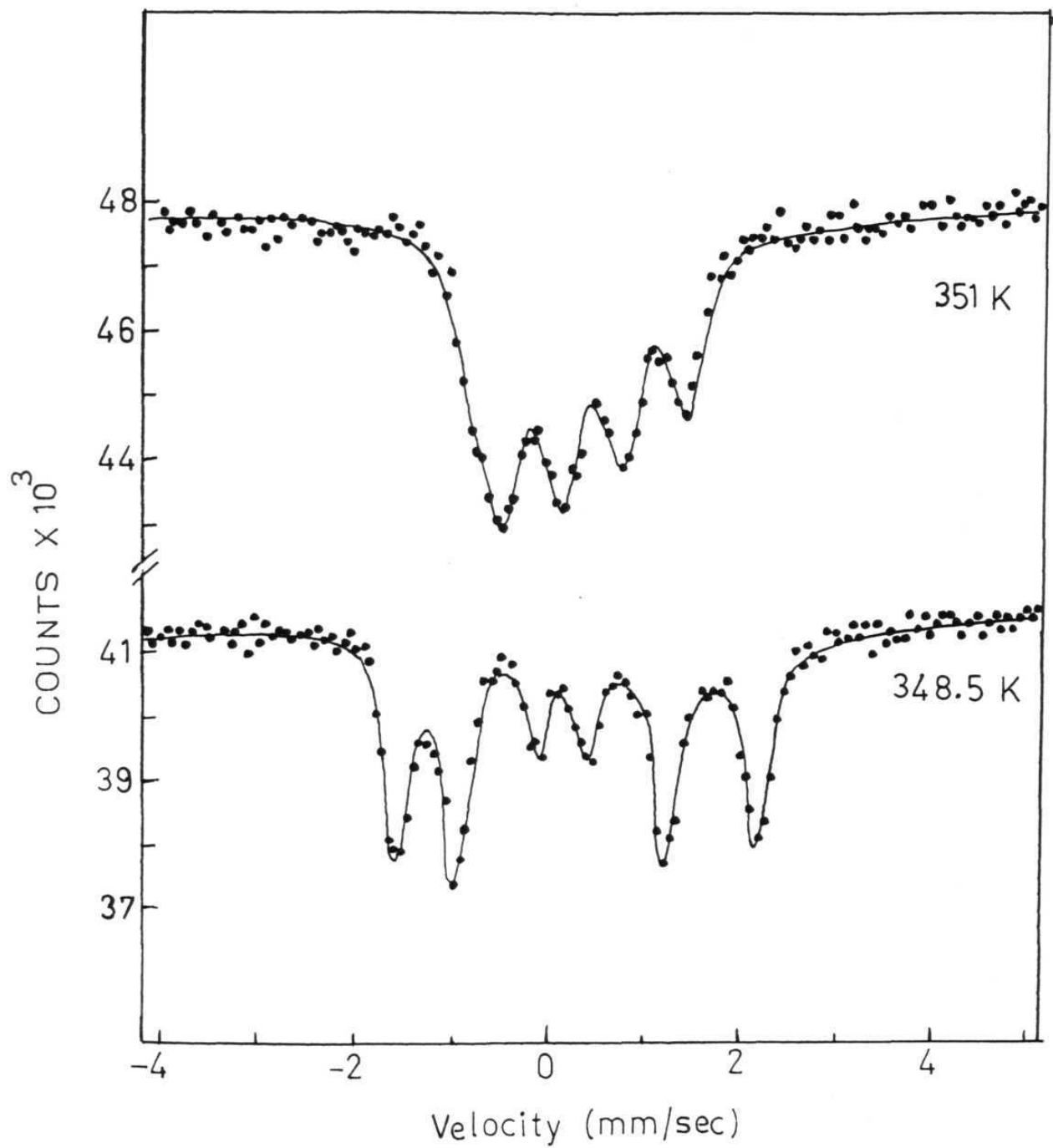
Fig.3.5 Mössbauer spectra of FeBO$_3$ at 348.5 and 351 K; solid lines are calculated spectra with least square fit Mössbauer data
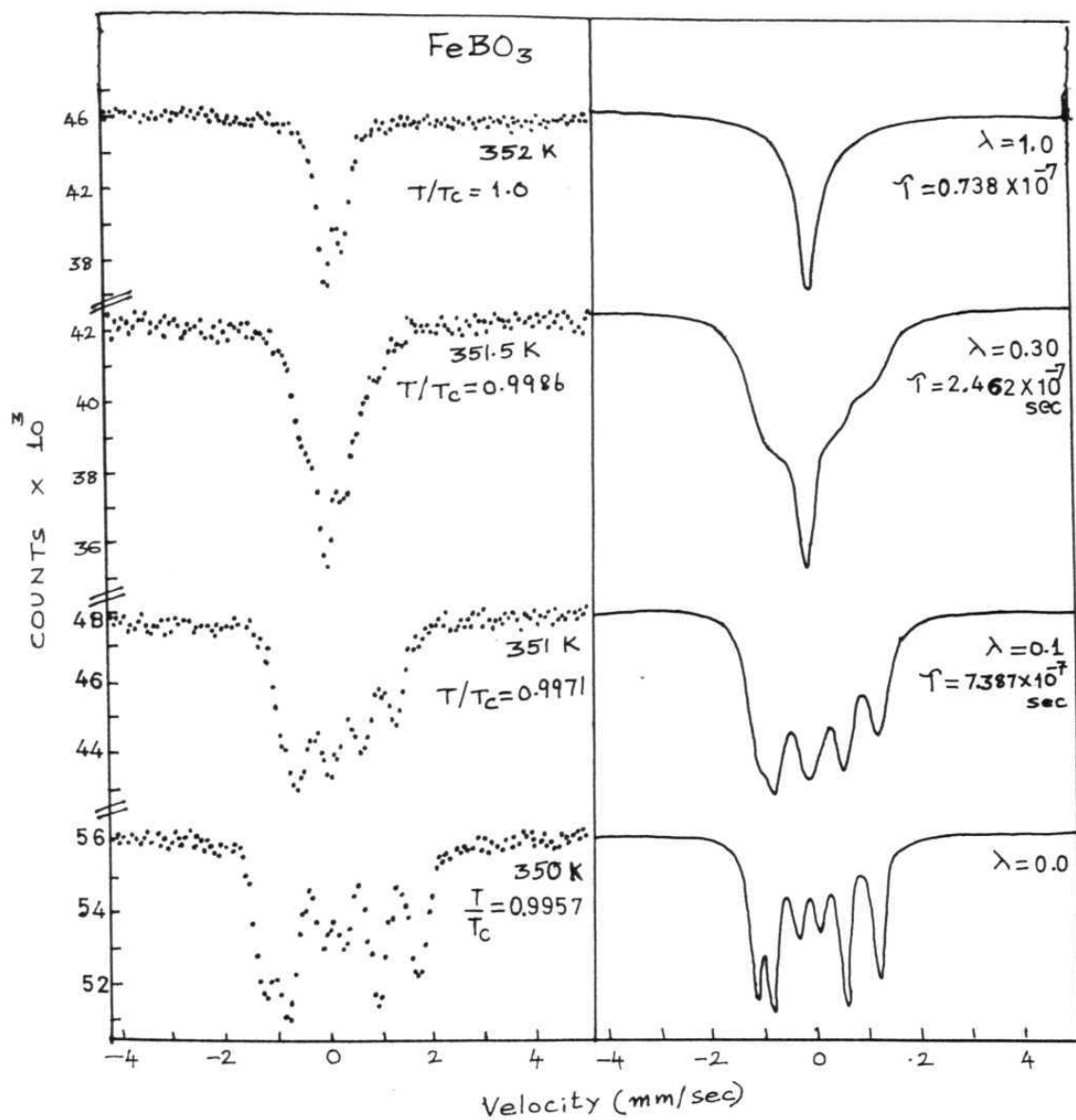
Fig.3.6 Comparison of experimental spectra of FeBO$_3$ at different temperatures with theoretical Mössbauer spectra based on relaxation effects.
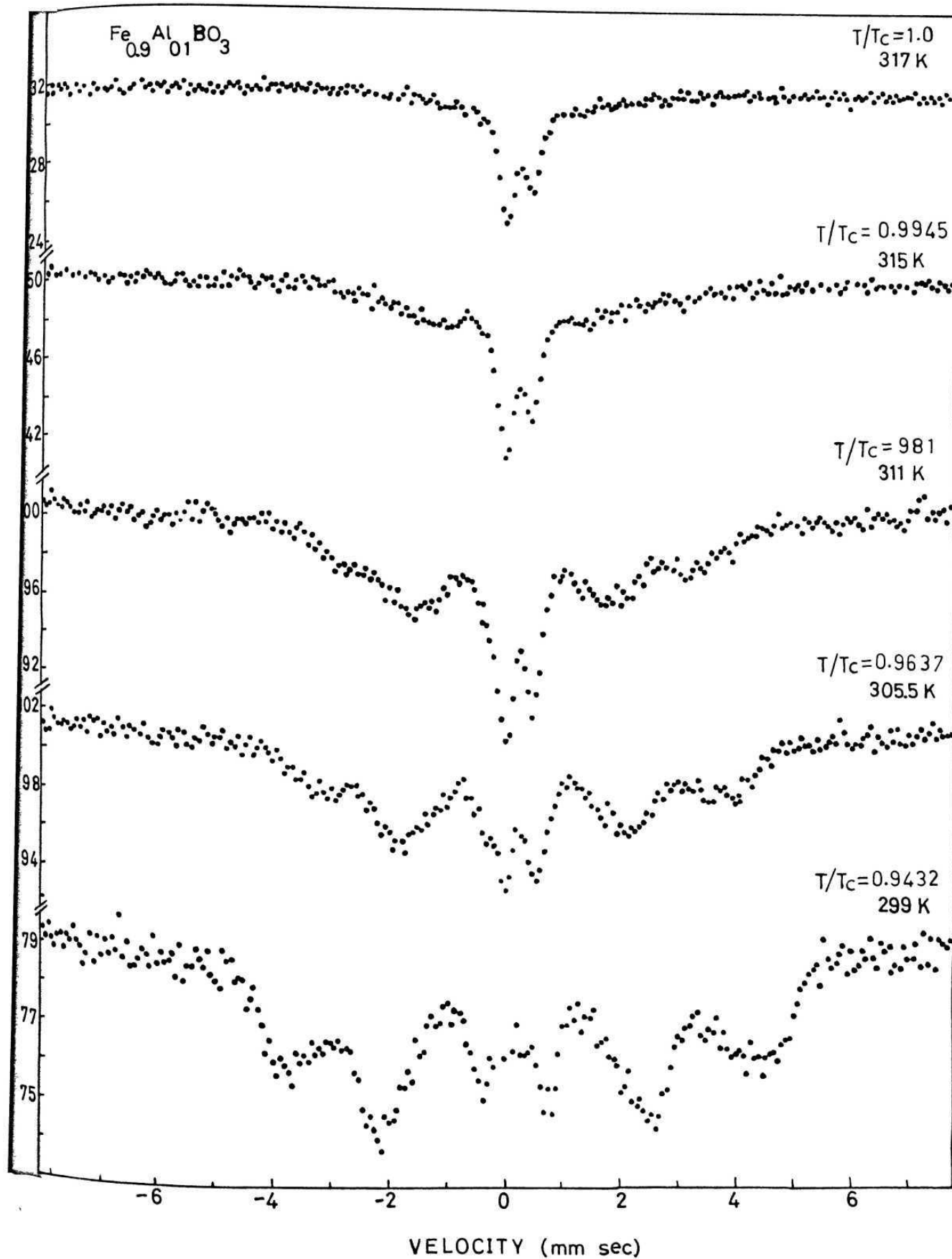
Fig.3.7 Mössbauer spectra of $Fe_{0.9}Al_{0.1}BO_3$ measured between 299 to 317 K.

takes into account the probabilities of different coordinations due to substitution and the consequent distributions in the hyperfine field as discussed in section 2.2.2. With this view in mind, attempts were made in this case to simulate the spectra for 10% diamagnetic substitution by Al^{3+} in octahedral symmetry as discussed in the earlier chapter. It was found, however, the spectrum based on this model obtained for $T/T_c = 0.99$ reproduced in Figure 3.8 showed poor agreement with the experimental spectrum shown in Figure 3.7, corresponding to 315 K.

Attempts to simulate the theoretical spectra employing expression 2.22 based on the relaxation model due to Blume also showed that unlike in the parent $FeBO_3$ the profiles of the experimental spectra could not be reproduced in these cases. Hence the model of van der Woude which is basically the same as that of Blume's but includes an order parameter, η, which differentiates the probability of spins being present up or down was tried. The theoretical spectra obtained using the latter model with Ω, the spin-flip frequency in the range 0.113 to 0.303 and $\eta = 0.45$ are compared with those of experimental spectra in Figure 3.9. The theoretical profiles show good agreement with the measured spectra. The spectra recorded at 317 K and above were found to be doublets with line widths
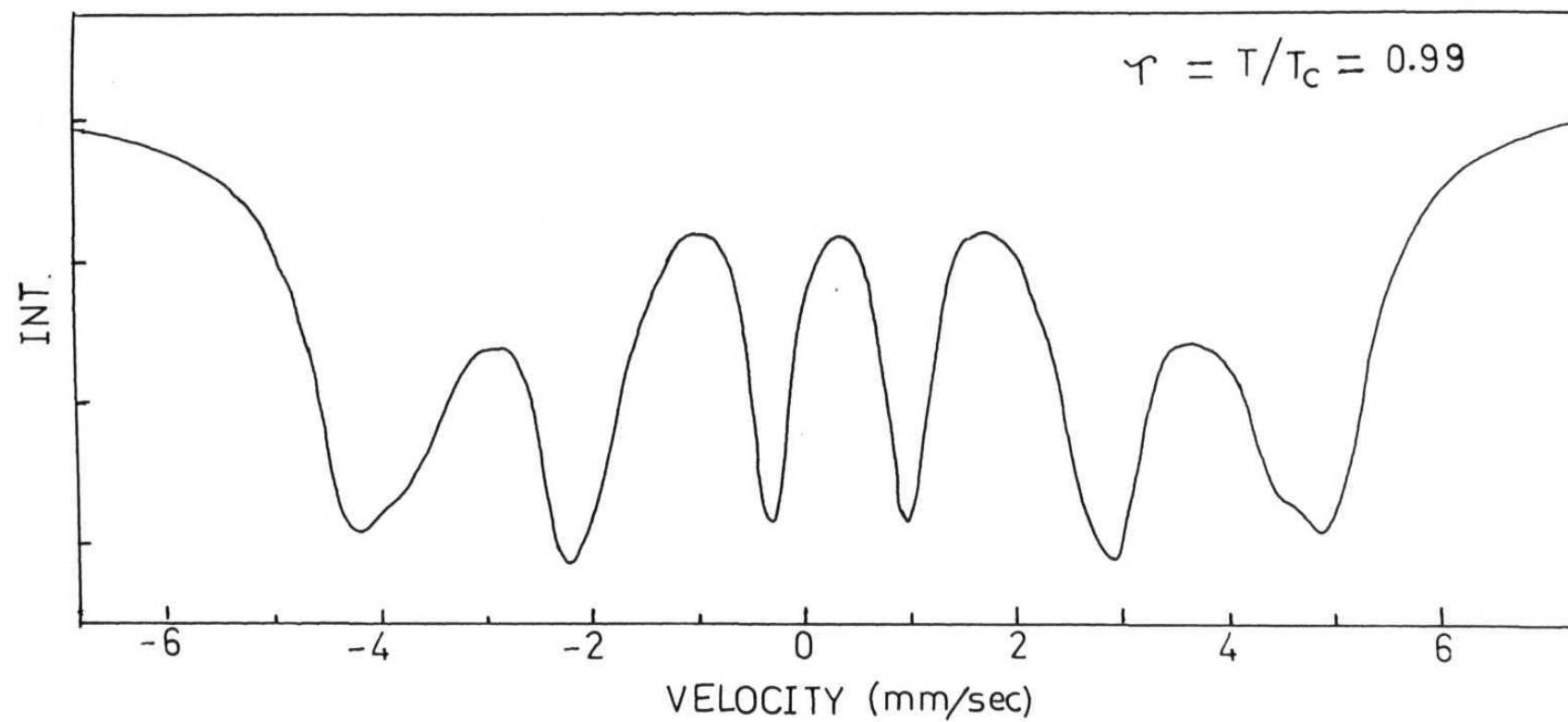
Fig.3.8 Theoretical Mössbauer spectrum simulated using the random distribution model (see text) for $\Upsilon = 0.99$
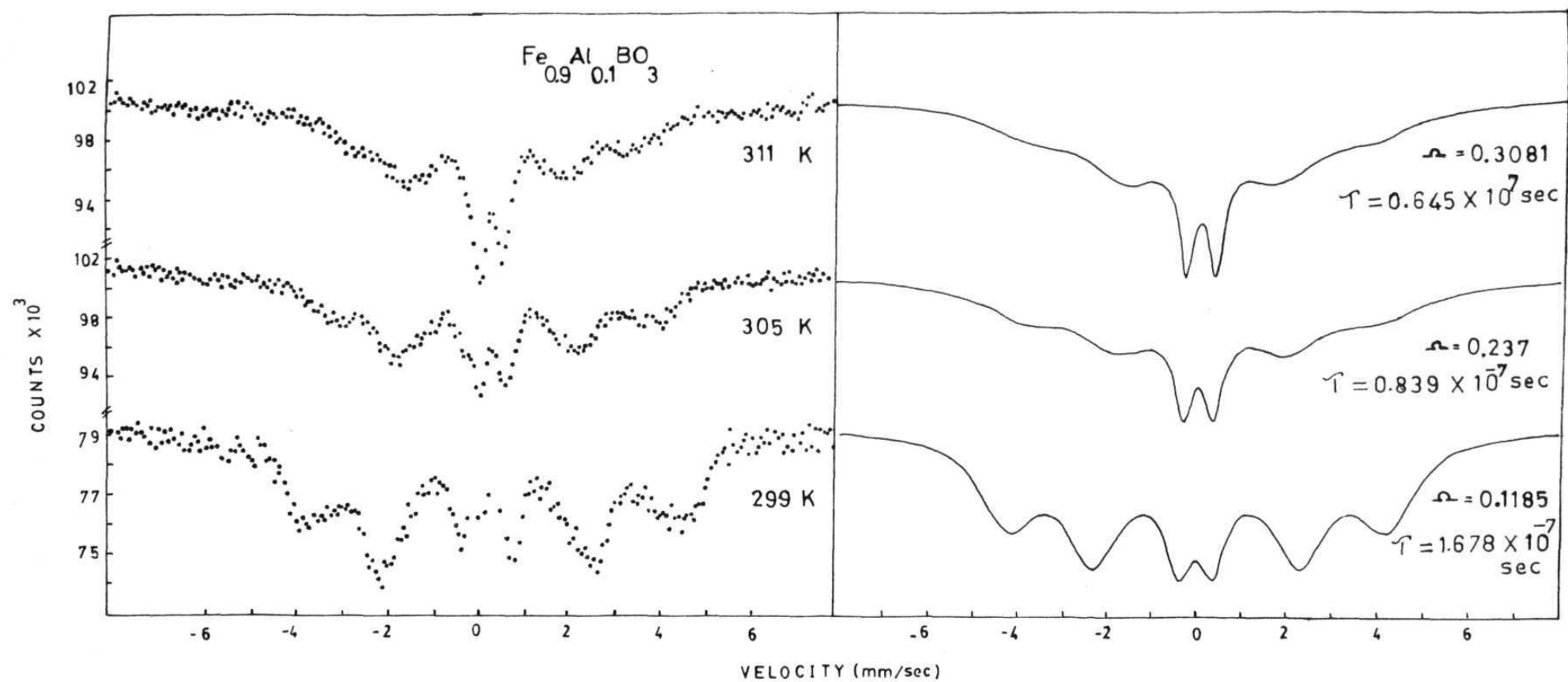
Fig.3.9 Comparison of experimental spectra of $Fe_{0.9}Al_{0.1}BO_3$ at different temperatures with theoretical spectra based on relaxation effects.

typical of paramagnetic spectra. The spectra however showed unequal intensities for the doublet. In these cases an estimate of the activation energy of 9.936×10^{-13} erg. degrees^{-1} is obtained using the expression

$$\Omega = \Omega_o \, e^{-Ea/kT} \qquad \ldots (3.1)$$

where E_a is the activation energy for the spin-flip process.

iii) $Fe_{0.9}Ga_{0.1}BO_3$

The Mössbauer spectra of 10% Ga^{3+} substituted $FeBO_3$ recorded in the range 77-320 K showed features similar to those of $Fe_{0.9} Al_{0.1} BO_3$. Representative spectra measured between 299 and 317 K are reproduced in Figure 3.10. The spectra based on the relaxation model of van der Woude and Dekker with Ω, the spin flip frequency lying in the range 0.166 to 0.379 and the order parameter $\eta = 0.45$ were found to give rise to theoretical spectra close to experimental situations (Fig. 3.11). The line profiles of spectra recorded at and above 319 K indicated that T_c for this sample to be 319 K. An estimate of activation energy obtained for the spin flip process is found to be 5.87×10^{-13} erg.degree^{-1} which is nearly the same as found for 10% Al^{3+} substituted $FeBO_3$.
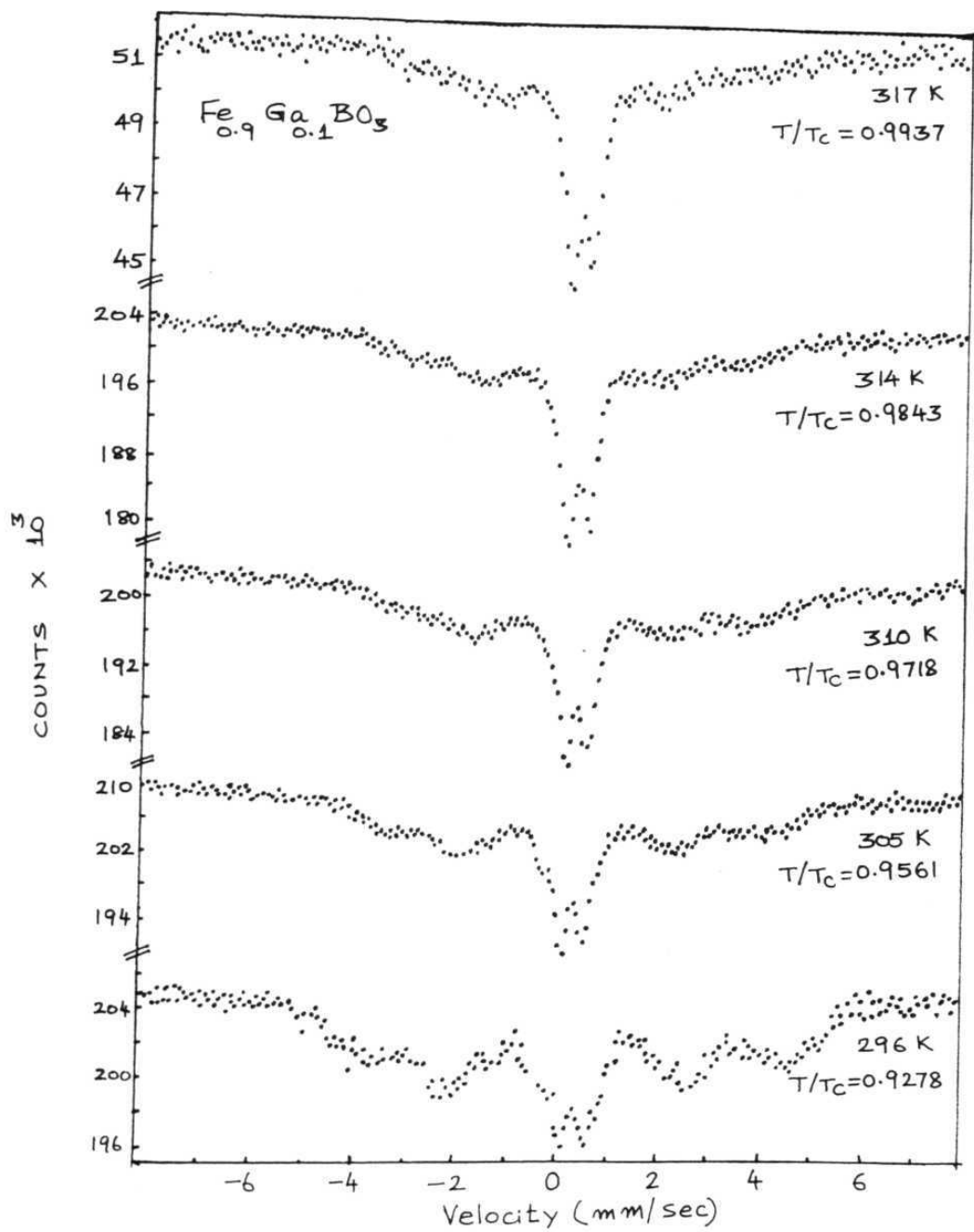
Fig.3.10 Mössbauer spectra of $Fe_{0.9}Ga_{0.1}BO_3$ measured between 296-317 K.
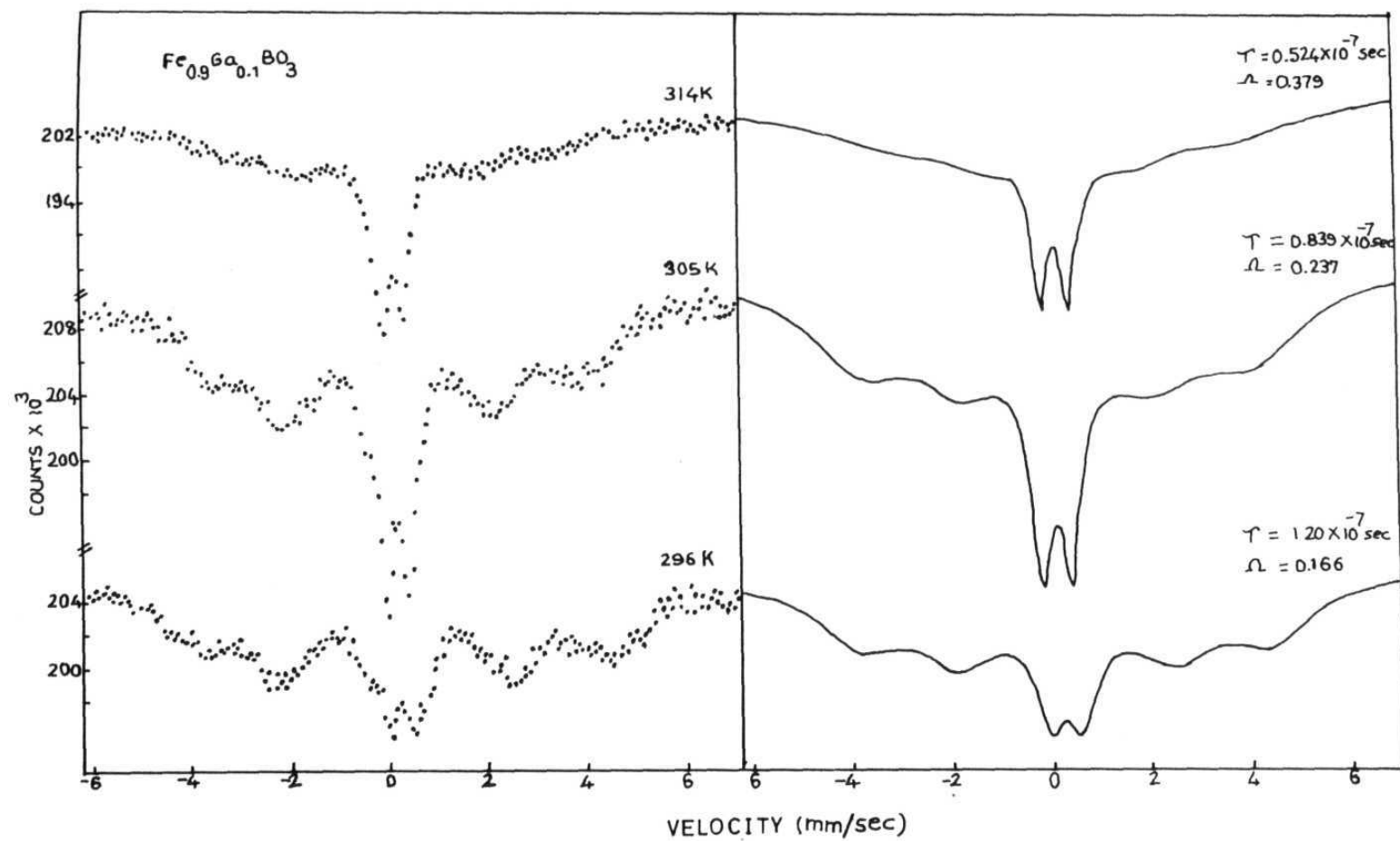
Fig.3.11 Comparison of experimental spectra of $Fe_{0.9}Ga_{0.1}BO_3$ at different temperatures with theoretical spectra based on relaxation effects.

iv) $Fe_{0.9}Cr_{0.1}BO_3$

The Mossbauer spectra of 10% Cr^{3+} substituted $FeBO_3$ recorded far away from T_c were similar to those of the parent and other solid solutions. However, those recorded close to T_c, reproduced in Figure 3.12 showed significant differences both from those of the parent as well as the Ga^{3+} and Al^{3+} substituted systems particularly in the region -2 to +2 mm/sec. Attempts to simulate these experimental spectra using the relaxation models which sucessfully reproduced the spectra for other solid solutions gave unsatisfactory results, particularly in the above mentioned velocity region.

A plot of $H_{eff}(T)/H_{eff}(O)$ vs T/T_c for $FeBO_3$ and substituted $FeBO_3$ is shown in Figure 3.13. It is found that all the data points closely follow the theoretical Brillouin curve for the $S = 5/2$ case.

The values of Ω, the spin flip frequency and Γ, the correlation time, and the activation energy obtained for the two substituted samples are given in Table 3.1. The hyperfine field at 80 K, the lowest temperature measured, the isomer-shifts and quadrupole splittings for the spectra measured in the paramagnetic states and the Curie temperatures for the
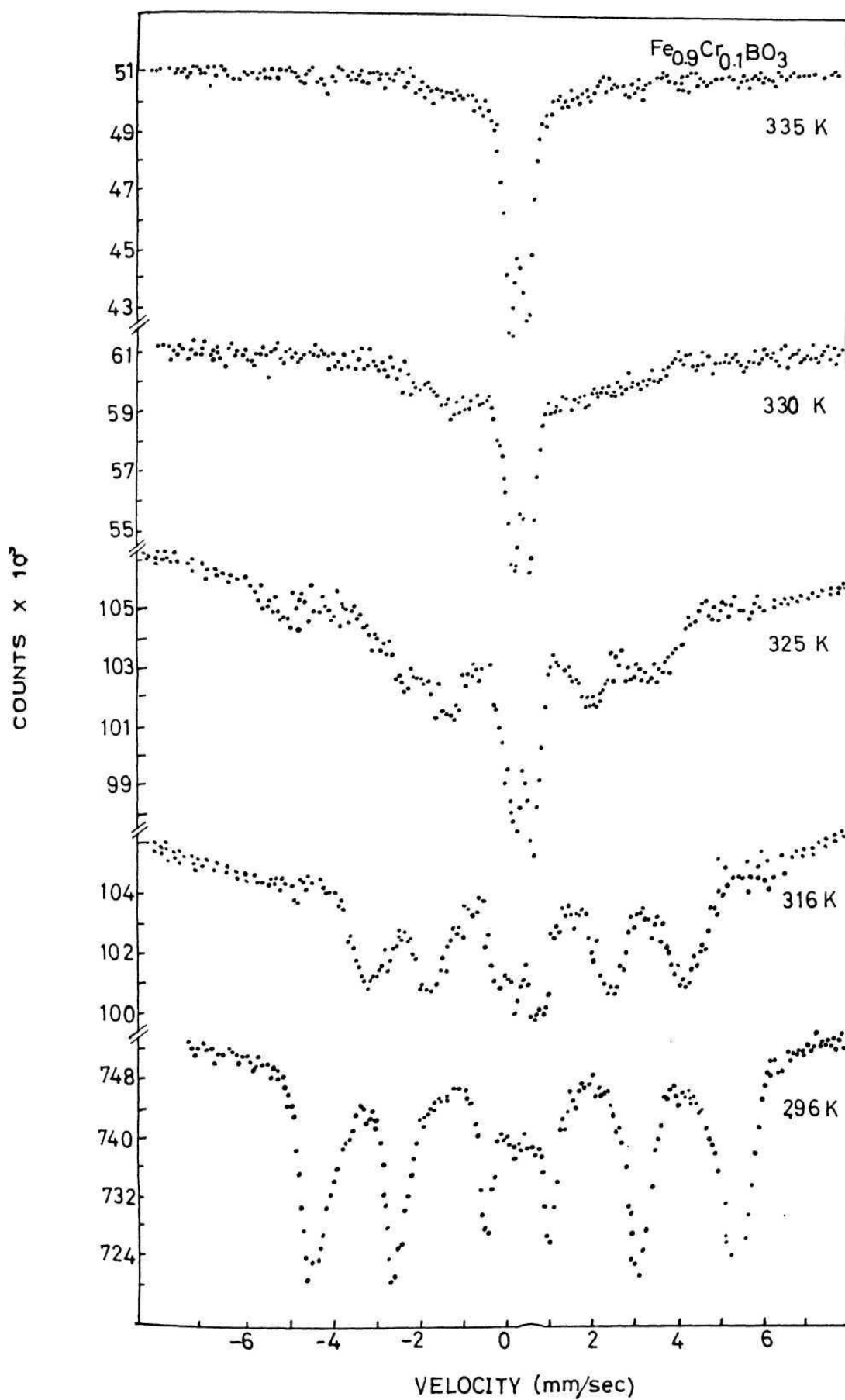
Fig.3.12 Mössbauer spectra of $Fe_{0.9}Cr_{0.1}BO_3$ in the range 296-335 K.
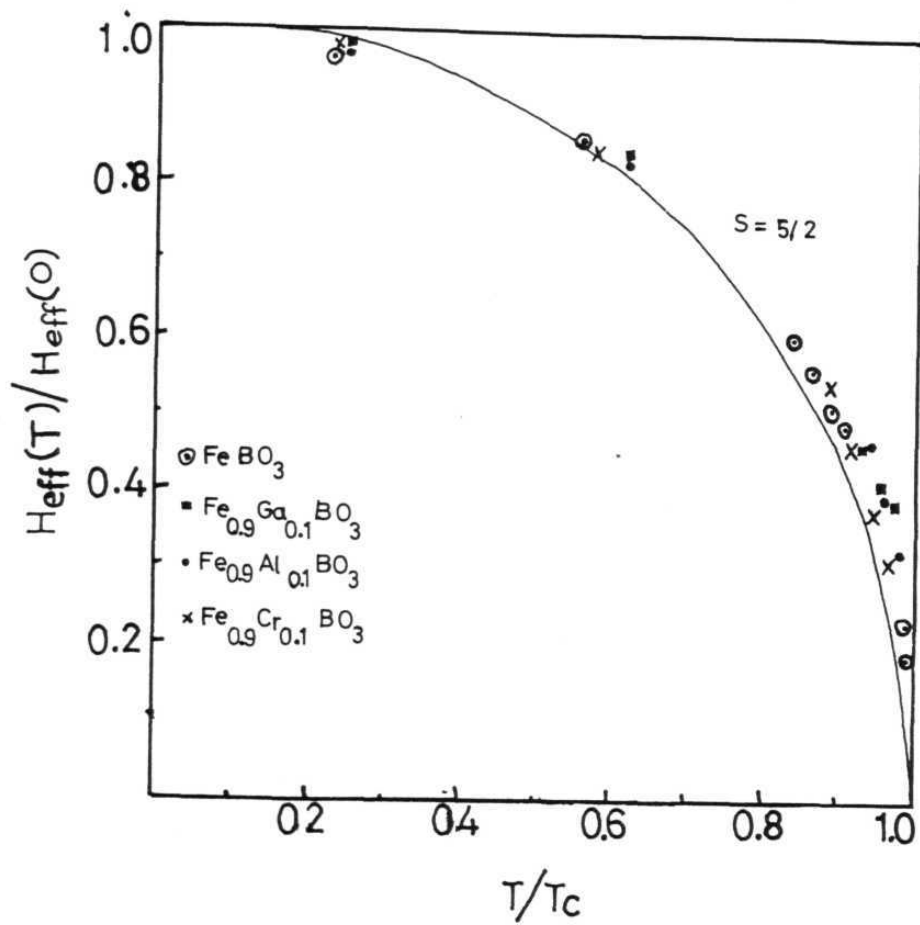
Fig.3.13 Plot of reduced hyperfine field vs reduced
temperature for the case of $FeBO_3$ and
different solid solutions. The continuous
line represents the Brillouin curve for
$S = 5/2$.

Table 3.1. The spin-flip frequency (Ω) correlation time (τ_s) and the activation energy (E_a) for spin-flipping process for 10% Ga^{3+} and Al^{3+} substituted $FeBO_3$.

Compound	Temp.(K) (±1)	Ω	τ_s(sec)x10^7	E_ax10^{13} (erg. degree^{-1})
$Fe_{0.9}Ga_{.1}BO_3$	296	0.166	1.20	5.87
	305	0.237	0.84	
	314	0.379	0.52	
$Fe_{0.9}Al_{.1}BO_3$	299	0.1185	1.678	9.93
	305.5	0.237	0.84	
	311	0.3081	0.64	

parent and the substituted systems are given in Table 3.2.

Attempts to understand situations giving rise to
'anomalous' Mössbauer spectra having superimposition of
'magnetic' and 'paramagnetic' profiles have been made both
from theoretical [15-19, 23-28] as well as experimental points
of view [29-37]. Detailed experimental investigations in these
studies in magnetically ordered materials are to our knowledge
confined to oxide systems such as the ferrites, where the pre-
paratory techniques introduce non-stoichiometry and inhomo-
genity. In that sense the data obtained in systems such as the
present one where the crystalline materials were prepared from
the flux techniques, should be more reliable. The anomalous
spectra were obtained for $FeBO_3$ just 1^O below T_c where time
dependent effects are unequivocal. In the case of the substi-
tuted borates they become evident even as far away as 15°
below their respective Curie temperatures. Such situations can
be explained on the basis of (i) electronic relaxation (ii)
superparamagnetic relaxation effects or (iii) possible hyper-
fine field distribution particularly in the case of solid solu-
tions. In the case of solid solutions different coordinations
can be expected to give rise to a distribution in the hyper-
fine field as discussed by Coey and other workers leading to
anomalous spectra [15,16,38]. It is found that such a model

Table 3.2. Quadrupole Splitting, Isomer Shift, Line width, H_{eff}(80 K) and T_c values for $FeBO_3$ and $Fe_{0.9}M_{0.1}BO_3$(M = Ga, Al and Cr).

Compound	Q.S. at T_c (mm/sec) ± 0.02	I.S[‡] (mm/sec) ± 0.02	FWHM at RT (mm/sec) ± 0.02	H_{eff}(80) ± 2 kOe	T_c.(K)
$FeBO_3$	0.36	0.30	0.33	545	352
$Fe_{.9}Al_{.1}BO_3$	0.45	0.28	0.38	533.5	317
$Fe_{.9}Ga_{.1}BO_3$	0.40	0.35	0.35	530.7	319
$Fe_{.9}Cr_{.1}BO_3$	0.38	0.32	0.34	539	335

‡ relative to Fe-foil.

does not reproduce the experimental results for 10% substitution in the said temperature range (Fig. 3.8), although it is found to be useful for accounting for observations away from T_c as discussed in the next chapter for Fe_3BO_6 case. Thus the utility of such models seem to be limited to situations where time dependent effects are not important. This is understandable as mean field approximations are far from satisfactory when time dependent effects are dominant.

In the parent compound where the time dependent effects appear important only very close to T_c the line shape expression of Blume and Tjon sucessfully reproduces the experimental spectra without introducing weight factors for different spin levels unlike in the case of solid solutions. In the molecular field approximation due to van der Woude it is equivalent to the situation of order parameter $\eta = 0$. In solid solutions good match with experimental spectra are obtained only if $\eta \neq 0$. The correctness of our analysis is also shown by unresolved intense central absorption in the spectrum of $FeBO_3$ at 351.5 K unlike in the solid solution spectra with resolved doublet structures. This trend is parallel to the trend shown by the theoretical spectra for $\eta = 0$ and $\eta \neq 0$ cases respectively [19]. The order parameter η is proportional to the magnetization. A finite value of η thus indicates polarisation of the

spin states implying that the collective behaviour of the spins has broken and partial order is present in the solid solutions.

Our results clearly show that relaxation effects are important. They occur only very close to T_c in the pure compound but could be easily observed over much wider ranges in solid solutions. Relaxation effects occur due to ionic spin fluctuations either due to the motion of the individual spins i.e., electronic relaxation effects or due to collective motion of large number of spins in a small region of the material i.e., superparamagnetic effects. The electronic relaxation effects may arise due to spin-lattice and spin-spin inter-actions. Fe^{3+} being an S state ion, the spin-spin relaxation mechanism is expected to be dominant. In this mechanism, the ion exchanges energy with another paramagnetic ion with which it is coupled through dipolar or exchange interactions. Relaxation effects arise as a result of the mutual spin-flip of one ion accompanied by that of another with identical Zeeman splitting so that the exchange is energy conserving. In this mechanism the population of the ionic levels vary with temperature resulting in temperature dependent lineshape.

Superparamagnetic effects in the Mössbauer spectra occur due to the presence of small regions, otherwise called clusters,

in a solid which are more magnetic than the rest of the solid and are magnetically decoupled from the rest of the solid, the cluster magnetisation fluctuating randomly among various easy directions of magnetisations due to thermal agitation. If V is the volume of the cluster, the relaxation time of the cluster magnetisation is given by [23, 39].

$$\tau_F = \tau_0 \exp(KV/k_B T) \qquad \qquad \dots (3.2)$$

where K is the anisotropy energy per unit volume, V is the volume of the cluster and k_B the Boltzmann constant. Thus a plot of log τ_F vs 1/T should lead to an estimate of τ_0. In the case of the solid solutions such a plot led to $\tau_0 = 5.37 \times 10^{-8}$ sec. and $\tau_0 = 5.01 \times 10^{-8}$ sec. for $Fe_{.9} Al_{.1} BO_3$ and $Fe_{.9} Ga_{.1} BO_3$ respectively, which is in the order expected for situations with superparamagnetic relaxation effects [19,23,39]. The superparamagnetic behaviour occurs for fine particles far below T_c as observed by the anomalous Mossbauer spectra. On the other hand, for large particle size this type of behaviour is observed as $T \longrightarrow T_c$ because then the anisotropy energy per unit volume and hence KV tends to zero. In a bulk material it is more appropriate to rewrite eq. (3.2) as

$$\tau_F = \tau_0 \exp(KV_{eff}/k_B T) \qquad \qquad \dots (3.3)$$

where V_{eff} characterises a spread in effective volume due to the inhomogenity intrinsic in the substituted materials. The inhomogenity gives rise to large clusters of magnetically independent regions. If the inhomogenity giving rise to clusters is important one would expect enhancement of relaxation region in magnetically diluted systems. In the parent $FeBO_3$ any such inhomogenities may be expected to be minimal resulting in a very small distribution of V_{eff} leading to the so called critical superparamagnetism with the relaxation effects becoming observable only very close to T_c. On the other hand substitution by nonmagnetic ion such as Al^{3+} or Ga^{3+} causes a significant change giving rise to clusters with a wider distribution in the value of V_{eff}. The collective motions of spins in the substituted systems are therefore highly damped affecting the relaxation processes. The large relaxation region with the effects seen even upto $(T_c - 15)$ in solid solutions thus arises predominantly due to superparamagnetic relaxation. It may be emphasised at this point that such an observation of the anomalous spectra over a wide range of temperature does not imply a distribution of T_c but signifies a range over which size effects become important [30]. Further, according to the super exchange relaxation model the spin-flip time, τ_F has been shown to decrease with increase in temperature which is found to be the case in our own observations in the systems under investigation [30] (Table 3.1).

It is suggested above that substitution of a non-magnetic ion should cause significant change in the nature of the clusters of magnetically independent regions present in the sample as shown in particular by the extension of observation of relaxation phenomena as far as 15° below T_c. It should be possible to get an estimate of the change brought about in the magnetic interaction by the substitution, provided a model independent method of obtaining the distribution of hyperfine fields discussed in section 2.2.4. is used. With this point of view a representative analysis of the hyperfine field distribution was carried out for both $FeBO_3$ as well as $Fe_{.9}Ga_{.1}BO_3$ close to T_c. Figures 3.14 and 3.15 show the Mössbauer spectra of $FeBO_3$ at 348.5 K and $Fe_{.9}Ga_{.1}BO_3$ at 296 K respectively along with the theoretical spectra simulated based on this approach. The plots of P(H), the probability of given hyperfine field vs H are shown in Figure 3.16. The widths of the distribution curves for $FeBO_3$ and $Fe_{.9}Ga_{.1}BO_3$ were found to be $\sim$ 35 gauss and $\sim$ 135 gauss respectively. The large width found for the latter clearly shows large distribution of magnetic fields present in the system. Thus 10% Ga^{3+} substitution brings about a large number of different near neighbours or clusters and hence a large field distributions in the substituted sample, in contrast to that of the parent material viz., $FeBO_3$. Further, attempts to reproduce the anomalous spectra close to
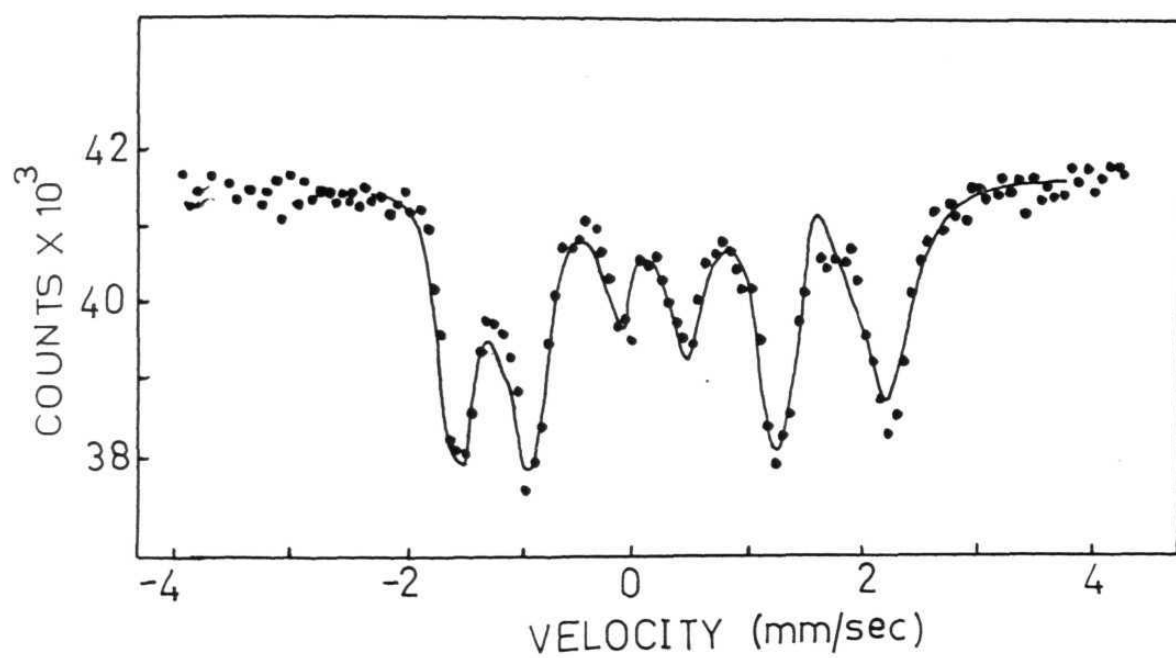
Fig.3.14 Mössbauer spectrum of FeBO$_3$ at 348.5 K. The solid line is
the composite theoretical spectrum based on the field distribution
using Window's method [20].
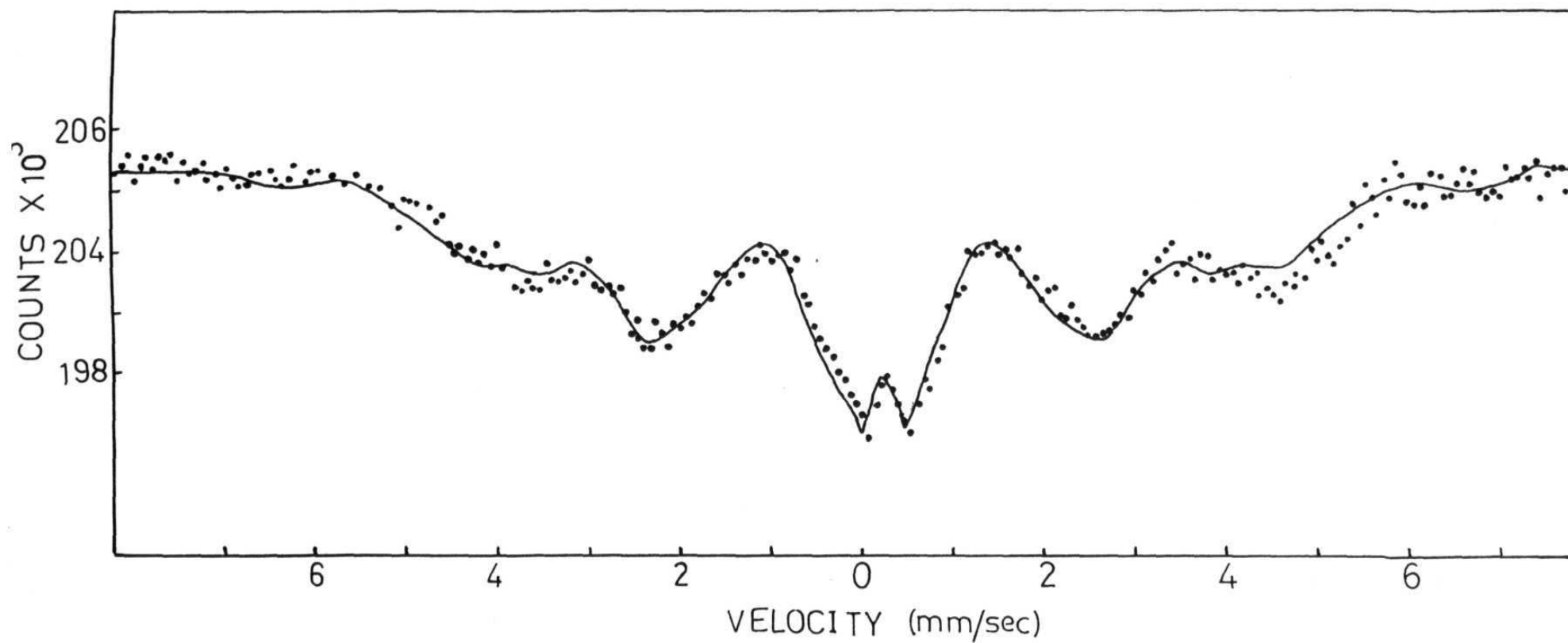
Fig.3.15 Mössbauer spectrum of $Fe_{0.9}Ga_{0.1}BO_3$ at 296 K. The solid line is the composite theoretical spectrum using Window's method [20].
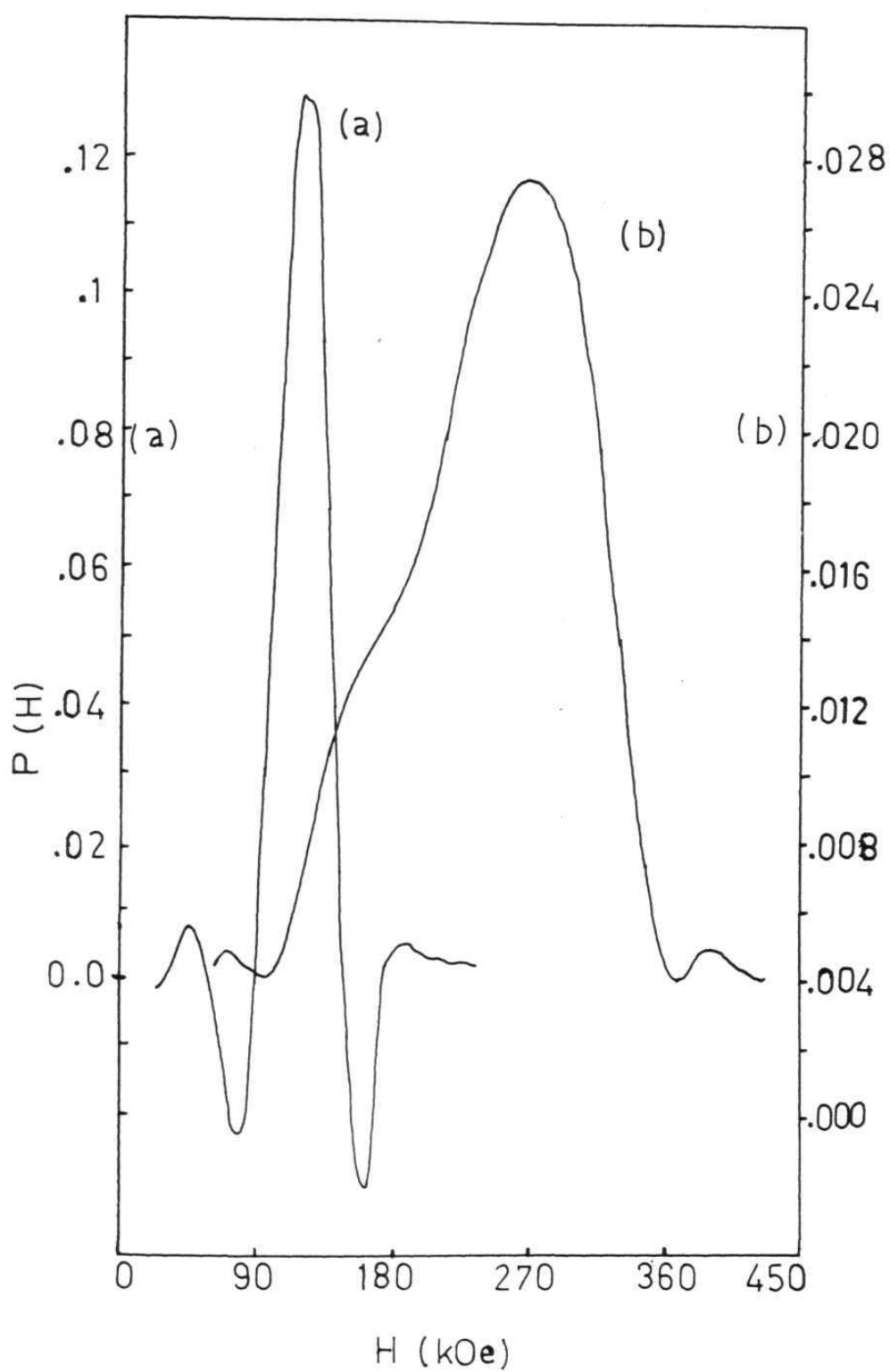
Fig.3.16 Hyperfine-field distribution P(H) of

(a) FeBO$_3$ at 348.5 K and

(b) Fe$_{0.9}$Ga$_{0.1}$BO$_3$ at 296 K.

T_c using this method of analysis were not successful indicating cluster formation leads to superparamagnetism and hence time dependent relaxation phenomena become important close to T_c.

It was found that the line profiles of the solid solution $Fe_{.9} Cr_{.1} BO_3$ could not be closely reproduced particularly in the central portion of the spectrum using either of the expressions based on the relaxation emchanisms viz., eqs. 2.22 or 2.26. The influence of substitution by another magnetic ion with a different spin state such as Cr^{3+} has always resulted in observations not well accounted. For instance (i) partial Cr^3 substitution of Fe^{3+} in $CaFe_2O_4$ led to several magnetic phases in equilibrium with each other [40], (ii) Cr^{3+} substituted $LiFeO_2$ shows anomalous susceptibility behaviour [41], (iii) a theoretical analysis predicts a sign reversal for the superexchange interaction parameters I(Fe, Cr) as a function of θ the super exchange angle [42], (iv) for certain compositions of $(Fe_{1-x} Cr_x)_2O_3$, the reduced field vs reduced temperature plots show quite unexpected results [43], (v) the anomalous spectra showing relaxation effects in the (Cr_2O_3/Fe_2O_3) in Al_2O_3 showed the existance of cross-spin relaxation [44].

Compositional dependence studies in the solid solution of $FeBO_3$-$CrBO_3$ shows competition between the two related

structures resulting in a weakly ferromagnetic to antiferro-magnetic interaction as one goes from iron rich to chromium rich composition. Although the overall profiles for the Cr^{3+} substituted $FeBO_3$ could be simulated with similar relaxation times, agreement in the central portions of the spectra were found to be poor. It may also be mentioned here that the results of the Mössbauer measurement, are treated here assuming a two level problem with regard to the spin states although for Fe^{3+}, $S = 5/2$. But the observed anomaly cannot be ascribed simply to this approximation only as the line profiles obtained in this two cases are closely similar [36,45].

3.4. Conclusions

Mössbauer study of $FeBO_3$ and the solid solutions $Fe_{0.9} Ga_{0.1} BO_3$, $Fe_{0.9} Al_{0.1} BO_3$ and $Fe_{0.9} Cr_{0.1} BO_3$ shows that their Curie temperatures are 352, 319, 317 and 335 K respectively. The reduced hyperfine field follows the Brillouin behaviour for $S = 5/2$ when plotted against reduced temperature. A static model assuming hyperfine field distribution due to different coordinations such as the one put forward by Coey [16] is found to be inadequate in explaining the spectra measrued close to T_c in these cases. It is found that the relaxation models well account for the profiles close to T_c.

Estimates of activation energies for the spin-flip have been found to be 9.93×10^{-13} erg/degree and 5.87×10^{-13} erg/degree for $Fe_{0.9} Al_{0.1} BO_3$ and $Fe_{0.9} Ga_{0.1} BO_3$ respectively. In the parent material viz., $FeBO_3$ relaxation effects are important only very close to T_c i.e 1^O below T_c. In the solid solutions relaxation effects dominate even 15° below T_c. It is found necessary to include η the order parameter signifying a differentiation in the probabilities of different spin states and a partial order, in the line-shape expression for simulating spectra close to experimentally observed results. The results show that the superparamagnetic relaxation effects due to the presence of clusters produced by substitution of magnetic by non-magnetic ions are important. Evidence for the presence of clusters is obtained by obtaining a distribution in the hyperfine field by a model independent approach due to Window [20] in analysing the spectra. Simple relaxation models have been found to be inadequate in fully reproducing the experimental spectra close to T_c for $Fe_{0.9}Cr_{0.1}BO_3$. The possible reasons for this have been pointed out in the light of experimental and theoretical observations in Cr^{3+} substituted systems in literature.

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5. Ref. 23, p.68.

A MÖSSBAUER STUDY OF HYPERFINE
INTERACTIONS IN THE BOROFERRITE
$Fe_{3-x}Ga_xBO_6(x=0, 0.12)$†
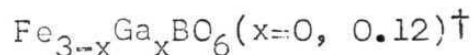
Abstract

Fe_3BO_6 and 4% Ga^{3+} substituted Fe_3BO_6 have been found
to undergo spin-reoreientation at 418 and 403 K respectively.
The hyperfine field in the vicinity of spin-reorientation
temperature (T_{SR}) shows no hysteresis effects either in
Fe_3BO_6 or in $Fe_{2.88}Ga_{0.12}BO_6$ inspite of being a first order
phase transition as shown by the change in the quadrupole
splitting. A comparison of our results has been made with
those reported for $\alpha-Fe_2O_3$. The reduced hyperfine field vs
reduced temperature in the case of Fe_3BO_6 and $Fe_{2.88}Ga_{0.12}BO_6$
shows that 8d site follows the Brillouin curve for S = 5/2
closely unlike the 4c site which shows consistently higher
values than expected for S = 5/2 and requires inclusion of
the biquadratic exchange term j/J = 0.015. The critical
exponent β, for the two sites show a 'splitting'. The
Mössbauer spectrum of $Fe_{2.88}Ga_{0.12}BO_6$ far away from T_c is
simulated using Coey's model and an exchange constant $J \sim 10$ cm^{-1}
has been evaluated.

4.1. Introduction

Study of magnetic interactions of the order-disorder type where one magnetic structure loses its stability and a new structure with a different magnetic symmetry becomes stable is of considerable theoretical and experimental interest [1-3]. Among the borates Fe_3BO_6 happens to be the only system exhibiting spin-reorientation and has been studied in some detail both by magnetic as well as Mössbauer measurements [4-6]. However these studies show differences in their observations and conclusions [5-7]. Further, two aspects, (i) the possible hysteresis effects suggested on the strength of microscopic models to explain spin-reorientation and (ii) the effect of substitution have not been so far investigated in this system. We report here the Mössbauer measurements on Fe_3BO_6 and $Fe_{2.88}Ga_{0.12}BO_6$ in the temperature range 77-518 K and compare our results with those of different workers on related systems such as α-Fe_2O_3 where results of parallel studies are available An attempt is made to explain the differences in the hyperfine fields at the inequivalent sites on the basis of structural factors and account for the deviation from the Weiss molecular field theory by considering the biquadratic exchange interaction terms. Employing Coey's model for simulating Mössbauer

spectra of diamagnetically substituted systems information
on coordination sites, associated hyperfine fields and
exchange interaction are derived.

4.2. Experimental procedure and analysis of data

The reported preparation of Fe_3BO_6 uses Bi_2O_3 flux or
the ceramic technique [4,8]. Muller has reported the forma-
tion of Fe_3BO_6 as a stable intermediate in a slow formation
of $FeBO_3$ from B_2O_3 flux [9]. This procedure is adapted for
the preparation of Fe_3BO_6 as follows. Ferric nitrate (B.D.H)
and boric acid (B.D.H) were used as the starting materials.
Stoichiometric mixture of boric acid and ferric nitrate is
dissolved in warm deionised water with a 400% excess of
boric acid. The solution is slowly evaporated to dryness.
The dried material is mixed thoroughly with acetone and loaded
into a platinum crucible. The mixture is heated slowly at
$500^{o}C$ and kept at that temperature for 12 hrs. and finally
at $800^{o}C$ for 2 days. After cooling to room temperature the
product is dissolved in hot water to remove excess B_2O_3.
After filtration the product is dried under vacuum. For the
substituted compound, required amount of gallium was taken
as Ga_2O_3 (Koch–Light Labs) and was converted to the nitrate
by dissolving in nitric acid and subsequently the ferric

nitrate and boric acid solutions were added. The subsequent steps were the same as described above. The ir spectra of both the compounds were found to agree well with the spectrum reported for Fe_3BO_6 [8]. Mössbauer spectra showed no contribution due to iron oxide or any other species. The powder X-ray diffractograms confirmed the formation of the compounds and absence of impurities. Mössbauer spectra were recorded as described earlier (section 2.1.1).

An estimate of η, the asymmetry parameter, Θ and ϕ the Euler angles giving the orientation of the electric field gradient (e.f.g) relative to the H_{eff}, the hyperfine field and $R = e.f.g/H_{eff}$ were obtained by comparing the experimental line positions with the theoretical plots similar to those described by Kundig [10a]. A computer programme based on this method is used for the purpose of analysing the line positions [10b]. R was then varied to get the theoretical line positions that matched with experimental within $\pm$ 0.04 mm/sec. Knowing H_{eff} from experimental positions e.f.g. was calculated from the value of R.

4.3. Results and discussion

The Mössbauer spectra of Fe_3BO_6 were recorded in the temperature range 77–520 K. The spectra recorded at 77K and room temperature show close similarity with those reported for the single crystal [4]. Fe_3BO_6 is known to have iron in two inequivalent sites in an orthorhombic unit cell [11]. In the low temperature spectrum the two hyperfine spectra arising due to the inequivalent sites overlap considerably unlike in the case of spectra measured at room temperature and above as shown in Figure 4.1. The higher temperature spectra show good resolution enabling easy identification of the two sextets with relative intensities in the ratio 2:1. The spectra recorded close to the spin reorientation temperature (T_{SR}) both above as well as below are reproduced in Figure 4.2 for comparison. The spin reorientation could be identified by the change in the splitting of the first and the last pairs of lines for both the sites and is found to occur at 418 K. The transition is found to be abrupt and takes place within 1° range. The T_{SR} value obtained is slightly higher than the value reported by susceptibility measurements viz., 415 K [4,12]. These spectra were analysed for hyperfine parameters viz., isomer-shift, quadrupole split and hyperfine field for the two sites from the line
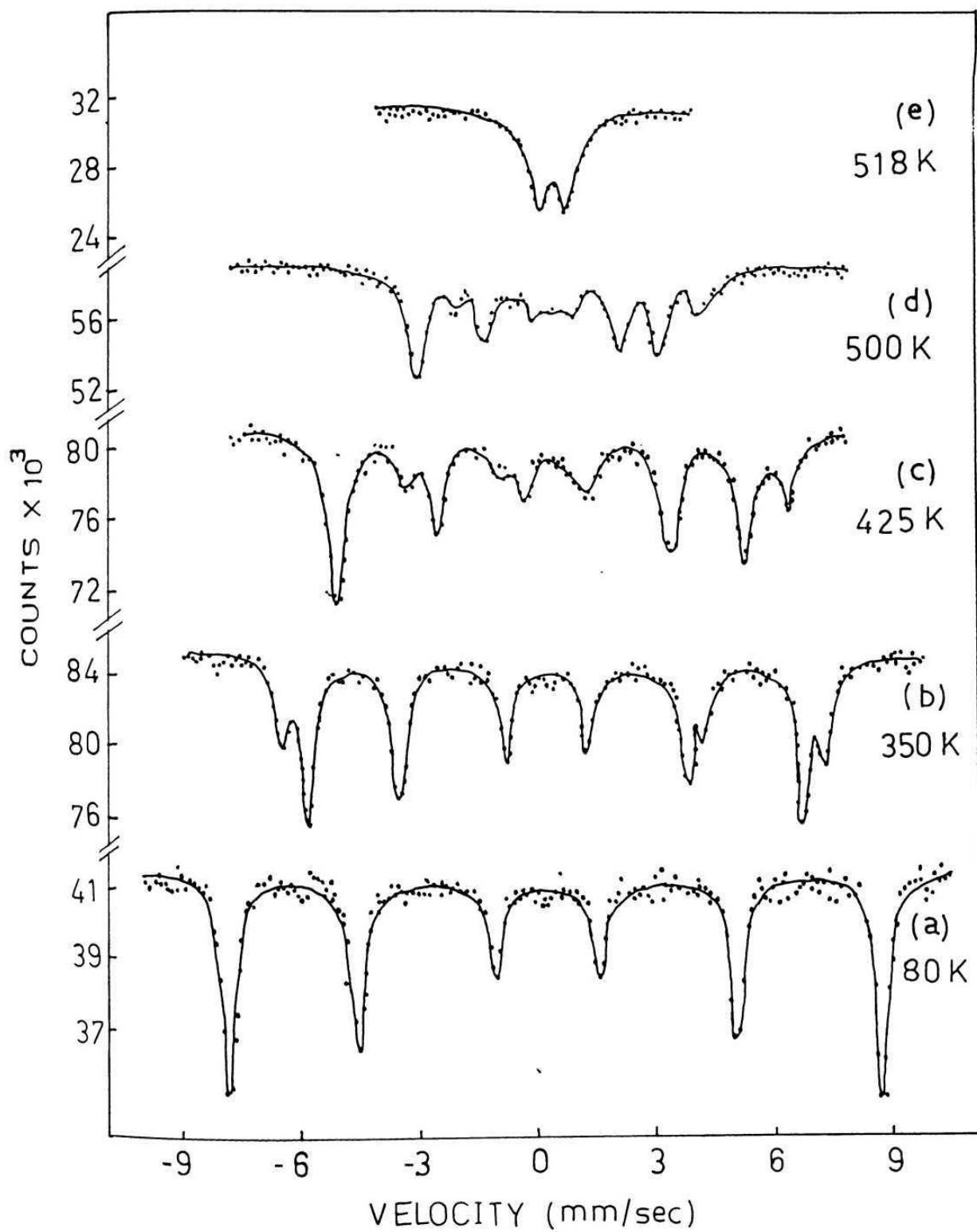
Fig.4.1 Mössbauer spectra of Fe_3BO_6 from 80 to 518 K.
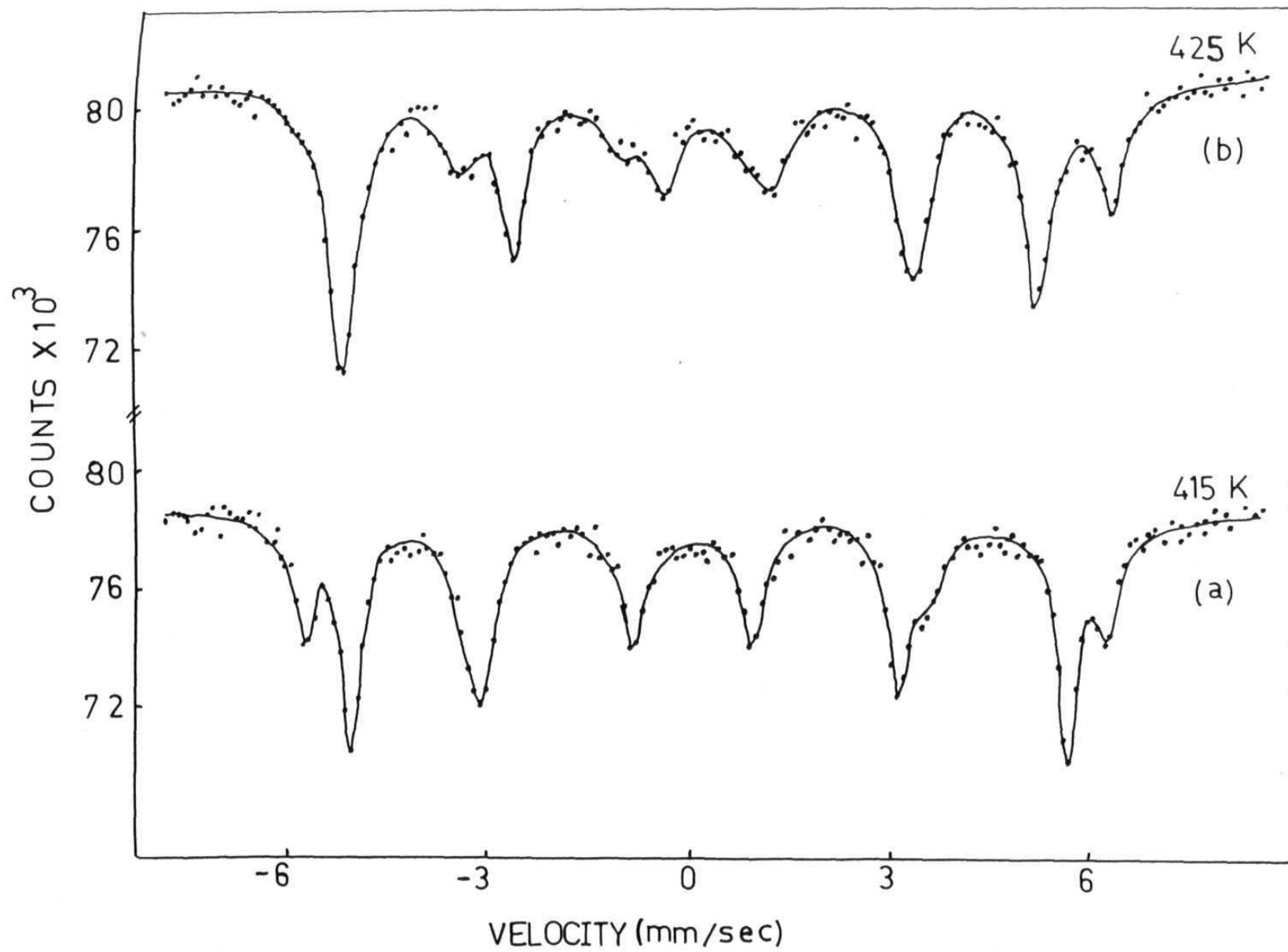
Fig.4.2 Mössbauer spectra of Fe_3BO_6 (a) below and (b) above T_{SR}.

positions as described in the experimental section and are given in Table 4.1. Further, the spectra were recorded below and above T_{SR} by heating and cooling the sample in a cyclic manner. It was found that the spectra could be fully reproduced for a given temperature irrespective of the heat treatment. This observation shows that Fe_3BO_6, unlike $\alpha-Fe_2O_3$ [2,13] does not show any thermal hysteresis behaviour. The variation in the isomer shift, quadrupols splitting and the hyperfine field as a function of temperature in the vicinity of T_{SR} are shown in Figure 4.3. The variation of $H_{eff}(T)$ vs T when extrapolated to $H_{eff}(T) = 0$ gave a Curie temperature of 518 K. This value is verified by the observation of a paramagnetic spectrum resulting from the collapse of the hyperfine spectrum at this temperature (Fig. 4.1). The Curie temperature thus determined is found to be significantly higher than 508 K reported from susceptibility measurements [4].

The plot of reduced hyperfine fields $H_{eff}(T)/H_{eff}(0)$ for the two sites as a function of reduced temperature is given in Figure 4.4. It is found that one of the two sites viz., (8d) followed a behaviour close to that predicted by the Brillouin function based on Weiss molecular field theory [14]. On the other hand the 4c site showed consistently higher values of $H_{eff}(T)/H_{eff}(0)$ for the reduced hyperfine

Table 4.1. Experimental values of ε and q.s. obtained from line positions below and above T_{SR}.

Site	T(K) (±0.5)	θ	ε(mm/sec)* (±0.04)	Q.S(mm/sec) (±0.04)
8d	350	90	-0.53	-0.53
	425	0	+0.79	-0.42
4c	350	90	-0.35	-0.35
	425	0	-0.98	+0.49

* $\varepsilon = \Delta_{12} - \Delta_{56}$ where Δ_{12} and Δ_{56} are the splittings between lines 1, 2 and 5, 6 respectively.
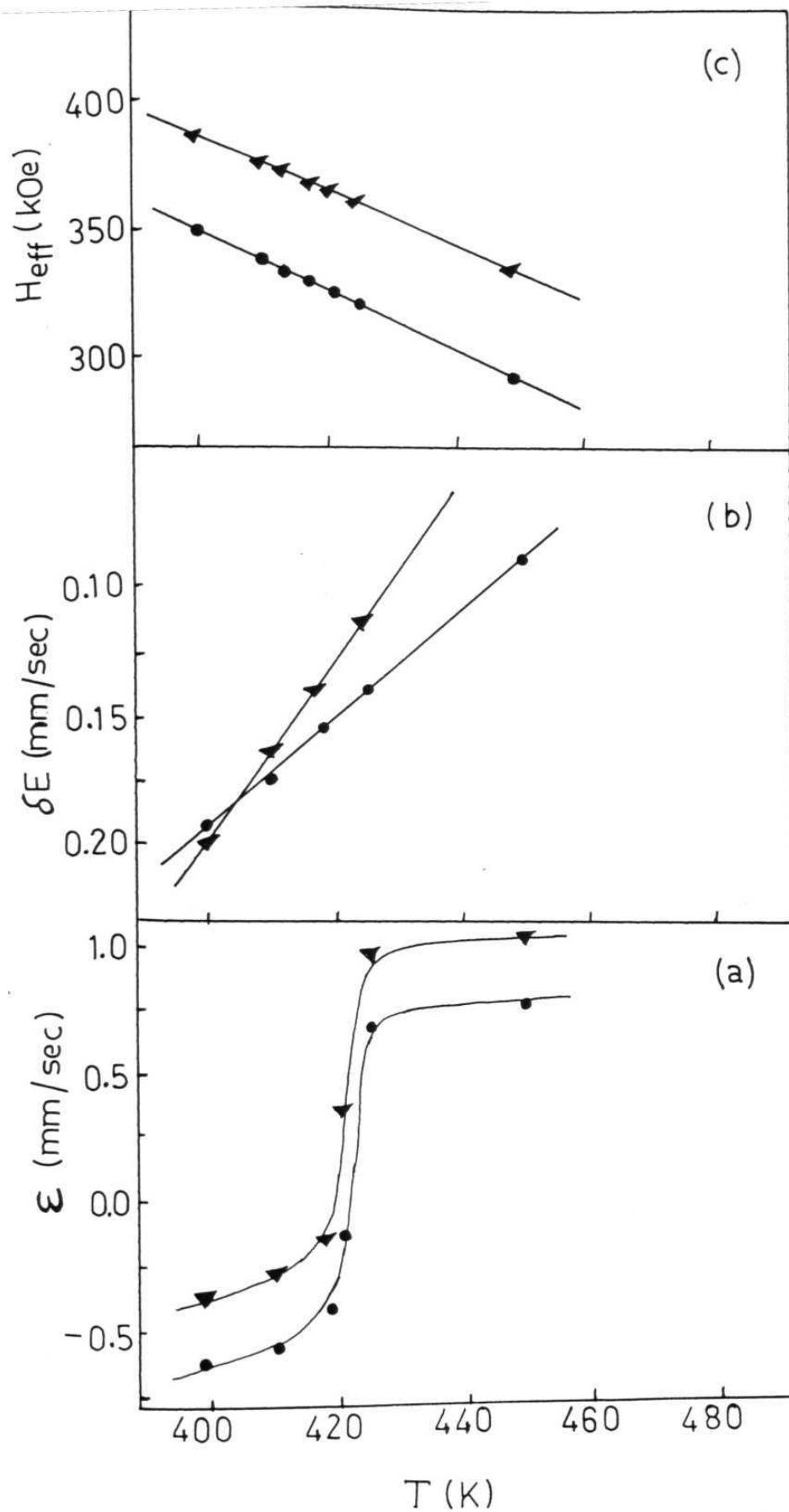
Fig.4.3 Plots of (a) ε (where $\varepsilon = \Delta_{12} - \Delta_{56}$) (b) Isomer-shift relative to ^{57}Co/Rh and (c) Effective magnetic field (H_{eff}) vs temperature in the vicinity of T_{SR}. • and ▼ are the experimental points for the 8d and 4c sites respectively.
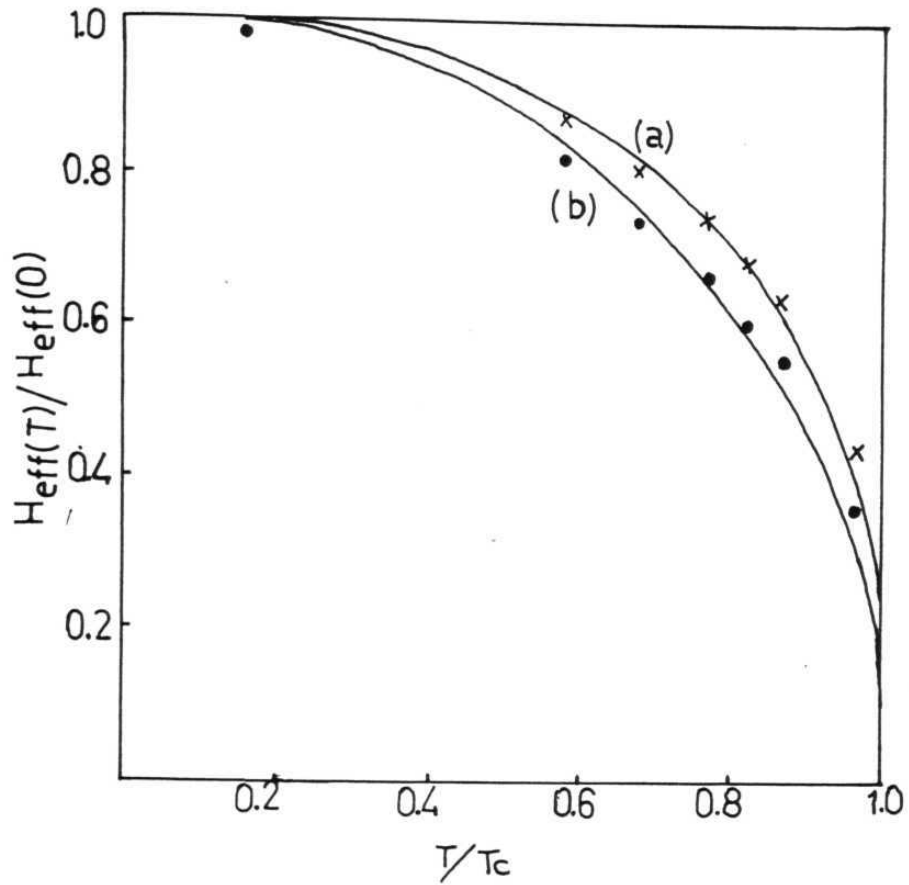
Fig.4.4 Reduced hyperfine field vs reduced temperature in the
case of Fe_3BO_6. Solid spheres and crosses are experimental
points for the 8d and 4c sites respectively. Solid line
(a) is the theoretical Brillouin curve for S = 5/2 and
(b) for S = 5/2 including biquadratic exchange
j/J = 0.015.

field with a significant deviation from the Brillouin curve
as shown in Figure 4.4. Such a deviation can be explained
on the basis of a biquadratic contribution to the linear
isotropic exchange interaction as suggested by Rodbell et al
[15]. The theoretical Brillouin Curve including the biquad-
ratic exchange term with a j/J value of 0.015 is found to
show close agreement with experimental data (Fig. 4.4).

An analysis of the temperature dependence of the hyper-
fine field can give information about the behaviour of the
system at the critical temperature T_c. At temperatures close
to T_c, $H_{eff}(T)/H_{eff}(0)$ will follow the power law $H_{eff}(T)/$
$H_{eff}(0) = D(1-T/T_c)^{\beta}$ and thus one can get the critical exponent
β for the two sites. The double log plots of $H_{eff}(T)/H_{eff}(0)$
vs $(1-T/T_c)$ are given in Figure 4.5. The values of β obtained
from the slopes of the plots were found to be 0.27 and 0.31
for the 4c and 8d sites respectively.

The Mössbauer spectra for the substituted sample
$Fe_{2.88}Ga_{0.12}BO_6$ were recorded from 77 to 494 K. Represen-
tative spectra are shown in Figure 4.6. The lines of the
two hyperfine spectra observed for the solid solution were
more broad and as a result showed less resolution of the
sextets. This sample is also found to show spin reorientation
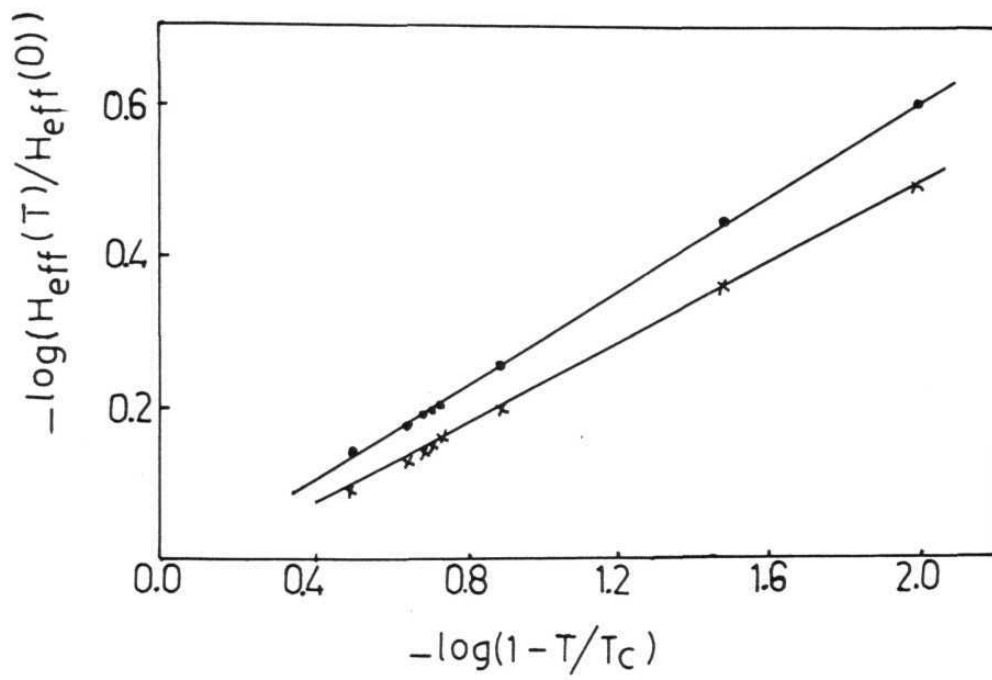
Fig.4.5 Double log plots of $H_{eff}(T)/H_{eff}(O)$ vs $(1-T/T_c)$ for Fe_3BO_6. Solid spheres and crosses are experimental points for 8d and 4c sites respectively.
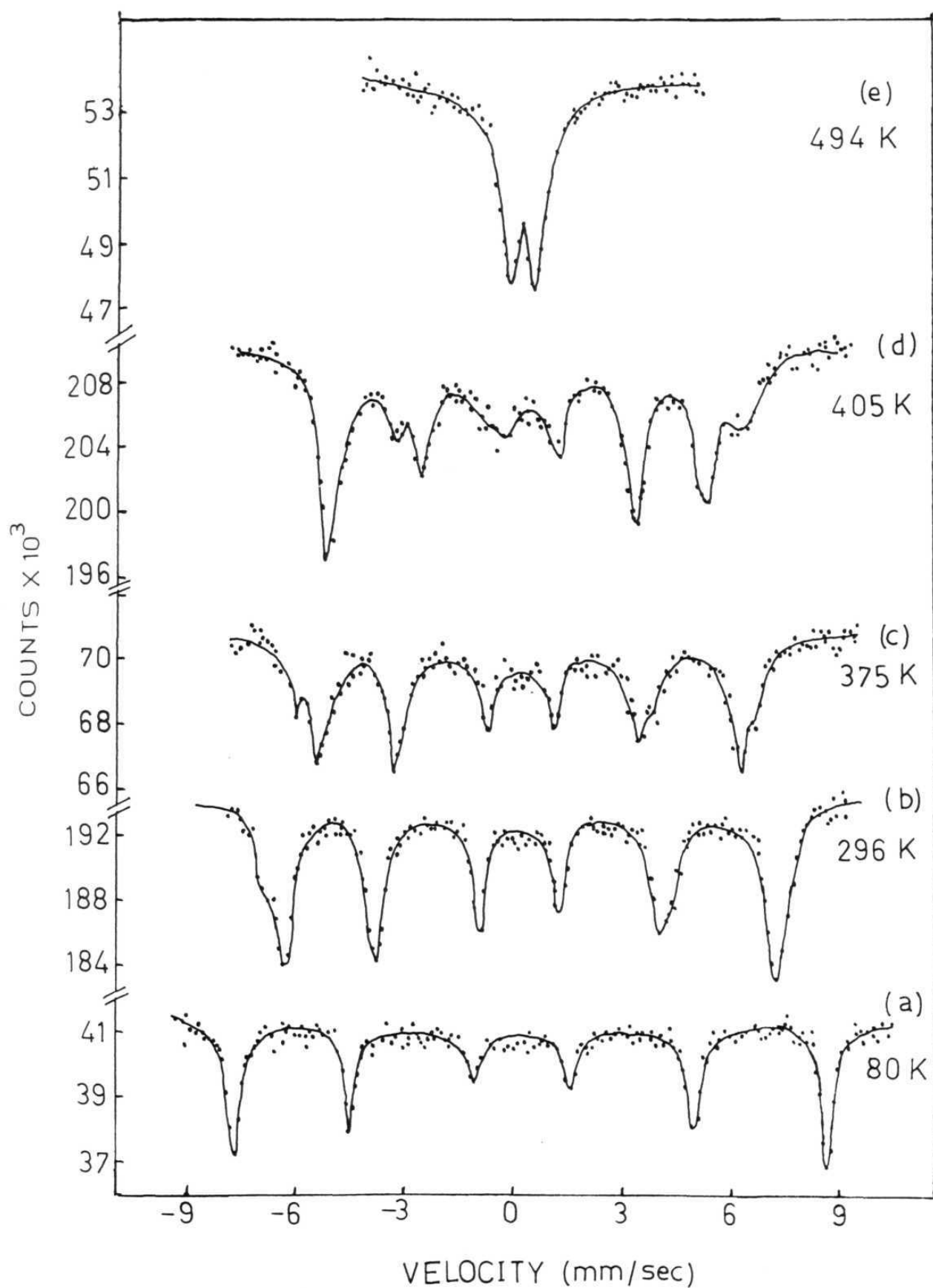
Fig.4.6 Mössbauer spectra of $Fe_{2.88}Ga_{0.12}BO_6$ from 80 to 494 K.

at 403 K as shown by significant changes in the Δ_{12} and Δ_{56} values for the two sites. .The temperature dependence of the hyperfine parameters showed a trend similar to that exhibited by the parent material (Fig. 4.3). $H_{eff}(T)$ vs T is found to lead to a Curie temperature of 494 K for the substituted sample compared to 518 K for the parent material. Further a plot of reduced magnetic field vs reduced temperature showed that the nature of the Brillouin plots did not significantly alter compared to the plots for the parent material and required inclusion of biquadrateic exchange term with a j/J value of 0.015 for the 4c site.

4.3.1. Nature of spin-transition

The phenomena of spin reorientation can proceed in two ways. (a) The magnetic moment vector may rotate continuously and coherently from the x-axis to the z-axis. (b) The magnetic moment vector jumps discontinuously from x-axis to the z-axis. The former is explained by the Landau's theory of second order phase transition. On the other hand, process (b) arises from the local first order phase transition. Kamzin and Bokov carried out detailed single crystal Mössbauer studies of Fe_3BO_6 in the temperature range 395–416 K in the presence of applied magnetic field and established

first order phase transformation for spin reorientation on the observation of coexistence of the two magnetic phases [16]. Consequently it is quite interesting to compare the behaviour for Fe_3BO_6 with that of $\alpha-Fe_2O_3$ as they show several differences in spite of both being shown to follow a first order transformation. For example in $\alpha-Fe_2O_3$, spin reorientation is accompanied by a break in the plots of isomer shift and hyperfine field vs temperature [17]. Further a thermal hysteresis behaviour is observed over a temperature range of 15° around T_{SR} and was explained on the basis of first order transition accompanied by a phase transformation [2]. Our results on Fe_3BO_6 show neither a break in the hyperfine field, isomer-shift vs temperature plots (Fig. 4.3) nor a thermal hysteresis behaviour and the transition occurs within 1°.

It is found that the line positions of the Mossbauer spectra recorded below and above T_{SR} could be reproduced using the Hamiltonian which includes the magnetic and quadrupolar interactions [10a, 10b] only if it is assumed that the magnetic field lies perpendicular and parallel to the principal axis of the electric field gradient tensor respectively (Table 4.1). Earlier studies show that the easy axis is parallel to 100 and 001 axis respectively below and

and above T_{SR} [4]. These results are consistent with our ana-
lysis if it is assumed that the principal e.f.g. axis lies
along the z-axis. Table 4.1 shows that the ε value correspond-
ing to $\Delta_{12} - \Delta_{56}$ does not change to simply -2ε which happens
to be the case for example in $\alpha\text{-Fe}_2\text{O}_3$ implying only an orien-
tation change in the latter. This clearly indicates a change
in the quadrupole splitting (Table 1) during spin reorientation.
Further, for the 4c site it is also found that a change in the
sign of e.f.g. is required to reproduce the line positions of
the hyperfine split spectrum. Our own results in this regard
are in general agreement with the preliminary report of Bayukov
et al but the signs in all the cases are just the reverse [18].
These results clearly show that spin reorientation is accom-
panied by structural change. However as isomershift is not
a sensitive parameter for $3d^5$ systems the structural change
is not shown up in isomer-shift vs temperature plot. The non-
observance of a break in the hyperfine field vs temperature
may be explained on the basis of relative contributions to
the hyperfine field from different sources. The effective
field at the nucleus is given by

$$H_{eff} = H_C + H_D + H_L \qquad \ldots (4.1)$$

where H_C is the contact field, H_D, the dipolar field and H_L

arises due to the orbital magnetic moment of the 3d electrons. H_C the contact field is the largest contribution and arises from spin density at the nucleus (~ -500 kOe). An estimate of the dipolar field may be obtained from the relationship

$$H_D = -2\mu_B q < \sum_S S \frac{3\cos^2\theta - 1}{r^3} >$$

$$= -\mu_B q \qquad\qquad \dots (4.2a)$$

for the case when the magnetization is along C axis and

$$H_D = \frac{1}{2} \mu_B q \qquad\qquad \dots (4.2b)$$

when the magnetization is perpendicular to the C-axis [17]. q in (4.2) may be obtained from quadrupole splitting as the values of the quadrupole moment is known. Thus using $Q = 0.3 \times 10^{-24} cm^2$ [17] the values of H_D obtained for the two sites below and above T_{SR} are given in Table 4.2. Thus spin reorientation involves a change in the hyperfine field equal to 13.7 kOe and 14.1 kOe for the 4c and 8d sites respectively. In the case of $\alpha-Fe_2O_3$ a change in the hyperfine field during spin transition is attributed to the dipolar field assuming the field due to spin-orbit coupling (H_L) to be negligible [13]. The absence of any such change in the field at T_{SR} in the present system thus implies that there is

Table 4.2. Estimates of dipolar contributions
for the 4c and 8d sites below and
above T_{SR}.

Site	T(K) (±0.5)	H_D(kOe) (±0.4)
8d	350	+5.4
	425	-8.6
4c	350	+3.6
	425	-10.1

a significant orbital contribution which cancels the contribution due to the dipolar term.

The microscopic models put forward for explaining reorientation of the easy axis of magnetization are based on the dependence of the thermodynamic free energy (F), on Θ, the angle between $<S>$ and the Z-axis which is of the form [1].

$$F = F_\Theta + A_o(T) + A_2(T)\sin^2\Theta + A_4(T)\sin^4\Theta \qquad \dots (4.3)$$

where $A_2(T)$ and $A_4(T)$ represent the second and fourth order single ion anisotropy contributions respectively. It is shown that in the case of spin jump mechanism, $A_4(T)<0$ and associated hysteresis effects are observable. To our knowledge the only attempt of correlation of the hysteresis width to any measurable parameter is due to Thomas and Stavely who pointed out that the loop area is related to the difference in the molar volumes of the two phases [19]. This has also been substantiated by experimental observations [20]. Thus the non-observance of hysteresis in our case despite the transformation being first order may be attributed to small changes in the molar volume during the transformation.

4.3.2. Temperature dependence of hyperfine field

The magnetic inequvalence of the 4c and 8d sites can be understood in terms of the stronger metal-metal interaction of the 8d iron sites where the concerned octahedra are edge-sharing compared to the 4c iron sites in which the octahedra are only corner sharing (Fig. 4.7). The deviations from the Weiss molecular field theory can be successfully accounted for by including a biquadratic contribution to the linear isotropic exchange interaction of the form

$$J. \, S_a . \, S_b - j(S_a . S_b)^2$$

where $J>0$ and the magnitude of j can differ depending upon the superexchange interaction [21]. The theoretical curve including such an interaction is found to give close agreement with experimental data for 4c site for j/J value of 0.015. Similar values have been obtained for other systems with $S = 5/2$[21,22].

4.3.3. The critical exponents

Our values of β, the critical exponents for the two sites are close to those of Kamzin et al who also observe a 'splitting' in the β values [23]. Irshinskii and Cherepanov have stated that after applying correction to the field,
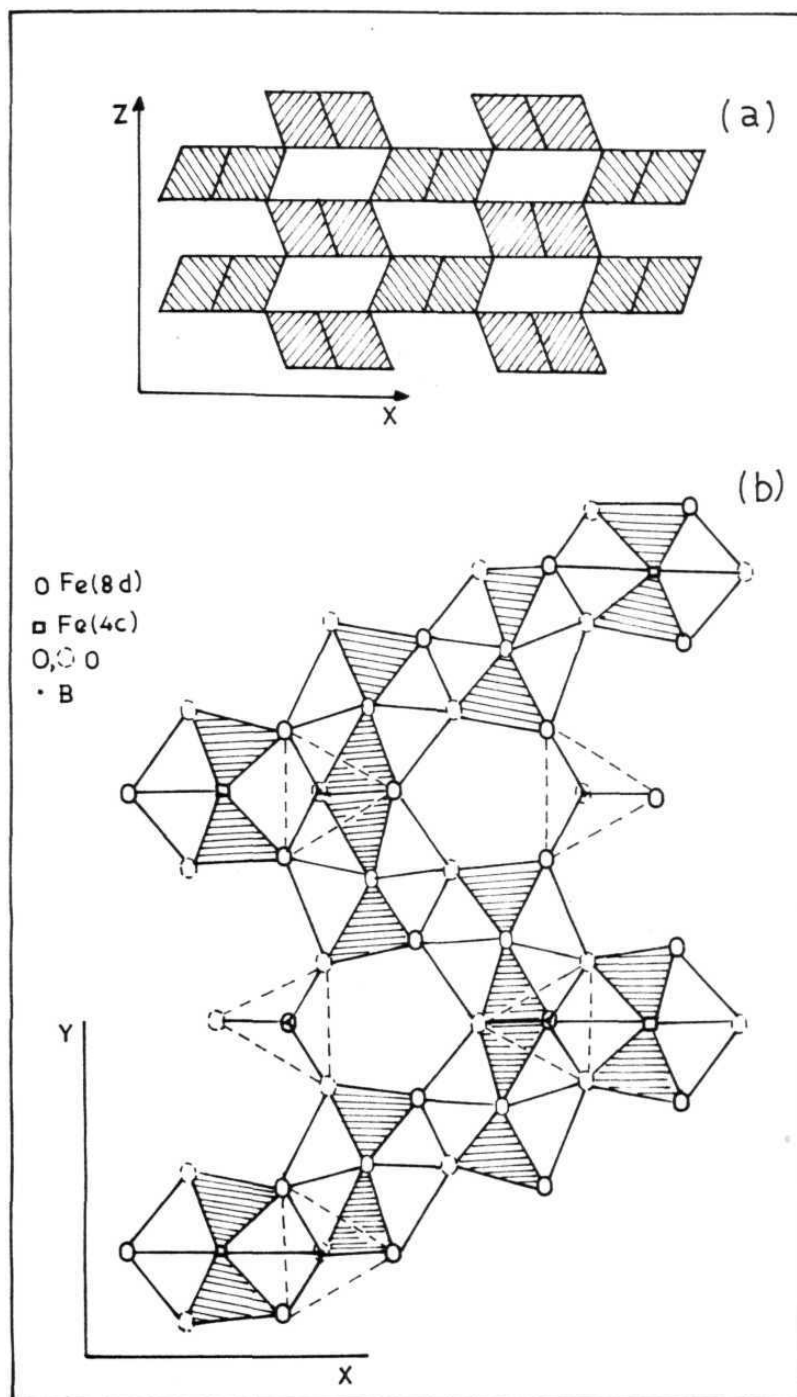
Fig.4.7 Schematic diagram of (a) FeO$_6$ octahedra in Fe$_3$BO$_6$ viewed along the y-axis contributing to interactions in the xz-plane; all the iron atoms occupy 8d sites and (b) viewed along z-axis; hatched portions depict planar ligands in the octahedra. O and represent O^{2-} ions above and below xy-plane respectively.

a single β value agreeing with that of Voigt and Ross based on magnetic measurements is obtained [7, 24]. It may be stated that although the line positions get shifted due to quadrupole interaction the splitting between the first and the last transitions is nott influenced and needs no correction for obtaining the internal magnetic field [2,17,24]. The 'split' in the β-values is not unreasonable in the case of Fe_3BO_6 as the extent to which the interaction of the two sites with the near neighbours are weakened by the linking non metal atoms differ significantly, resulting in a corresponding change in β which is known to depend on the dimensionality in the magnetic interaction.

4.3.4. Mössbauer studies of the substituted compound $Fe_{2.88} Ga_{0.12} BO_6$
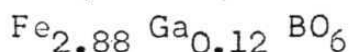
The temperature dependence of isomershift, quadrupole splitting and hyperfine field for the substituted system $Fe_{2.88} Ga_{0.12} BO_6$ is found to follow closely the behaviour of the parent material. Our results show that 4% substitution by the diamagnetic Ga^{3+} ion in Fe_3BO_6 leads to a decrease in the T_{SR} which is found to occur at 403 K compared to that of the parent occuring at 418 K. On the other hand the Curie temperature decreases as expected as the magnetic

interaction will be weakened by the presence of the non-magnetic ion. Different substitutents are known to influence the T_{SR} differently as illustrated by the reported observations presented in Table 4.3 [3,25-29]. To our knowledge the only attempt at rationalisation of the effect of substitutent on T_{SR} is due to Gratz and Nowotny [3]. These authors show that an enhancement or decrease in T_{SR}, can be explained in cases where a detailed knowledge of the crystalline electric field and molecular field parameters are available [3].

The Mössbauer spectra of 4% substituted sample show the following features. The room temperature spectrum, for example shows less resolved profile (Fig. 4.6). The spectra near the Curie temperature showed in contrast with that of parent material the simultaneous presence of paramagnetic with magnetic spectra as shown in Figure 4.8. The latter situation is complex for analysis for both the effects of hyperfine field distribution due to magnetic dilution as well as relaxation play a role. However considerable information can be elicited from the Mössbauer spectra of mixed crystals recorded away from T_c employing the model of Coey [30-32]. In this model a binomial distribution is assumed for calculating the probability of the possible near neighbour environments for a given coordination around the iron site, for a given

Table 4.3. Effect of substitution on spin reorienta-
tion behaviour in systems containing
Fe/R.E.

System	Effect of dopant on T_{SR}	Ref.
$(Ho_{1-x}Y_x)Co_2$	T_{SR} increases	3
$(Nd_{1-x}Y_x)Co_2$	T_{SR} decreases	3
$\alpha-(Fe_{1-x}Cr_x)_2O_3$ $(0.005<x<0.02)$	T_{SR} decreases	25
$Er(Fe_{1-x}Co_x)_3$ $(0<x<0.4)$	almost same	26
$(x>0.4)$	T_{SR} increases	
$\alpha-(Fe_{1-x}Al_x)_2O_3$ $(x = 0.048)$	T_{SR} decreases	27
$\alpha-(Fe_{1-x}Rh_x)_2O_3$	T_{SR} increases	28
$\alpha-(Fe_{1-x}Sn_x)_2O_3$	T_{SR} decreases	29
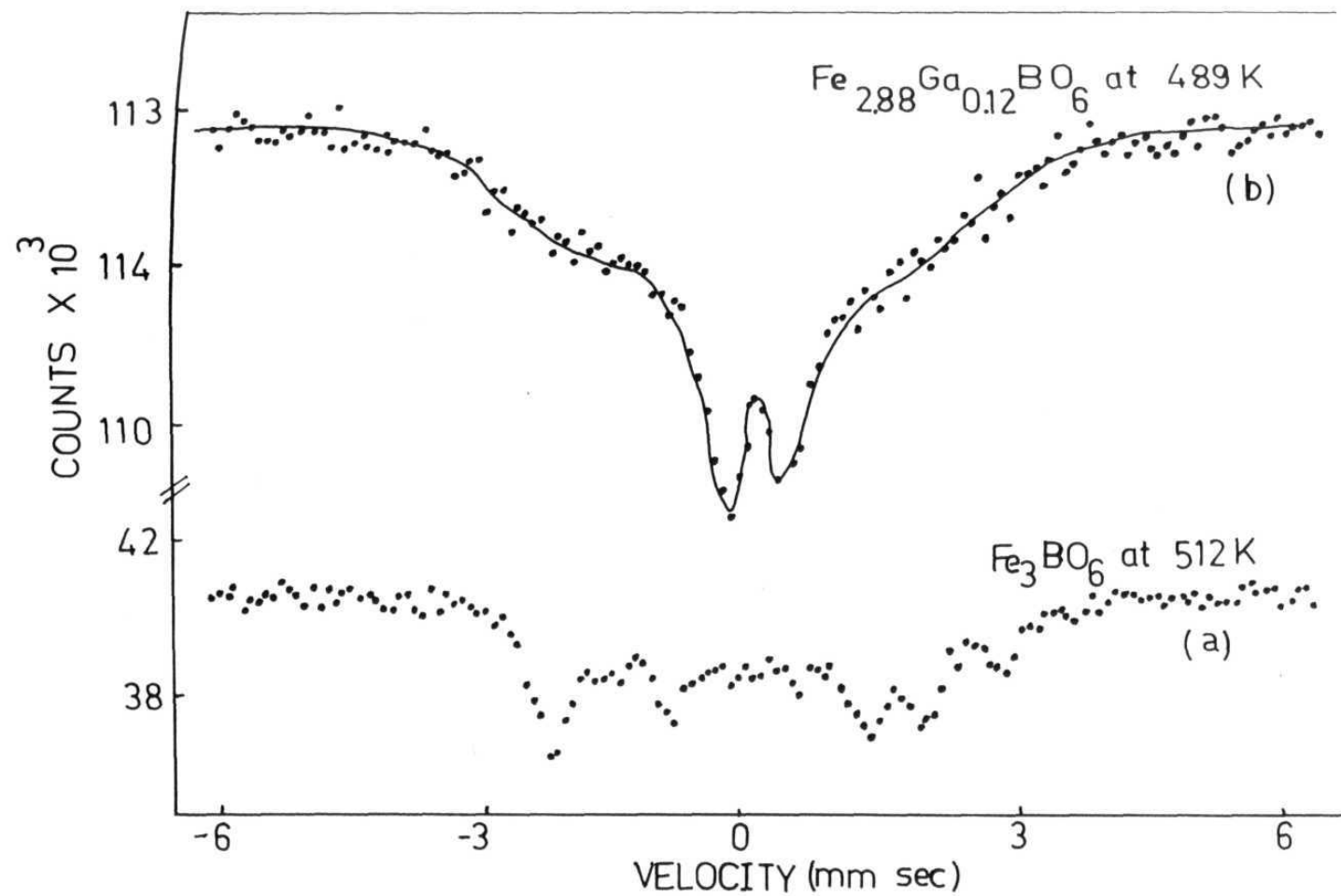
Fig.4.8 Mössbauer spectra of (a) Fe_3BO_6 and (b) $Fe_{2.88}Ga_{0.12}BO_6$ close to their Curie temperatures, 518 and 494 K respectively.

concentration of the non magnetic ion. The further details of analysing the spectra on the basis of this model are given in section 2.2.2. In the present case the Mössbauer site is assumed to be sorrounded by Z Fe^{3+} ions and $(N-Z)$ Ga^{3+} ions where $N = 6$. The original model does not take into account quadrupole interaction which can be introduced in the following manner. Line positions were first calculated assuming no quadrupole interaction. Subsequently the positions were shifted such that the resultant splittings of the lines will correspond with the observed orientation of the electric field gradient with respect to the magnetic field. The quadrupole splitting is then varied to get the best match. It is found that the spectrum simulated as discussed in section 2.2.2. for $\Upsilon = 0.7$ for $x = 0.04$ agreed quite well with the measured room temperature spectrum as shown in Figure 4.9. The match also explains the large line broademing due to different coordination sites brought about by substitution. The line widths for the substituted specimen for the outer— most lines were found to be ~ 0.65 mm/sec compared to ~ 0.35 mm/sec for the parent material supporting the applicability of the model for the present case. The probabilities of different coordinations and their resultant hyperfine fields are given in Table 4.4. The model assumes a random distri- bution of non—magnetic ions in the place of magnetic ions.
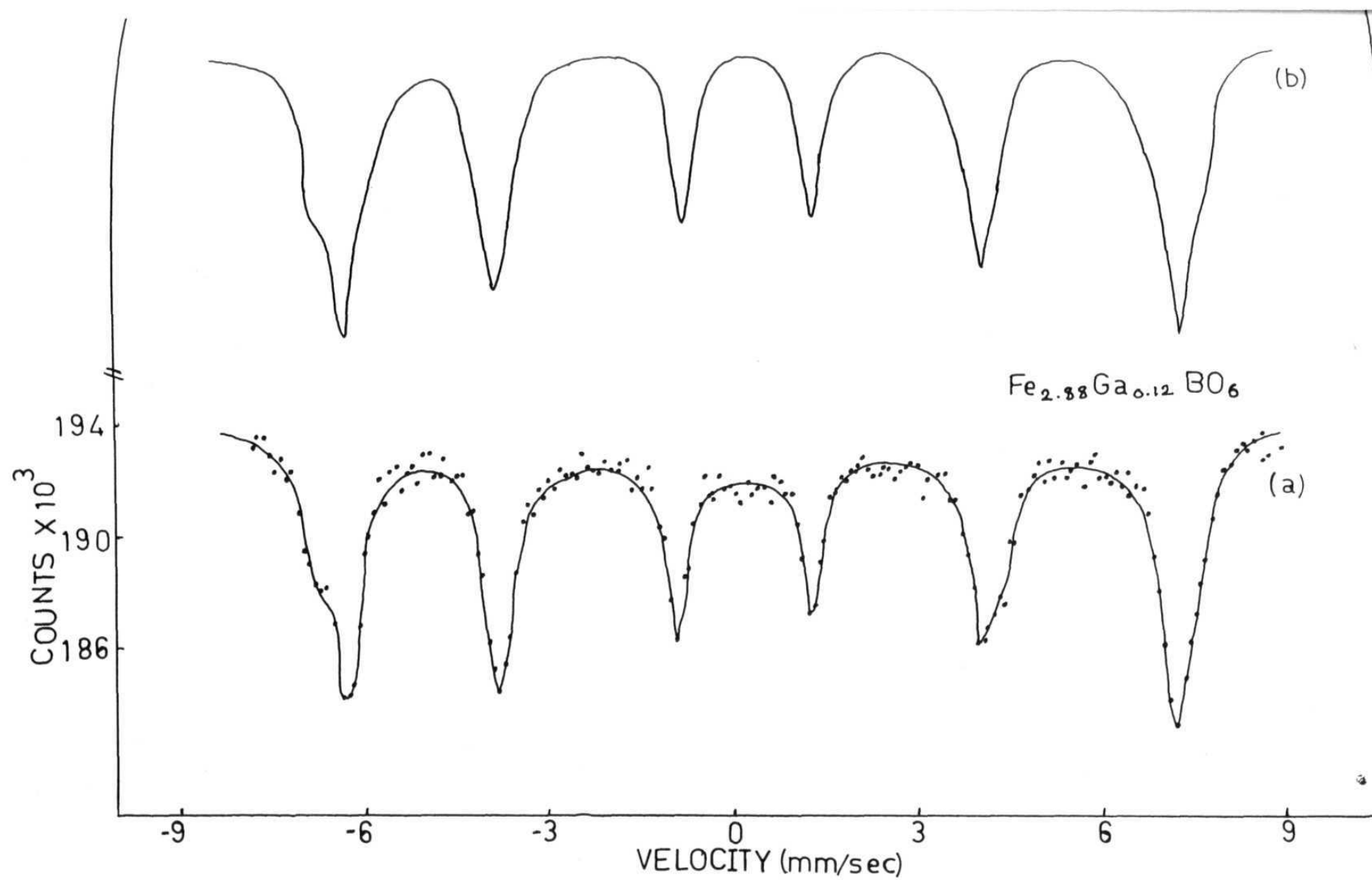
Fig.4.9 Comparison of (a) experimental Mössbauer spectrum at 296 K with (b) theoretical spectrum based on the random substitution model.

Table 4.4.   Nearest neighbour probabilities and the
corresponding fields for a random distri-
bution of two types of atoms in a lattice
with six nearest neighbours for x = 0.04.

Number of magnetic neighbours	Probability (%)	H_{eff} (kOe)	
		4c	8d
1	< 0.1	130.0	121.5
2	< 0.1	195.6	186.8
3	0.11	252.0	239.2
4	2.04	294.4	279.6
5	19.57	326.3	310.0
6	78.27	350.2	332.6

Thus agreement with theoretical spectrum also implies that Ga^{3+} ions show no preference between 4c and 8d sites. The value for which the theoretical fit gave a good match with experiment is found to be 0.7 and corresponds to an average J value of $\sim$10 cm^{-1}.

For materials with x < 0.5, the $\langle Z \rangle_{av}$, the average over different coordinations is given by $\langle Z \rangle_{av} = 6(1-x)$ for octahedral systems [27]. T_c for the solid solution is proportional to $\langle Z \rangle_{av}$ and the value thus obtained for x = 0.04 would correspond to 496 K. This is in good agreement with the experimentally determined value viz., 494 K.

4.4. Conclusions

Mössbauer measurements of hyperfine parameters close to T_{SR} shows no hysteresis effects unlike in the case of α-Fe$_2$O$_3$ although in both cases the spin-reorientation has been shown to follow first order. Thus, measurement of hysteresis effects alone cannot be considered conclusive in stating whether the reorientation takes place by first or second order mechanism. However, as is characteristic of first-order change, significant change in structure is indicated by the changes in the quadrupole interactions.

The temperature dependence of hyperfine field for the 8d site follows closely the Brillouin function for $S = 5/2$. The deviation of the 4c site from the Brillouin curve has been explained by including the biquadratic exchange interaction giving rise to $j/J = 0.015$. 4% substitution of Fe^{3+} by Ga^{3+} brings down T_{SR} from 418 to 403 K. It is found that Ga^{3+} has no site preference. Unlike in the case of experimental spectra close to T_c it is found that static model such as that of Coey can be employed for simulating the experimental spectra at temperatures far away from T_c. An exchange constant $J \sim 10$ cm^{-1} has been obtained on the basis of this model.

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PART - B

5.1. Introduction

Organic acids complex with transition metals and the rare earths with ease. Despite their long history significant amount of work on this subject appear even in current literature. The reasons are not far to seek. As for example, the carboxylic acids lend themselves to a comparative study of complexes of the same carboxylic acid with different metal ions, of different carboxylic acids with the same metal ion and of the transition metal ions with the rare earths in analogous situations[1,2]. Such a comparative study shows several revealing features. By way of illustration, we may cite examples mainly from the simple mono and dicarboxylic acids such as formic, acetic, malonic and maleic acids and transition metal ions such as Fe^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+} as some of our own studies pertain to systems closely related to these.

5.2. Structural features

Some of the distinguishing structural features in the transition metal complexes with organic acids are (1) one or more of the oxygen atoms, even in the case of mono carboxylic acids can coordinate to the metal ion, (2) depending on the

structure both intermolecular and intramolecular hydrogen bonding can occur which are revealed in the study of their crystal structures. In copper formate tetrahydrate (CuFTH), for instance, each copper atom is sorrounded by four oxygen atoms of four different formate ions in an approximately square planar configuration at a distance of 2.0 $\overset{o}{A}$, with two water molecules above and below at 2.36 $\overset{o}{A}$ (Fig. 5.1(a)). The remaining water molecules are hydrogen bonded either to the coordinated water molecule (O_{III}) or to the oxygen atom (O_{II}) of the COO$^-$ group [3]. On the other hand Fe(II), Zn(II) and Mn(II) give rise to isomorphous formates with structural features strikingly different from that of CuFTH (Fig. 5.1(b)) [4,5]. In these systems the metal ion occupies two crystallographically inequivalent sites, one coordinated to six carboxylic oxygens (site I) and the other by two carboxylic oxygens in trans position and four water molecules in a plane (site II) [4].

In the case of the next higher monocarboxylic acid in the homologous series viz., acetic acid, the transition metal ion Co^{2+} forms a simple acetate wherein the metal ion is coordinated to two -COO$^-$ groups and four water molecules with intermolecular hydrogen bonding between them (Fig. 5.2(a)) [6]. On the other hand in Cu^{2+} acetate monohydrate one

(a)

H_2O

(b)

M = Zn, Fe, Mn
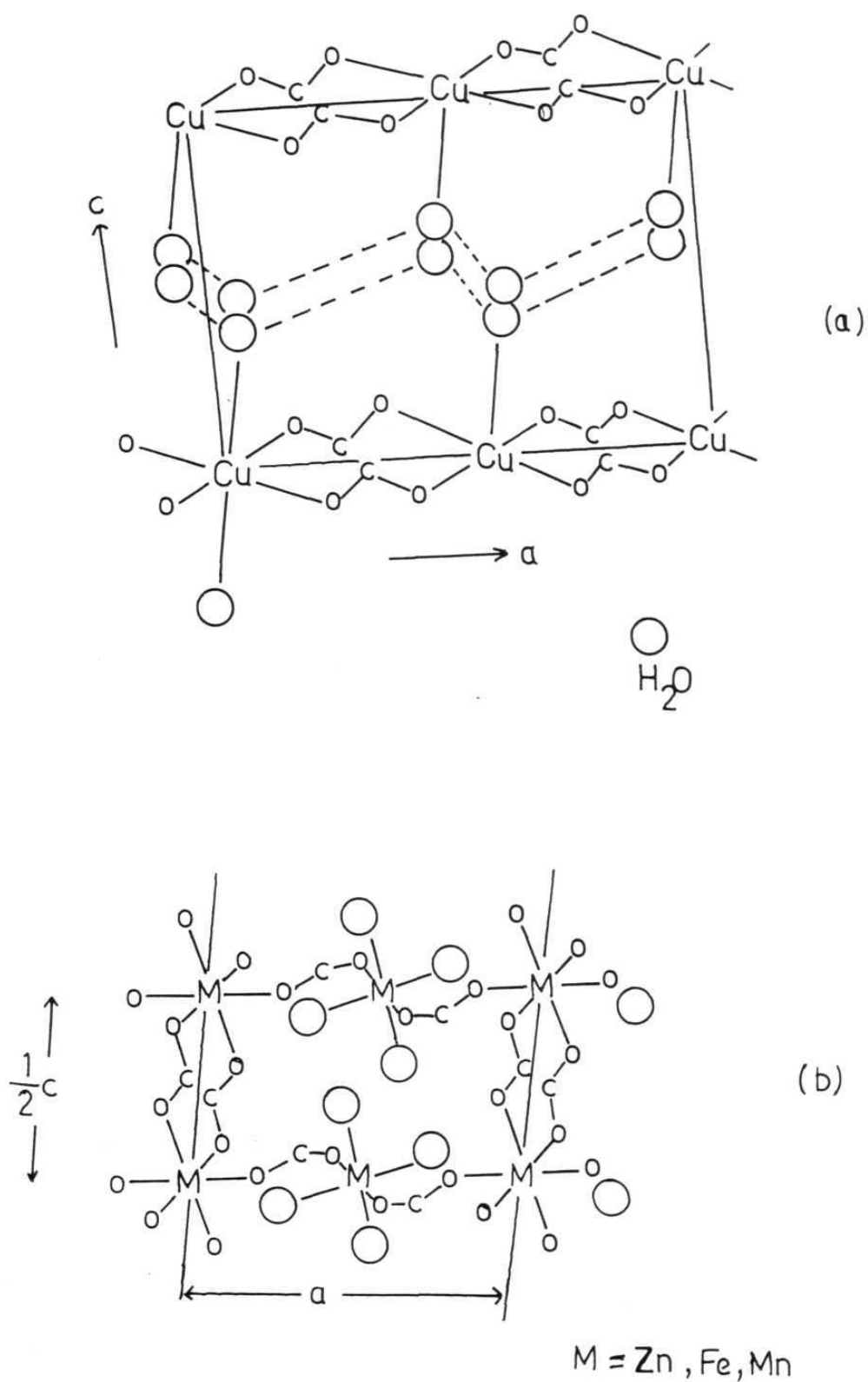
Fig.5.1 Crystal structures of (a) Cu(II) formate tetrahydrate and
(b) M(II) formate (M = Fe, Zn and Mn) dihydrate.
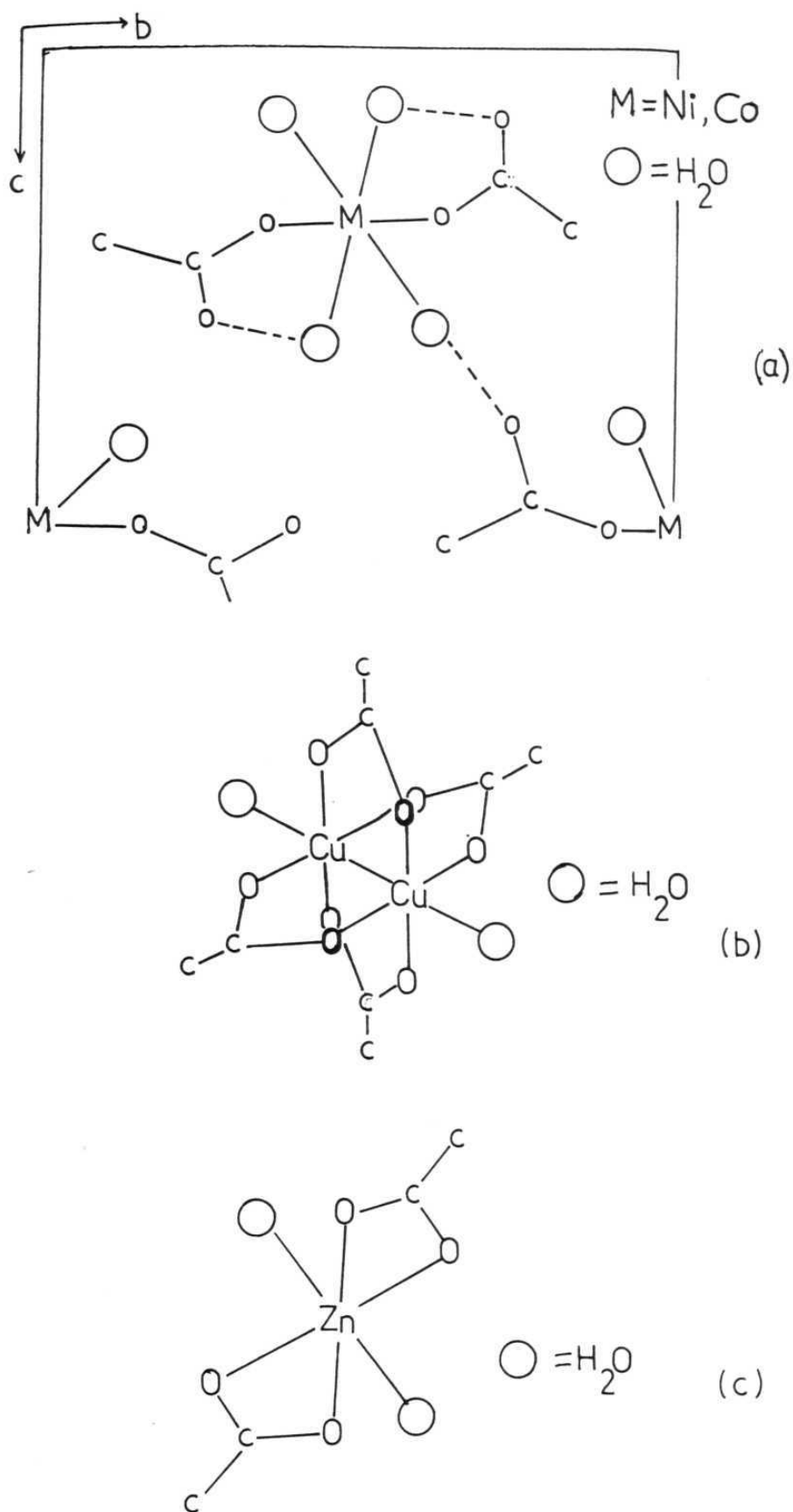
Fig.5.2 Crystal structures of (a) Co(II) acetate tetrahydrate
(b) Cu(II) acetate monohydrate and (c) Zn(II) acetate
dihydrate.

carboxylic acid group is coordinated to two metal ions
(Fig. 5.2(b)) [7]. Yet in another instance viz., zinc acetate
dihydrate, the ⊸COO⁻ group chelates with the metal ion forming
a four membered ring as shown in Figure 5.2(c).[8]. Similar
features have been observed in the higher members of the
monocarboxylic acid series [2].

The di and poly carboxylic acids exhibit additional
interesting features stemming from the fact that their disso-
ciation constants pK_a for the acid groups in the case of
higher members differ significantly, unlike the first dicar-
boxylic acid viz., oxalic acid, enabling formation of both acid
as well as normal complexes. For instance in the case of
Cu(II) oxalate two types of structures have been proposed on
the basis of magnetic studies (Fig. 5.3(a,b)). In both the
cases, both the carboxylic acid groups are coordinated to the
metal ion [9]. Fe^{2+}, Co^{2+} and Ni^{2+} also form oxalates with a
structure analogous to the polymeric copper oxalate dihydrate
[10,11]. Ferrous oxalate dihydrate has been reported to exist
in two allotropic modifications, α and β forms, which show
difference in the X-ray and infrared data but are indistin-
guishable by Mössbauer spectra [10,12-14]. A dibasic acid
higher up in the series such as malonic acid however behaves
differently from oxalic acid on account of steric considerations
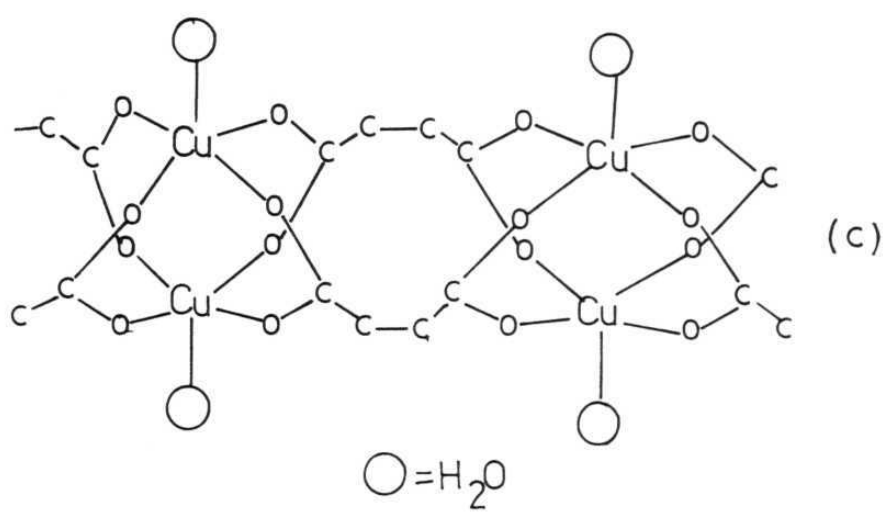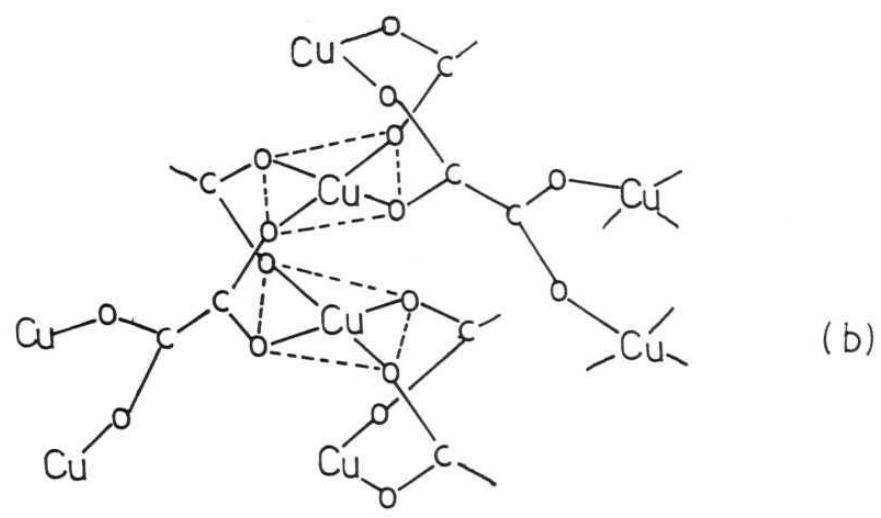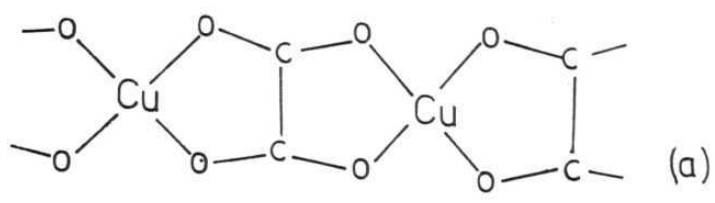
Fig.5.3 (a), (b) proposed structures for Cu(II) oxalate and
(c) Cu(II) succinate [9].

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arising due to the separation of the two carboxylic acid groups by a $-CH_2-$ group reducing the spatial restriction in bonding and a significant difference in the pK_1 and pK_2 values ($pK_1 = 2.83$, $pK_2 = 5.69$). In these cases one of the carboxylic acid groups is deprotonated and the oxygen atom of the OH^- group is coordinated to the metal ion. The other $-COOH$ group also is coordinated but through the oxygen of the $-C=O$ group with hydroxyl ion remaining intact [15]. Detailed crystal structure work on malonates of Ca^{2+} and Mg^{2+} have been reported and are typically different due to the difference in their coordination behaviour [16,17]. Fe^{2+} has been shown to form an octahedral compound isomorphous with Mg^{2+} where malonic acid acts as a bidentate ligand forming an acid complex in profound contrast to the ferrous oxalate dihydrate which exists in polymeric form as discussed earlier. Very little is known about the other transition metal malonates. The crystal structure data also provide evidence for considerable inter and intramolecular hydrogen bondings in the malonates [17]. The next higher acid viz., succinic acid forms a dimer with Cu^{2+} and the individual dimeric units are joined by two $-CH_2-CH_2-$ bridges from opposite corners [18] (Fig 5.3(c)). The Cu-Cu separation within the dimeric unit is 2.61 Å. The Cu-Cu separation between nearest copper atoms in adjacent dimers in the chain is 6.44 Å. Our own work pertains to a

Mössbauer study of iron maleate tetrahydrate and electron spin resonance studies of Cu^{2+} and Mn^{2+} doped in zinc maleate tetrahydrate. References to crystal structures of the related maleates are included at the appropriate place in the course of discussion of our results.

5.3. Mössbauer studies

Mössbauer studies of simple carboxylic acid complexes of iron, tin and the rare-earths, europium and dysprosium provide illustrations how informations both on structure as well as hyperfine interactions can be obtained by this spectroscopic technique [15,19-26]. A survey of the study of iron(III) carboxylates by this technique is included by Catterick and Thornton in their review on polynuclear carboxylates [2]. An account of preliminary Mössbauer data on some of organic acid salts of both iron(II) and iron(III) is reported by Y. Takashima and Y. Tateishi [27]. The method has also been exploited in the study of decomposition products of carboxylates in particular, which reveal several interesting features. For instance, the decomposition study of strontium tris oxalato iron(III) in the absence of air shows that at $300^{\circ}C$, the oxidation state of the iron changes to +2 completely, and reverts to +3 by $400^{\circ}C$. At $700^{\circ}C$

a significant percentage is present as +4, which is gradually reduced to +3 with increasing temperature [28]. As our own study pertains to a Fe(II) compounds we shall briefly survey here related Mössbauer studies. The study of iron(II) formate dihydrate by Hoy and deBarros is remarkable for being able to distinguish the two inequivalent sites discussed in the earlier section (p.129), by the difference in their quadrupole splittings. Lowering of temperature even upto 6K does not show any metal-metal interaction [19].

A number of investigations have been reported on ferrous oxalate dihydrate, including one from our own laboratory [14,20,21,29]. The interest in the system arises from the hyperfine split spectrum below 15 K giving rise to a significant combined quadrupole and Zeeman interaction effect resulting in forbidden transitions. The metal-metal interaction below 15 K has been explained on the basis of superexchange mechanism via oxalate ions. The inability to distinguish by Mössbauer spectra the two forms reported on the basis of X-ray data and the effect of replacing H_2O by D_2O in the dihydrate also have been investigated in detail [20,29]. Further, some reports are available on the decomposition products of ferrous oxalate dihydrate which indicates the intermediate formation of $\gamma-Fe_2O_3$ [14,30-32]. The preliminary X-ray

data and detailed Mössbauer studies on iron(II) malonate
dihydrate revealed the presence of discrete octahedra with
monomeric structure and the absence of metal-metal interaction
down to 1.2 K. This study is an illustration of the forma-
tion of a monomer in the higher dicarboxylic acid in view of
the large difference in the pK_1 and pK_2 values and separation
of the metal ions for steric reasons. A combined study of
Mössbauer and differential thermal analysis (DTA) showed
that ferrous malonate dihydrate when heated in the range
$120-210^{\circ}C$ becomes anhydrous, with the microsymmetry of the
central metal ion changing from octahedral to tetrahedral
coordination. Further heating showed the intermediate forma-
tion of $\gamma-Fe_2O_3$ as in the case of the oxalate [15]. In the
present work, by way of extension of these studies we report
the preparation, structural and decomposition studies of
iron(II) maleate tetrahydrate by Mössbauer, optical, DTA
and thermogravimetric studies.

5.4. Electron spin resonance studies.

Electron spin resonance (ESR) studies of carboxylic
acid complexes have been an attractive area in the application
of the technique for the study of microsymmetry, metal-metal
interaction and hyperfine interaction studies on transition

metal ions and rare-earth ions. It has been gainfully employed particularly in the study of Cu^{2+} and Mn^{2+} carboxylic acid complexes in the pure form, in powder or in single crystals and in isomorphous lattices doped with the transition metal ions as well. In the last mentioned cases detailed informations can be obtained. We present here an account of Cu^{2+} and Mn^{2+} ESR studies in simple monocarboxylic and dicarboxylic acid complexes, related to our own studies of Cu^{2+} and Mn^{2+} ions doped in zinc maleate tetrahydrate. In the case of Cu^{2+} and Mn^{2+} complexes ESR studies have been reported for formate, acetate and propionate both in their pure forms as well as on Cu^{2+} and Mn^{2+} doped in the respective diamagnetic zinc lattices [33-46]. In the case of Cu^{2+} doped in $Zn(HCOO)_2 \cdot 2H_2O$, Cu^{2+} shows preferential substitution of site-I of the two sites available (Fig. 1b) in which the metal ion is coordinated to six formate groups in a distorted octahedron [37]. Further, the Cu^{2+} ions in this site exhibit exchange coupling when the concentration of the dopant is increased. Temperature dependence studies give $|J| = 33 \pm 1$ cm^{-1} [37]. At higher concentrations copper ions go to the second site as well. The spin-Hamiltonian parameters have been deduced to be $g_{||} = 2.416$, $g_{\perp} = 2.077$ for site I and $g_{||} = 2.42$ and $g_{\perp} = 2.066$ for site II. Billing and Hathaway investigated the ESR and optical spectra of pure $Cu(HCOO)_2 \cdot 4H_2O$ in single

crystals and deduced $g_{||}$ = 2.35 and $g_{\perp}$ = 2.06 with the metal ion situated in D_{4h} symmetry with $d_{x^2-y^2}$ ground state [34]. For Mn^{2+} doped in $Zn(HCOO)_2 \cdot 2H_2O$, Morigaki and Abe deduced from single crystal ESR studies that there is no site preference unlike in the case of Cu^{2+} [38]. They obtained the ESR parameters g_1 = 2.005, D_1 = 295, E_1 = 30, A_1 = -92 for site I and g_2 = 1.993, D_2 = 455, E_2 = 28 and A_2 = -91 G for site II. The normal ESR and half field resonance of $Mn(HCOO)_2 \cdot 2H_2O$ have been studied by Karra and Kemmerer [36]. Of the two sites present in $Mn(HCOO)_2 \cdot 2H_2O$, the resonances due to site II were too broad to observe. From the normal ESR and half field measurements of site I it was concluded that the above material is a quasi-two dimensional magnet.

Cu(II) acetate monohydrate happens to be one of the earliest instances studied by Bleaney and Bowers where the measurements were accounted in terms of a singlet ground state with an excited triplet state, whose population varied with temperature [39]. This observation gave an impetus to investigate a number of copper(II) carboxylates with copper-copper interactions culminating in a review by M. Kato et al [47]. Paramagnetic resonance in single crystals of

$Mn(CH_3COO)_2 4H_2O$ was studied down to 1.3 K [41]. An interesting observation in this case is a shift of the resonance field at < 3 K which has been attributed to ferromagnetic character below T_c = 3 K [41]. The ESR studies of zinc doped $Cu(CH_3COO)_2H_2O$ have been studied by Kokoszka et al [42], and Kawamori et al [43]. These authors investigated the effects of dipolar and exchange interactions and from dilution studies derived the relationship between the hyperfine tensor components for the doublet and the triplet species and compared their results with the predictions of Slichter [48]. A set of 30 allowed ESR transitions arising from a single type of Mn^{2+} ions has been reported for $Mn^{2+}/Zn(CH_3COO)_2 2H_2O$ and analysed to give the spin-Hamiltonian parameters g_z = 2.0013, g_x = 2.0014 and g_y = 2.004, D = 248, E = -25.3, A_z = -89.6, A_x = -89.9 and A_y = -89.3 G. The observation of the forbidden transitions have been reported and the values Q' = 0.402 G and Q" = 4.7 G have been deduced for the axial and rhombic components of quadrupole interaction terms for the ^{55}Mn nucleus respectively [45]. The single crystal ESR studies of zinc doped copper propionate monohydrate by Fujiwara indicate that there exists super-exchange interaction via the bridging carboxyl groups similar to that of copper acetate monohydrate [46].

A number of ESR studies have been reported where the transition metal ion is doped in organic acid complexes of non-transition metal ions such as Ca^{2+}, Sr^{2+} and Cd^{2+}. The results in such studies are of interest as they provide a non-isomorphous host lattice and the doped Cu^{2+} or Mn^{2+} can occupy substitutional or interestitial sites. From the angular variation studies of Mn^{2+} and Cu^{2+} doped in $Sr(CH_3COO)_2 \cdot 0.5H_2O$, Jain and Upreti concluded that the unit cell symmetry of the parent lattice is triclinic in contrast to the X-ray report suggesting monoclinic symmetry [49]. Further, these authors showed that Cu^{2+} and Mn^{2+} occupy different sites.

Although considerable work has been reported on mono-carboxylic acid complexes, ESR studies of transition metal ions in polycarboxylic acid complexes is relatively meagre. Recently Karmakaz et al reported a Cu^{2+} doped cadmium oxalate trihydrate single crystal ESR study[50]. In yet another recent work, an ESR study of Mn^{2+} in cadmium oxalate tri-hydrate has been reported by the same authors analysing the allowed and forbidden transitions in terms of the spin-Hamiltonian including a rhombic crystalline electric field. Mn^{2+} substitutionally replaces Cd^{2+} in this case and gives a g-value slightly anisotropic [51]. The ESR studies of Mn^{2+}

and VO^{2+} doped in $K_2C_2O_4 \cdot H_2O$ single crystals have been reported by Jain [52]. The dopants have been found to go into interstitial sites. The doublet separation of forbidden hyperfine transitions corresponding to $m = \pm 1$ for Mn^{2+} have been observed and analysed. A value of 0.44 G for Q' and 0.09 G for Q" have been obtained.

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CHAPTER 6

EXPERIMENTAL METHODS AND METHODOLOGY

Abstract

The experimental details pertaining to ESR
spectral measurements of single crystals, differential
thermal analysis, thermogravimetric analysis and optical
spectral measurements are presented. A description of
the appropriate spin Hamiltonian for the case of Cu^{2+}
and Mn^{2+} ESR spectral analysis is given. The steps involved
in the derivation of the g and A tensors for the Cu^{2+} case
are also presented. The various expressions required for
the analysis of allowed and forbidden ESR transitions for
the case of Mn^{2+} leading to evaluation of the spin-
Hamiltonian parameters are also given.

6.1. Experimental measurements

6.1.1. Electron spin resonance (ESR) measurements

First derivative ESR spectra were recorded in JEOL-FE-3X X-band spectrometer employing 100 KHz modulation. For angular variation study the sample was mounted on a Teflon sample holder and rotated about three mutually perpendicular axes. The Z-axis was found by recording in a plane which gives the maximum spread in the spectrum and designated as X'Z-plane. Spectra are recorded in two other planes Y'Z and X'Y' chosen such that the three planes are mutually perpendicular. Each of the three crystal planes were explored at 10° interval. The spectrometer settings were optimised to record intense, resolved hyperfine lines. DPPH was used as field marker.

The g value of a peak in an ESR spectrum can be calculated using the relationship

$$gH = 2.0023 \ H_{DPPH}$$

where H is the magnetic field at the ESR peak of the sample and H_{DPPH} is the field of DPPH resonance. The ESR positions could be measured to 0.1 mm on the 40 cm wide chart paper which

corresponds to an accuracy of $\pm$ 5G for magnetic field scans of 2500 G. This gives an accuracy of $\pm$0.003 in the g values.

6.1.2. Differential thermal analysis (DTA)

The DTA measurements were made on a unit fabricated in our laboratory. The block diagram of the same is given Figure 6.1. The unit consists of (i) a furnace (ii) specimen holder made up of nickel (iii) ceramic support for keeping the holder in position (iv) a light spot galvanometer for measuring the differential thermocouple output (v) Keithley digital multimeter (model 174) for measuring the e.m.f output of the thermocouple measuring the temperature of the nickel block and (vi) chromel-alumel (25 s.w.g) thermocouples. The heating rate of the furnace was controlled manually using a variac. In all the measurements a heating rate of 4-5°/min was employed. Initial standardisation of the set up was carried out by recording the DTA of ammonium nitrate [1].

6.1.3. Thermogravimetric measurements

The thermogravimetric analysis (TGA) was carried out on a home made unit. The unit consists of (i) a balance (ii) a furnace (iii) sample holder made up of Corning glass and
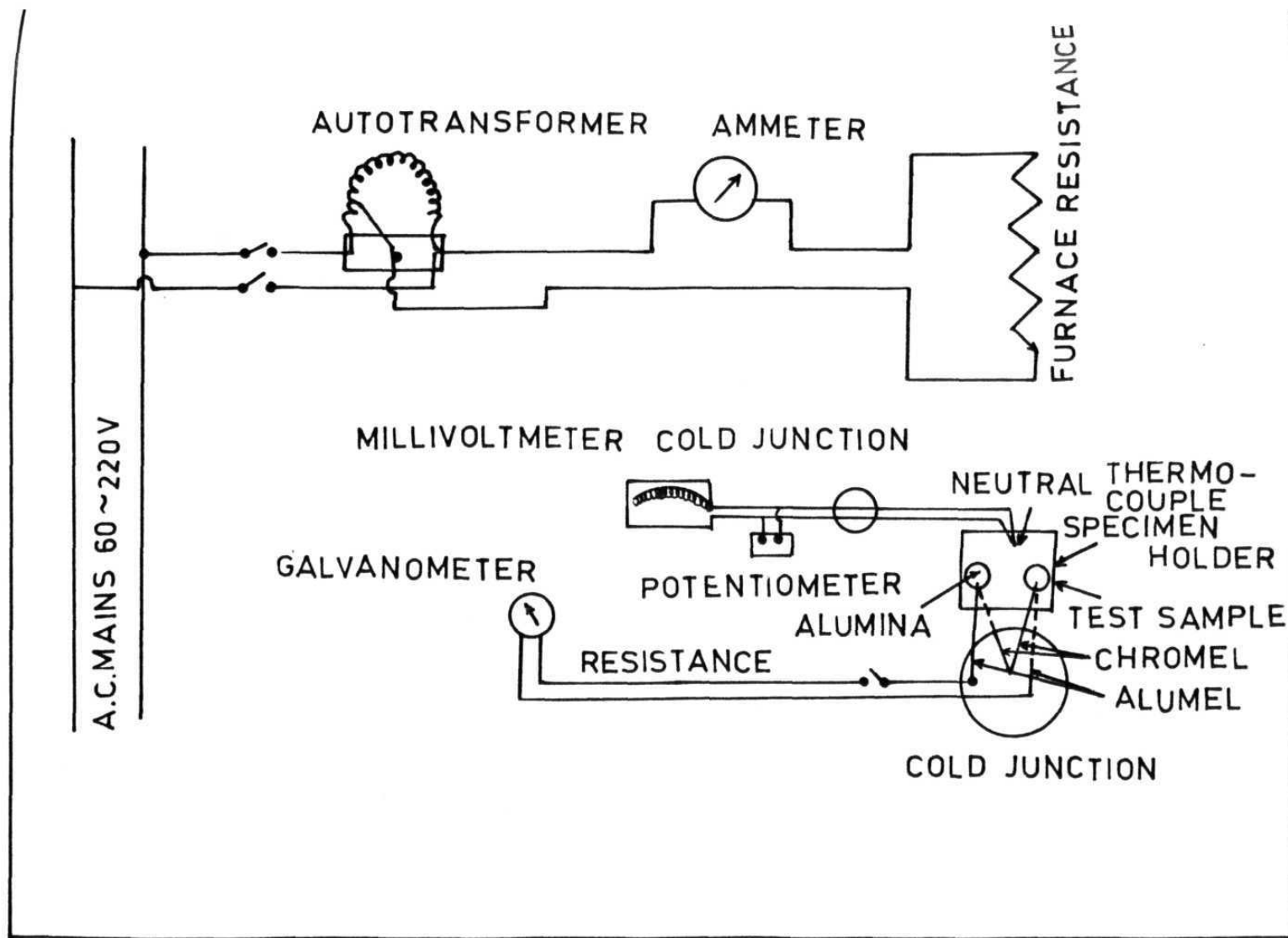
Fig.6.1 Experimental set up used for differential thermal analysis (DTA)

(iv) a digital multimeter (Keithley model 174). The heating rate of the furnace was controlled manually using a variac. A heating rate of 4-5°/min was employed. The sample was placed in the sample holder hanging at the centre of tubular furnace with the help of an insulated copper wire attached to a single pan balance. The weight loss was monitered by the balance and the corresponding temperature was noted by measuring the e.m.f of a thermocouple placed near the sample holder.

6.2. Methodology

This part of the thesis concerns with a Mössbauer study of iron maleate tetrahydrate and its decomposition products and single crystal ESR studies of Cu^{2+} and Mn^{2+} doped zinc maleate tetrahydrate (ZnMTH). The methodology employed for the Mössbauer studies has been presented earlier in chapter 2. Here we confine to a brief discussion of (i) the spin-Hamiltonian (ii) the splitting of the energy levels for the Cu^{2+} and Mn^{2+} cases and (iii) the formalisms used for obtaining the g-tensor and the ground state in the case of Cu^{2+}/ZnMTH and hyperfine constants from an analysis of the allowed and forbidden transitions of Mn^{2+}/ZnMTH from the experimental spectra.

6.2.1. Total Hamiltonian and the effective spin-Hamiltonian

The total Hamiltonian for an ion in a crystalline electric field with an applied magnetic field may be written as

$$H_{total} = H_V + H_{LF} + H_{LS} + H_{SS} + H_{HI} + H_Q + H_{SH} + H_{SI} + H_{II}$$

$$\ldots (6.1)$$

where the significance of the different terms of the total Hamiltonian and the order of magnitude of each term are given in Table 6.1 [2].

The effective spin-Hamiltonian contains those parts of the total Hamiltonian which are relevant for the purpose of ESR i.e., the spin vectors only. The energy levels of the paramagnetic ion can be represented by this Hamiltonian using the ficititious or effective spin S. This is given by

$$H_{spin} = \beta_e(g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) + D[S_z^2 - \tfrac{1}{3}S(S+1)] +$$

$$E(S_x^2 - S_y^2) + (A_x S_x I_x + A_y S_y I_y + A_z S_z I_z) - \beta_N g_N H \cdot I +$$

$$\frac{e^2 qQ}{8I(2I-1)} \quad (3\cos^2\theta - 1) \, [I_z^2 - \tfrac{1}{3}I(I+1)] \qquad \ldots (6.2)$$

Table 6.1. Hamiltonian operators in order of approximate decreasing magnitude[2].

Hamiltonian	Interaction	Magnitude(cm^{-1})	Expanded form.
V	Electron–Electron	10^5	$\sum\limits_{k>j-1}^{n} \dfrac{e^2}{r_{kj}}$
LF	Ligand Field	10^4	$\sum\limits_{k} - eV(xk.yk.zk)$
LS	Spin–Orbit	10^2–10^3	$\lambda.\hat{L}.\hat{S}$
SS	Electron–Electron dipde	10^{-1}–1	$\beta e^2 r_{12}^{-3} [\hat{S}_1.\hat{S}_2 - \dfrac{3(\hat{S}_1.\hat{r}_{12})(\hat{S}_2.\hat{r}_{12})}{r_{12}^2}$
HI	Nuclear Zeeman	10^{-1}–10^{-3}	$-g_N \beta_N \hat{H}.I$
Q	Nuclear Quadrupole	10^{-3}	$Q'[I_z^2 - \frac{1}{3} I(I+1)]$ were $Q' = \dfrac{3eQ}{4I(2I-1)} \dfrac{\partial^2 V}{\partial Z^2}$
SH	Electron Zeeman	–	$\beta_e (\hat{L}.g\hat{S}).H$
SI	Electron spin–Nuclear Spin	10^{-2}–10^{-4}	$A.\hat{I}.\hat{S}$
II	Nuclear Spin–Spin	–	$\sum\limits_{i>j} I_i J_{ij} I_j$

where g_x, g_y and g_z are the principal components of the g tensor, A_x, A_y and A_z are the principal components of the hyperfine coupling tensor, D and E are the axial and rhombic components of zero field splitting respectively, and the significance of the other terms have been pointed out earlier (Table 6.1.) The importance of the various terms relevant to our studies with $Cu^{2+}(3d^9)$ and $Mn^{2+}(3d^5)$ are given below.

6.2.2. $Cu^{2+}(3d^9)$ Case

The ground state of Cu^{2+} with a d^9 configuration is ^2D with S = 1/2. The orbital splittings for the different stereochemistries are shown in Figure 6.2. The magnetic properties of the lowest orbital singlet are modified by an admixture of the excited states through spin-orbit interaction resulting·in anisotropic g-values. Figure 6.3 shows the splitting of the ^2D state in the presence of crystalline fields, spin-orbit coupling and magnetic field. In the case of trigonal symmetry with an orbital doublet ground state, the structure will distort itself so as to resolve the degeneracy by Jahn-Teller effect. In either case the ground state is a Kramer's doublet and ESR spectra are readily observed at room temperature.
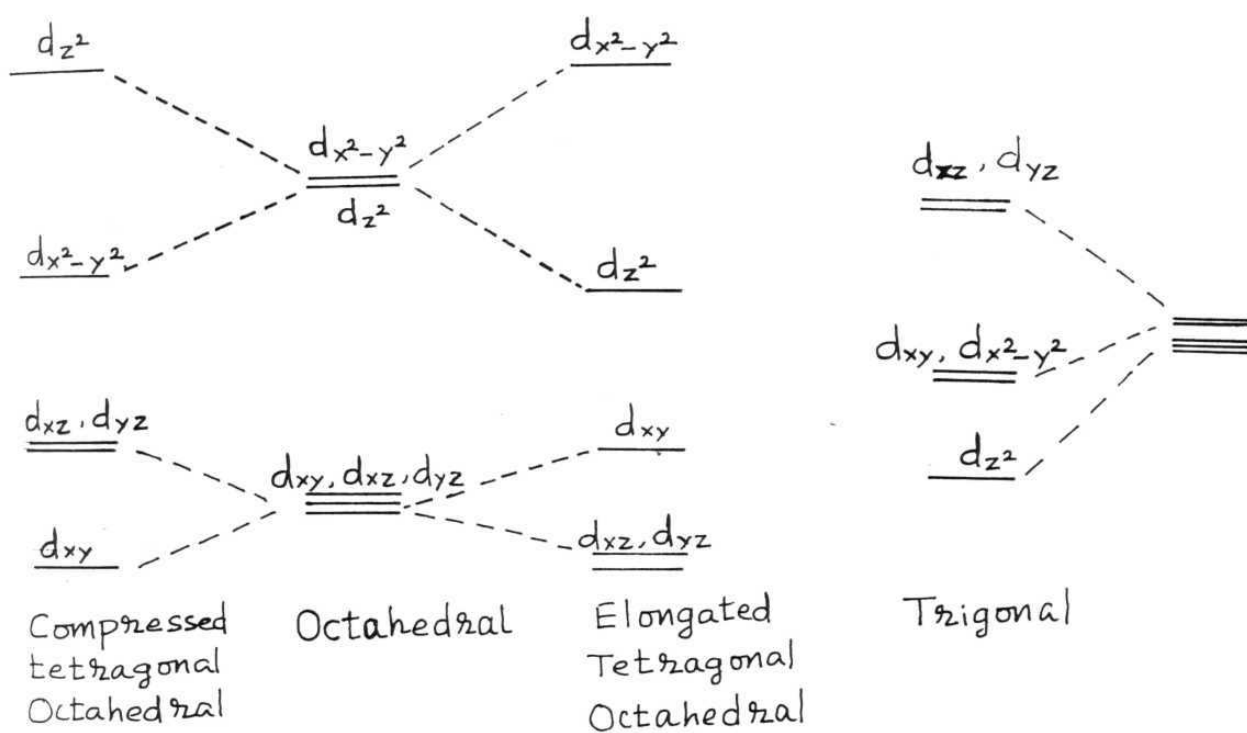
Fig.6.2 The d-orbital splittings for different geometries in $Cu^{2+}(d)^9$
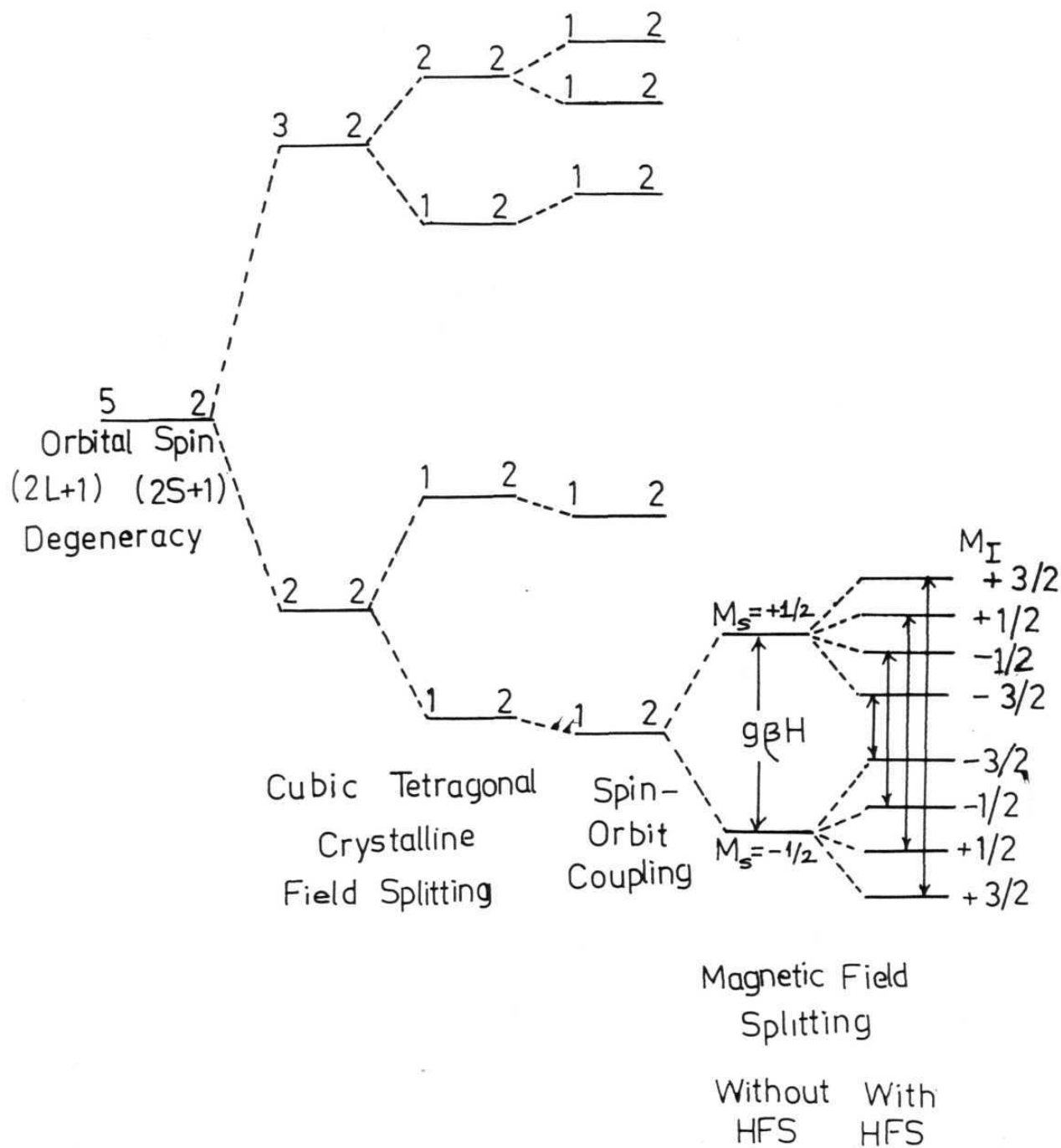
Fig.6.3 Splitting of the ^{2}D state of Cu^{2+} under the action of crystalline fields, spin-orbit coupling and Magnetic field.

For Cu^{2+} ion the Eq. 6.2 may be written as

$$H_{spin} = \beta_e(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) +$$
$$(S_x A_x I_x + S_y A_y I_y + S_z A_z I_z) - \beta_N g_N H \cdot I +$$
$$Q'[I_z^2 - \frac{1}{3} I(I+1)] \qquad \qquad \ldots (6.3)$$

The D and E terms are not included since for S = 1/2, the zero field terms do not exist. Determination of the g-tensor in the case of copper is helpful in fixing the ground state and understanding the stereochemistry. One method of determining the g and A tensors from experimental measurements on single crystals is due to Schonland [3], the details of which are given in section 6.2.4.

6.2.3. $Mn^{2+}(3d^5)$ Case

The ground state of high spin $Mn^{2+}(3d^5)$ is ^6A. The presence of crystalline electric field does not split this orbital singlet ground state as the ion is spherically symmetric. There are no other sextuplet terms and the next higher state is ^4G. Since there is no other sextuplet term of the $3d^5$ configuration, the ground state cannot mix with any other by spin-orbit coupling and so there is no

zero field splitting. However if there is an axial distortion, the zero field splitting does occur and three Kramers doublets appear. It has been shown by Van Vleck and Penney that this splitting comes in due to higher order admixtures involving the spin-orbit coupling and the axial field [4]. Further it is shown that the contribution to zero field splitting from spin-spin interaction also is significant. The contribution due to spin-spin interaction and the spin-orbit coupling have been calculated by Watanabe [5]. However, the results calculated by Watanabe appeared to be smaller than the values measured experimentally. Yet another mechanism suggested which contributes to zero field splitting through axial splitting is due to Blume and Orbach [6]. These authors showed that the $^6T_1$ term of the ground state ^6A has the right symmetry to mix with the linear combinations $(^4_i T_4)$ of the excited states ^4G, ^4P and ^4F through spin-orbit coupling generating the axial field responsible for zero field splitting.

In the absence of a magnetic field the axial crystalline field splits the $^6S_{5/2}$ state as discussed above into three Kramer's doublets viz., $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$, each being 2-fold spin degenerate. The separations between the $\pm 5/2$ and $\pm 3=2$, $\pm 3/2$ and $\pm 1/2$ states are 4D and 2D respectively,

where D is the zero field splitting (Figure 6.4). When the
magnetic field is applied the spin degeneracy is lifted giving
six electronic levels with -5/2 lying lowest. Since the
nuclear spin of ^{55}Mn with natural abundance of 100%, is 5/2,
each electronic level is further split into six levels. The
splitting between the hyperfine components is given by the
term $A \cdot M_S \cdot M_I$. Thus the separation between the hyperfine compo-
nents will be five times as large in the case of the outer
electronic levels as for the central levels. Since the
electronic spin magnetic quantum number M_S(max) corresponds
to the case in which the magnetic moment of the electron is
parallel with the external magnetic field, it represents the
lowest energy for the electron spin, and hence the largest
negative electronic quantum number (M_S) will be lowest.
Considering the nuclear magnetic quantum numbers associated
with the electronic levels the nuclear levels $+M_I$ will lie
lowest in energy for the above case. This results from the
fact that the hyperfine coupling constant A is usually positive
so that the net hyperfine interaction contribution will be
negative for the case of $-M_S$ and $+M_I$. For the higher electro-
nic levels reverse will be the case because for a positive
M_S value, a negative M_I value gives negative contribution due
to the hyperfine interaction. Thus applying the selection
rules _viz._, $\Delta M_S = \pm 1$ and $\Delta M_I = 0$ for the allowed transitions,
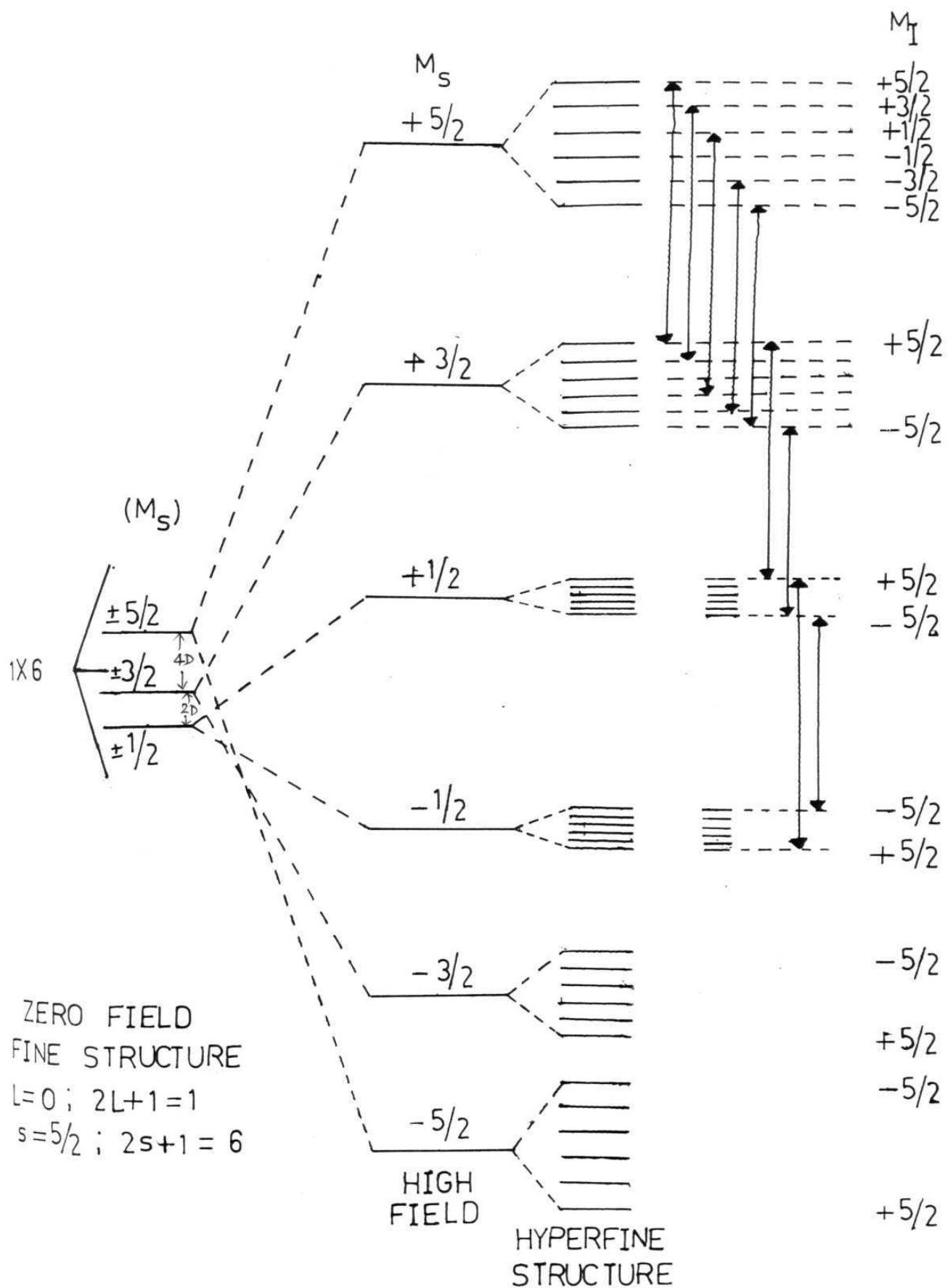
Fig.6.4 Splitting of the ^6S state of Mn^{2+} under the action of crystalline field, magnetic field and hyperfine interactions.

a 30 line spectra will be obtained for Mn^{2+} ion in axial crystalline fields as designated in Figure 6.4.

The effective spin Hamiltonian viz., (6.2) for Mn^{2+} ($3d^5$) may be written as

$$H = g\beta HS + D'[S_z^2 - \frac{1}{3} S(S + 1)] + E'[S_x^2 - S_y^2]$$

$$+ \frac{a'}{6}[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S + 1) (3S^2 + 3S - 1)] + SA'I$$

$$\ldots (6.4)$$

where the first term represents the Zeeman splitting energy, second and third terms represent the axial and rhombic zero field splittings respectively. The fourth term is the cubic field part while the last term represents the hyperfine interaction. The constants D', E', a' and A' are related to D, E, a and A through a multiplication factor of $g\beta$ (viz., D' = g\beta D etc).

The above spin-Hamiltonian can also be written in the form of crystal field parameters as follows for Mn^{2+} in orthorhombic (or lower) symmetry [7]

$$H = \beta[S_z g_z B_z + g_x(S_x B_x + S_y B_y) + \tfrac{1}{3} b_2^0 O_2^0 +$$

$$\tfrac{1}{3} b_2^2 O_2^2 + \tfrac{1}{60}(b_4^0 O_4^0 + b_4^2 O_4^2 + b_4^4 O_4^4) +$$

$$[S_z A_z I_z + A_x(S_x I_x + S_y I_y)] \qquad \dots (6.5)$$

where O_n^m is an operator function having the same transformation properties as the corresponding spherical harmonics Y_n^m and the coefficients b_n^m are parameters to be determined by experiment. The relationship between the b_n^m and D, E, a are

$$a = 120\, b_4^0$$

$$D = 3b_2^0$$

$$F = 180\, b_4^0$$

We have retained the terms a, D and E corresponding to expression (6.4), for our discussion.

The spin Hamiltonian given above is derived from zero order wavefunctions $|M, m_I\rangle$, which would be appropriate to an ion in a very large magnetic field, are admixed by the off diagonal terms in this Hamiltonian. If we consider the second order admixtures arising from the cross products of the terms in D and A of the type

$$(S_z S_+) \ (S_- \ I_+), \quad (S_z S_-) \ (S_+ I_-)$$

then a nuclear state $|m_I\rangle$ becomes admixed with states $|m_I \pm 1\rangle$ by amounts of order $3D \sin 2\theta/4g\beta H$ and forbidden transitions of the type $\Delta M_S = \pm 1$, $\Delta m_I = \pm 1$, occur [8]. They have intensities of the order of the square of the respective admixture coefficients relative to the intensities of the allowed transitions in which m does not change. The expressions derived from this Hamiltonian using which the forbidden transitions are analysed are given at the end of this chapter.

6.2.4. Analysis of angular variation data for the case of Cu^{2+}.

(a) Evaluation of g and A tensors.

The g value of a hyperfine pattern is determined by measuring the magnetic field at the centre of the hyperfine pattern. The hyperfine coupling constant (A) is given by the field separation between adjacent hyperfine components. However if the spacings between consecutive peaks are unequal, then the average of all such spacings is taken to be the value of A. This has been adopted in the cases of $Mn^{2+}/(ZnMTH)$ and $Cu^{2+}/(ZnMTH)$, in evaluating the value of A, as the adjacent spacings were unequal.

(b) Least square fit.

In an angular variation experiment the ESR spectra are recorded for rotations of the single crystal about any three mutually perpendicular (but not necessarily crystallographic) axes, at intervals of 5° or 10°, depending upon the amount of information present in the spectra. We have recorded the ESR spectra at 10° intervals as this was sufficient to get the angular variation of g and A. The g^2 values thus obtained are plotted against Θ, the angle which the d.c. magnetic field makes with one of the reference axes, for rotations about the Z or Y axes. Each of the three plots obtained is fitted, by the method of least squares to the relationship,

$$g_{xy}^2(\Theta) = g_{xx}^2 \, Cos^2\Theta + g_{yy}^2 \, Sin^2\Theta + 2g_{xy}^2 \, Sin\Theta \, Cos\Theta \qquad \dots \ (6.6)$$

with similar equations for $g_{yz}^2(\Theta)$ and $g_{zx}^2(\Theta)$. As g_{xx}^2, g_{yy}^2 and g_{zz}^2 occur twice during the three rotations, they serve as checks on the correct mounting of the crystal for the rotations (for example see Table 7.1 for these values in the case of $Cu^{2+}/ZnMTH$).

Equation (6.6) could be rewritten as

$$g^2(\theta) = U + V \, Cos \, 2\theta + W \, Sin \, 2\theta \qquad \ldots (6.7)$$

where $U = (g_{xx}^2 + g_{yy}^2)/2$, $V = (g_{xx}^2 - g_{yy}^2)/2$ and $W = g_{xy}^2$.
Equation (6.7) could also be used for fitting experimental g^2 values. Then the maximum and minimum g^2 values are deter-mined using the θ values given by

$$\tan 2\theta = W/V$$

Appendix III gives the listings of a HI-BASIC programme for DCM Spectrum-7 to least square fit the measured g values to eq.(6.7) to get the values of U, V, W, g_{max}^2 and g_{min}^2.

(c) Diagonalization of g and A tensors.

The g^2 matrix to be diagonalized is

$$\{g^2\} = G = \begin{bmatrix} g_{xx}^2 & g_{xy}^2 & g_{xz}^2 \\ g_{yx}^2 & g_{yy}^2 & g_{yz}^2 \\ g_{zx}^2 & g_{zy}^2 & g_{zz}^2 \end{bmatrix} \qquad \ldots (6.8)$$

The various elements of G are obtained from a least square fit of the experimental data to the relations of the type given in eq.(6.7). The eigen value problem

$$|G - \lambda I| = 0$$

is solved to get the principal g-values, which occur as the positive square roots of λ_1, λ_2, λ_3 which are the roots of the equation

$$\lambda^3 + p^2\lambda + q\lambda + r = 0 \qquad \qquad \cdots (6.9)$$

where $p = -(g_{xx}^2 + g_{yy}^2 + g_{zz}^2)$,

$$q = [(g_{xx}^2 \, g_{yy}^2 + g_{yy}^2 \, g_{zz}^2 + g_{zz}^2 \, g_{xx}^2) - (g_{xy}^2 + g_{yz}^2 + g_{zx}^2)]$$

and

$$r = (g_{xx} \, g_{yz}^2)^2 + (g_{yy} \, g_{zx}^2)^2 + (g_{zz} \, g_{xy}^2)^2 - g_{xx}^2 \, g_{yy}^2 \, g_{zz}^2 -$$

$$2g_{xy}^2 \, g_{yz}^2 \, g_{zx}^2$$

Schonland has developed a method to obtain the g^2 matrix [6.8] by just knowing accurately the g_{max}^2 and g_{min}^2 for crystal rotations about three mutually perpendicular axes [3]. In this procedure the full angular variation curve fitted by the least square method to eq.(6.7) can be used to obtain accurate values for g_{max}^2 and g_{min}^2 for each rotation. If the axis of rotation is $i(i = x, y \text{ or } z)$, the parameters α and δ may be defined as

$$\alpha_i = (g_{max}^2(i) + g_{min}^2(i))/2$$

$$\delta_i = (g_{max}^2(i) + g_{min}^2(i))/2 \qquad \ldots (6.10)$$

we thus get α_x, α_y, α_z and δ_x, δ_y, δ_z. After computing α and δ values, the matrix elements of g tensor can be set up as follows.

$$g_{xx} = \alpha_y + \alpha_z - \alpha_x$$

$$g_{yy} = \alpha_z + \alpha_x - \alpha_y$$

$$g_{zz} = \alpha_x + \alpha_y - \alpha_z$$

$$g_{zy} = g_{yz} = \pm \sqrt{(\delta_x + \alpha_y - \alpha_z)(\delta_x - \alpha_y + \alpha_z)}$$

$$g_{xz} = g_{zx} = \pm \sqrt{(\delta_y + \alpha_z - \alpha_x)(\delta_y - \alpha_z + \alpha_x)}$$

$$g_{xy} = g_{yx} = \pm \sqrt{(\delta_z + \alpha_x - \alpha_y)(\delta_z - \alpha_x + \alpha_y)}$$

$$\ldots (6.11)$$

The G matrix is then diagonalized by the Jacobi method [9]. The matrix elements which are found to be imaginary are rejected and their values are taken as zeros. The diagonalization of the G-matrix (6.8) gives the principal g values.

The principal A values can also be computed using the same procedure. Initially g^2A^2 values for all the three axes are calculated and least square fit using the eq.(6.7) to give $g^2A^2_{max}$ and $g^2A^2_{min}$ values. These $g^2A^2_{max}$ and $g^2A^2_{min}$ values are then used to calculate α and δ defined in a similar manner as in 6.11 which are used to set up the matrix elements of the form $g^2_{ij} A^2_{ij}$. The diagonalisation of the corresponding matrix gives the principal g^2A^2 values from which the principal A values can be computed.

6.2.5. Analysis of angular variation data for the case of Mn^{2+}.

(a) Allowed transitions

Equation 6.4 may be written in the form

$$H = g\beta HS + D' \left[S^2_z - \tfrac{1}{3} S(S+1)\right] + E'\left[S^2_x - S^2_y\right] +$$

$$\tfrac{a'}{6}\left[S^4_x + S^4_y + S^4_z - \tfrac{1}{5} S(S+1)(3S^2 + 3S - 1)\right] + SA'I$$
$$\ldots (6.12)$$

neglecting the other terms which do not undergo any change during the transition. For the case of axial symmetry, it has been shown that the line-positions in terms of magnetic fields exhibit a variation given by $(3Cos^2\theta - 1)$ [10].

However, the effect of diagonal terms results in a deviation in the experimental situation from strict adherence to such a variation. The analysis of the line-positions for obtaining the hyperfine parameters, D, E, a and A are fairly simplified by locating the spectrum corresponding to H $\parallel$ Z as shown by the largest split of the external lines and the absence of forbidden transitions [10]. In such a case the hyperfine terms are related as follows [11].

(a) for fine structure (H $\parallel$ Z)

$$H(M = \pm\, 5/2 \rightarrow \pm\, 3/2) = H_o \mp 4D + \frac{9E^2}{(H+D)} - \frac{5E^2}{(H+3D)} \mp 2a$$

$$H(M = \pm\, 3/2 \rightarrow \pm\, 1/2) = H_o \mp 2D \mp \frac{9E^2}{(H+D)} \pm \frac{9E^2}{(H-D)} -$$

$$\frac{5E^2}{(H\pm3D)} \pm \frac{5}{2}\, a$$

$$H(M = +\, 1/2 \rightarrow -\, 1/2) = H_o - \frac{9E^2}{(H-D)} + \frac{5E^2}{(H+3D)} + \frac{5E^2}{(H-3D)}$$

$$\dots (6.13)$$

(b) for hyperfine structure (H $\parallel$ Z)

$$H(m \longrightarrow m) = H - Am - \frac{A^2}{2H}\left[I(I+1) - m^2 + (2M-1)m\right]$$

$$\dots (6.14)$$

The parameters D, E, a and A are calculated using the above expressions in an iterative manner till a good match between H_{cal} and H_{obs} are obtained. The computer programme to calculate self consistently the D, E, a .and A using the above expressions is given in appendix IV. The values D, E, a and A thus obtained are used in analysis of the forbidden transitions described below.

(b) Forbidden transisions.

The spin Hamiltonian used in the analysis of forbidden transitions is derived from the perturbation approach and is of the form

$$H = \beta \widetilde{g}.H.S + D[S_z^2 - \tfrac{1}{3} S(S+1)] + E[S_x^2 - S_y^2] + S.\widehat{A}.I -$$

$$\gamma \beta_N H.I + Q'[I_z^2 - \tfrac{1}{3} I(I+1)] + Q''(I_x^2 - I_y^2)$$

$$\ldots (6.15)$$

where Q' and Q" represent respectively the axial and rhombic components of the quadrupole coupling constants of ^{55}Mn nucleus. The significance of the other terms have been discussed earlier.

The above Hamiltonian is applicable only when the applied magnetic field is along Z-axis of the crystal.

However, if the magnetic field is not along the Z-axis but makes an angle Θ to Z-axis and ϕ to X-axis in the XY-plane, equation (6.15), takes the form [12],

$$H = g\beta H S_{z'} + \sigma \left[S_{z'}^2 - \frac{1}{3} S(S+1) \right] + \rho S_+^2 + \rho^* S_-^2 +$$

$$\frac{\lambda}{2} (S_{z'} S_+ + S_+ S_{z'}) + \frac{\lambda^*}{2} (S_{z'} S_- + S_- S_{z'}) + A S_{z'} I_{z'} +$$

$$\frac{A}{2}(S_+ I_- + S_- I_+) - \gamma \beta_N H I_{z'} + P \left[I_z^2 - \frac{1}{3} I(I+1) \right]$$

$$\ldots (6.16)$$

taking the Z' axis along H. Here

$$S_+ = S_{x'} + i S_{y'} \quad ; \quad S_- = S_{x'} - i S_{y'}$$

$$\sigma = \frac{1}{2}[D(3\cos^2\Theta - 1) + 3E \sin^2\Theta \cos 2\phi],$$

$$\rho = \frac{1}{4} [D\sin^2\Theta + E(\cos^2\Theta \cos 2\phi - \sin^2\phi) + 2iE\cos\Theta \sin 2\phi],$$

$$\lambda = \sin\Theta [(D-E\cos 2\phi)\cos\Theta + iE\sin 2\phi],$$

$$P = \frac{1}{2}[Q'(3\cos^2\Theta - 1) + 3Q'' \sin^2\Theta \cos 2\phi]$$

In the above expression the small anisotropy in the hyperfine constant and g value are neglected for simplicity.

In the perturbation approach we approximate $g\beta H \gg |D|$, $|E|$, $|A|$ and the eigen values of the above Hamiltonian to

a third order are

$$E_{|M,m\rangle} = g\beta HM + \sigma[M^2 - \tfrac{1}{3}S(S+1)] + AMm +$$

$$\frac{A^2}{2g\beta H}[m\{M^2-S(S+1)\} + M\{I(I+1) - m^2\}] -$$

$$\gamma\beta_N Hm + P[m^2 - \tfrac{1}{3}I(I+1)] + \frac{|\lambda|^2}{(2g\beta H)^2}\cdot\frac{2Am}{M}[\{M^2-$$

$$S(S+1)\}^2 - M^2] + \frac{|P|^2}{(g\beta H)^2}2AMm[2M^2 + 1 - 2S(S+1)]$$

$$+ \frac{A^2\sigma}{(2g\beta H)^2}[\{S(S+1) - M(M+1)\}\{I(I+1) -$$

$$m(m-1)\}(2M+1) - \{S(S+1) - M(M-1)\}\{I(I+1) -$$

$$m(m+1)\}(2M-1) + \frac{A^3}{(2g\beta H)^2}[\{S(S+1) -$$

$$M(M+1)\}\{I(I+1)-m(m-1)\}(m-M-1) +$$

$$\{S(S+1)-M(M-1)\}\{I(I+1)-m(m+1)\}(M-m-1)]$$

$$\dots (6.17)$$

The energy levels of allowed and forbidden hyperfine lines can be obtained by substituting the appropriate M and m values and applying the selection rules viz., $\Delta M = \pm 1$, $\Delta m_I = 0$ for allowed lines and $\Delta M = \pm 1$, $\Delta m_I = \pm 1$ or ± 2 for forbidden lines. The forbidden lines are analysed in pairs to simplify the

calculations. The distance between two forbidden transitions viz.,ΔH (in gauss) can be obtained by substituting the M and m values. Thus we get for M = +1/2 $\longrightarrow$ -1/2 sextet

$\Delta m = \pm 1$ Transitions

$$\Delta H = {}^{H}|1/2,\ m+1\rangle \longrightarrow |-1/2,\ m\rangle - {}^{H}|1/2,\ m\rangle \longrightarrow |-1/2,m+1\rangle$$

$$= (17A^2/2H_o) + 2(\gamma\beta_N/g\beta)H_o - (2m+1)\ [2P-(8A^2\sigma/H_o^2) +$$

$$(25A^3/3H_o^2) + (\gamma\beta_N/g\beta)A]$$

$\Delta m = \pm 2$ transitions

$$\Delta H = {}^{H}|1/2,m+1\rangle \longrightarrow |-1/2,m-1\rangle - {}^{H}|1/2,m-1\rangle \longrightarrow |-1/2,m+1\rangle$$

$$= (17A^2/H_o) + 4(\gamma\beta_N/g\beta)H_o - 2m[4P + (16A^2\sigma/H_o^2) +$$

$$(25A^3/H_o^2) + 2(\gamma\beta_N/g\beta)A]$$

M = +3/2 $\longrightarrow$ +1/2 sextet

$\Delta m = \pm 1$ transitions

$$\Delta H = {}^{H}|3/2,m+1\rangle \longrightarrow |1/2,m\rangle - {}^{H}|3/2,m\rangle \longrightarrow |1/2,m+1\rangle$$

$$= -2A + 2(\gamma\beta_N/g\beta)H_o - 2P(2m+1) - (|\lambda|^2 256A/3H_o^2) +$$

$$(|\rho|^2\ 52A/H_o^2) + (A^2/H_o)(2m+8.5) + (A^2\sigma/H_o^2)(14m+9)-$$

$$(A^3/H_o^2)(m^2 + 19m-(51/4))$$

$M = +5/2 \longrightarrow +3/2$ sextet

$\triangle m = \pm 1$ transitions

$$\triangle H = {}^{H}|5/2,m+1\rangle \longrightarrow |3/2,m\rangle - {}^{H}|5/2,m\rangle \longrightarrow |3/2,m+1\rangle$$

$$= -4A + 2(\gamma\beta_N/g\beta)H_o - 2P(2m+1) - (40A|\lambda|^2/3H_o^2) +$$

$$(56A|\rho|^2/H_o^2) + (A^2/H_o)(4m+6.5) + (A^2\sigma/H_o^2)(18m+8) -$$

$$(A^3/H_o^2)(2m^2-m-33)$$

$M = -3/2 \longrightarrow -1/2$ sextet

$\triangle m = \pm 1$ transitions

$$\triangle H = {}^{H}|-1/2,m+1\rangle \longrightarrow |-3/2,m\rangle {}^{-H}|-1/2,m\rangle \longrightarrow |-3/2,m+1\rangle$$

$$= -2A - 2(\gamma\beta_N/g\beta)H_o + 2P(2m+1) - (256A|\lambda|^2/H_o^2) +$$

$$(52A|\rho|^2/H_o^2) + (A^2/H_o)(2m-6.5) - (A^2\sigma/H_o^2)(4m+5) -$$

$$(A^3/H_o^2)(m^2-17m - (123/4))$$

$M = -5/2 \longrightarrow -3/2$ sextet

$\triangle m = \pm 1$ transitions

$$\triangle H = {}^{H}|-3/2,m+1\rangle \longrightarrow |-5/2,m\rangle - {}^{H}|-3/2,m\rangle \longrightarrow |-5/2,m+1\rangle$$

$$= -4A - 2(\gamma\beta_N/g\beta)H_o + 2P(2m+1) - (40A|\lambda|^2/3H_o^2) + (56A|\rho|^2/H_o^2$$

$$+ (A^2/H_o)(4m-2.5) - (18mA^2\sigma/H_o^2) - (A^3/H_o^2)(2m^2+5m-30)$$

$$\ldots (6.18)$$

Using the above equations for H_{cal}, trial values
of Q' and Q" are given as input paremeters and the calcula-
tions are done in an iterative manner. The iteration is
continued till a good fit is obtained between H_{cal} and H_{obs}.
A computer programme used for this purpose is given in the
appendix V.

The intensities of ESR hyperfine lines (both allowed
as well as forbidden) of ions in sufficiently strong crystalline
fields exhibit strong angular variations when the static
magnetic field direction is varied with respect to the crystal
field directions. The intensities of the forbidden lines will
follow the expression

$$\left(\frac{3D \sin^2\theta}{4g\beta H}\right)^2 \left\{1 + \frac{S(S+1)}{3M(M-1)}\right\}^2 \left\{I(I+1) - m^2 + m\right\} \quad \ldots \ (6.19)$$

It is evident from the above expression that the intensities
of forbidden lines will be zero at $\theta = 0°$ and maximum at
$\theta = 45°$.

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PREPARATION AND MÖSSBAUER STUDIES OF
FERROUS MALEATE TETRAHYDRATE
$(Fe(C_4H_3O_4)_2 4H_2O)$†
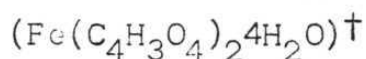
Abstract

$Fe(C_4H_3O_4)_2 \cdot 4H_2O$ is shown to be monomeric with a
structure isomorphous with the Mn(II) analogue and the unit
cell dimensions are determined to be a = 7.27, b = 9.60 and
c = 5.24Å α = 105.9, β = 87.8 and γ = 115.6°. The temperature
dependence of quadrupole splitting and optical spectral data
give $\sim$ 10,000 cm^{-1}, $\sim$ 650 cm^{-1}, $\sim$ 190 cm^{-1} and $\sim$ 1400 cm^{-1}
for the 10 Dq, tetragonal field, rhombic field and the
splitting of the e_g level respectively. The quadrupole split-
ting data indicate that the distortion from cubic symmetry
increases in the following order, oxalate<malonate<maleate.
DTA, TGA and Mössbauer studies indicate elimination of one
molecule of maleic acid at 235°C. The resulting intermediate
product is found to be a stable divalent compound with less
distortion and is attributed to the formation of maleato
(2-) iron (II).

7.1. Introduction:

In this and the next two chapters we report the studies of ferrous maleate tetrahydrate (hereafter FeMTH), Cu^{2+} doped zinc maleate tetrahydrate (hereafter Cu^{2+}/ZnMTH) and Mn^{2+} doped zinc maleate tetrahydrate (hereafter Mn^{2+}/ZnMTH), as part of a programme of detailed investigations of hyperfine interactions and decomposition behaviour of organic acid complexes which give rise to situations of interest presented earlier. In the case of the first candidate **viz.**, FeMTH Mössbauer spectroscopy provides a suitable technique to study structure and related properties. The latter two systems can be best studied by electron spin resonance technique. In this chapter we give an account of preparation and Mössbauer studies of FeMTH and its decomposition products. X-ray data establishing the octahedral structure isomorphous with the Mn^{2+} analogue are also presented. Crystal-field parameters have been derived from an analysis of temperature dependence of quadrupole splitting for the d^6 case and optical spectral data conveniently obtained in the solid state using the photoacoustic spectral technique. The results of differential thermal analysis and thermogravimetric studies carried out to facilitate Mössbauer studies of decomposition products are also presented. A brief note on the Mössbauer spectrum of the single crystal,

originally taken up for an e.f.g. tensor analysis but yet to be completed is also included.

7.2. Experimental

FeMTH was prepared by dissolving iron powder (500 mg) (electrolytic grade, Sarabhai Chemicals) in a hot aqueous solution containing a 100% excess of maleic acid (Reidel), concentrating the resultant solution to half the original volume and cooling to room temperature. For the manganese analogue, the stoichiometric amount of manganese chloride (BDH) was converted into hydroxide by adding ammonia. The excess of ammonia was eliminated by slow heating and the resultant solution was dissolved in aqueous solution containing a 100% excess maleic acid. The crystals obtained were separated and dried in vacuum. Light yellow and colourless crystals were obtained for the iron and manganese salts, respectively.

The Mössbauer spectra were recorded as discussed in section 2.1.1. DTA and TGA were recorded on home made units, details of which are given in sections 6.1.2. and 6.1.3. Details of X-ray measurements also are given earlier in Section 2.1.4.

7.3. Results and Discussion

7.3.1. X-ray studies

FeMTH is found to be highely soluble in water. Its solubility in water and the similarity of the molecular formula with that of MnMTH, CoMTH, ZnMTH, NiMTH and CuMTH suggest a monomeric structure. Of these the crystal structures of CuMTH and MnMTH have been reported [1,2]. For the maleates CoMTH, ZnMTH and NiMTH preliminary crystal structure data are available [3,4]. We prepared these maleates to investigate whether FeMTH is isomorphous with any one of them. Figure 7.1 shows the X-ray powder diffractograms of FeMTH and MnMTH in the form of histograms. The d-values and the intensities of the respective lines of FeMTH were found to be close to that of MnMTH (Table 7.1). A comparison of the d-values of the two maleates show them to be isomorphous. MnMTH crystallizes in the triclinic unit cell with $P\bar{1}$ space group. The cell parameters are reported to be a = 7.35, b = 9.77, c = 5.18 Å and α = 106.9, β = 94.6 and γ = 116.6° [2]. The unit cell contains one molecule of MnMTH and the central metal ion is situated at (OOO) position in an octahedral geometry. The metal ion is coordinated to four water molecules and two maleate groups as shown in Figure 7.2. An analysis of X-ray
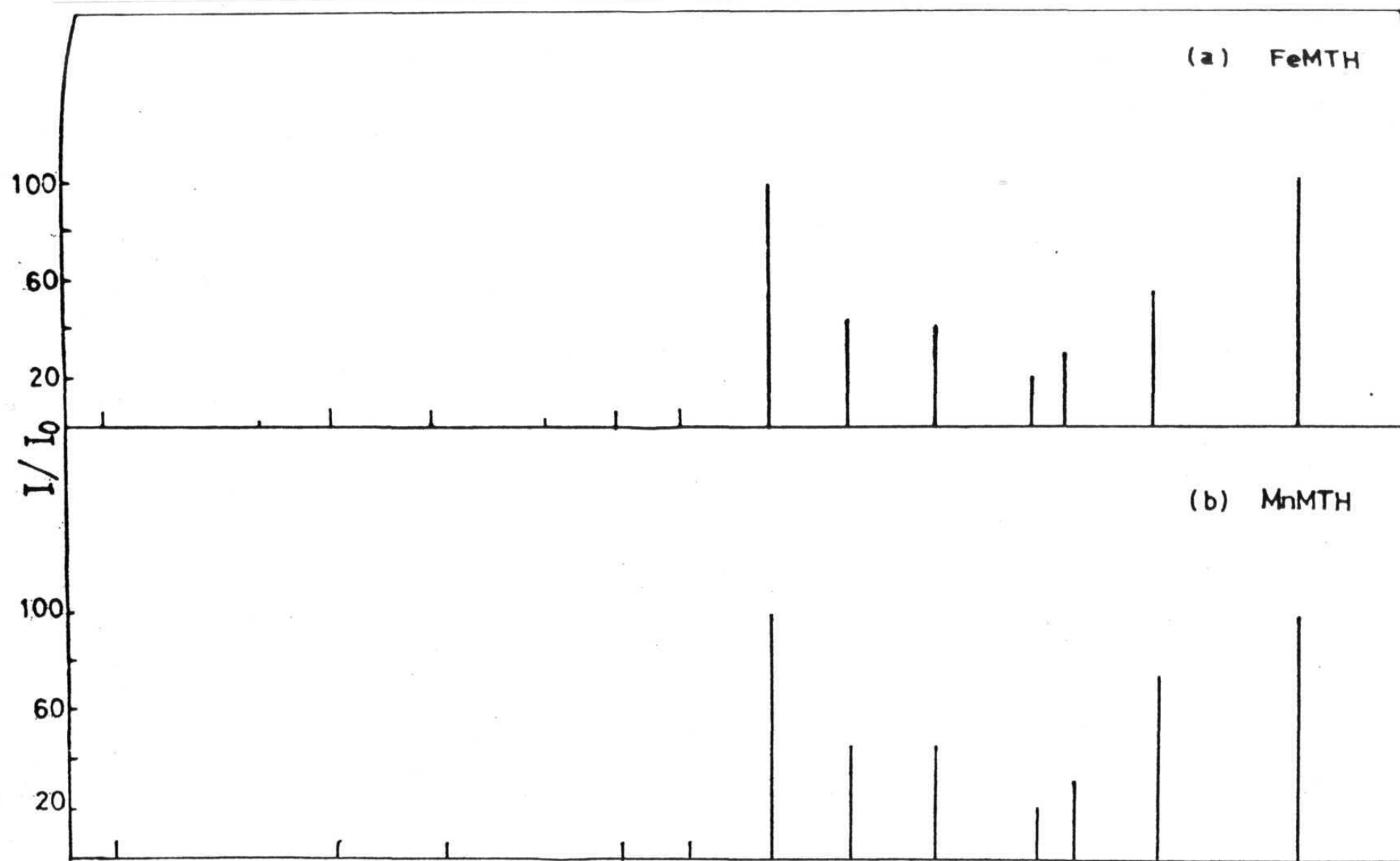
Fig.7.1 X-ray diffractograms of (a) Ferrous Maleate Tetrahydrate and (b) Manganese Maleate Tetrahydrate.

Table 7.1. X-ray data of tetraquabis [Maleato(-1) iron(II) and manganese(II).

FeMTH d_{obs}	Relative intensity	MnMTH d_{obs}	Relative intensity
6.56	100	6.69	100
5.02	75	5.06	80
4.40	30	4.41	30
4.15	20	4.18	20
3.68	40	3.71	45
3.30	45	3.34	45
3.02	100	3.07	100
2.86	5	2.85	5
2.66	5	2.70	5
2.65	3	2.67	3
2.29	5	2.32	5
2.28	3	2.26	5
2.11	5	2.13	8
1.75	5	1.75	5

Fig.7.2 Crystal structure of Manganese Maleate Tetrahydrate

data of FeMTH complex using a least square fit programme for the refinement of cell parameters lead to a = 7.27, b = 9.60, c = 5.24 Å and α = 105.9°, β = 87.8° and γ = 115.6°.

7.3.2. Mössbauer studies

The Mössbauer spectra of FeMTH were recorded in the range 15-320 K. Figure 7.3 shows a representative Mössbauer spectrum recorded at 15.5 K. All the spectra show large quadrupole splitting with sharp line widths of ∽ 0.30 mm/sec. Table 7.2 gives the Mössbauer parameters for these spectra. The isomer shifts, quadrupole splits and the line width values are typical of Fe^{2+} in high spin state with only one type of iron present. The increase in isomer shift with decrease in temperature is in accordance with the theoretical prediction for the second order doppler shift [5]. The absence of magnetically split spectra up to 15 K shows the absence of any strong metal-metal interactions either directly or indirectly through the ligand atoms unlike in the case of ferrous oxalate dihydrate [6]. The significantly large quadrupole splitting of 3.15 ± 0.02 mm/sec for this compound is in accordance with the crystal structure for the isomorphous manganese complex which shows the metal ion to be in a considerably distorted octahedral environment [2]. The quadrupole
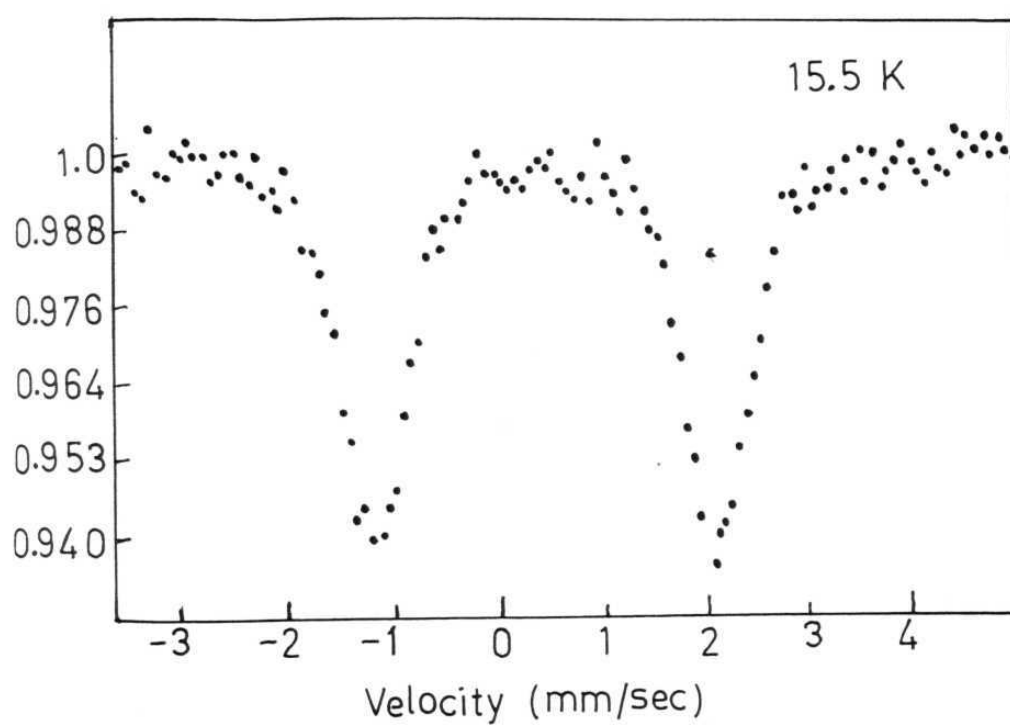
Fig.7.3 Mössbauer spectrum of Ferrous Maleate
Tetrahydrate at 15.5 K.

Table 7.2. Mössbauer parameters of Iron(II) maleate tetrahydrate between 15.5 and 323 K.

Temp (K)	I.S[‡]. (mm/sec) ($\pm$0.02)	Q.S. (mm/sec) ($\pm$0.02)	(mm/sec) (0.015)
323	1.23	2.99	0.34
303	1.26	3.15	0.31
196	1.26	3.29	0.26
80	1.37	3.51	0.29
15.5	--	3.24	0.28

‡w.r.t Fe-foil.

splitting for the FeMTH is found to be significantly larger than that of iron(II) oxalate dihydrate and iron(II) malonate dihydrate [6,7]. Although one would expect less distortion in complex formation with monodentate ligands, the quadrupole splitting at any given temperature in these systems show that the distortion from cubic symmetry at the metal site is in the order: oxalate < malonate < maleate. Thus the differences in the bonding of the anions with the transition metal ions mentioned above, the size of the anions and possibly hydrogen bonding in these systems discussed in detail in literature play a significant role in deciding the crystal symmetry and the local symmetry at the metal site [2,8,9].

The variation of quadrupole splitting with temperature in the range 15-320 K is given in Figure 7.4. The data were fitted to a theoretical curve by diagonalising a 15 x 15 matrix to obtain the energy levels arising from the $^5T_{2g}$ level of Fe^{2+} (^5D) state. The terms corresponding to tetragonal (∂) and rhombic (ϵ) distortions were included in the calculations of the electric field gradient (e.f.g) as discussed in section 2.2.1. The contributions to the e.f.g from the ^5E_g levels were ignored. The matrix elements and the computer programme developed earlier in this laboratory for the purpose of such an analysis were made use of for
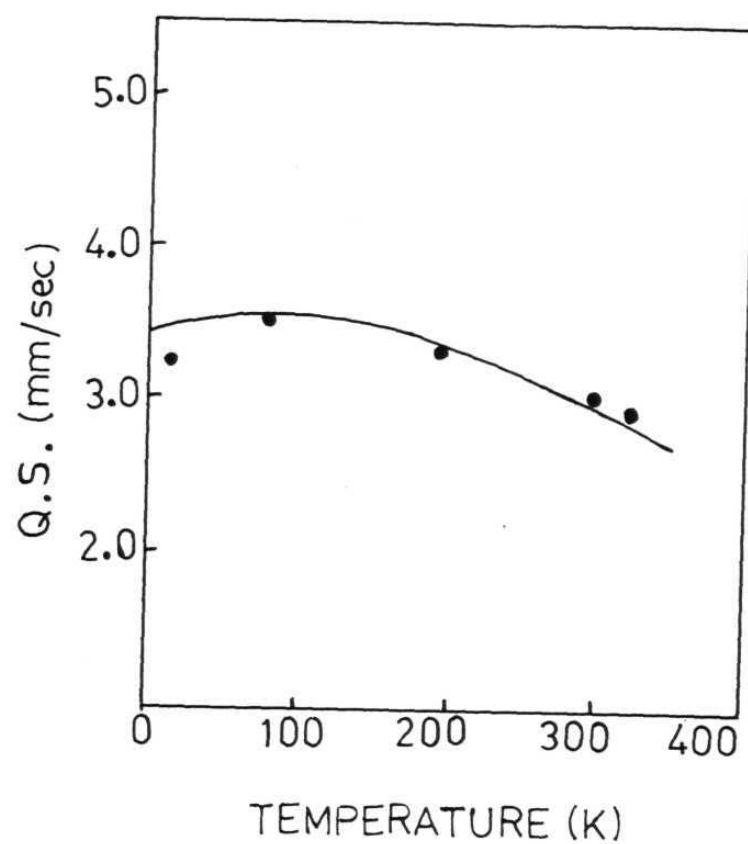
Fig.7.4 Plot of q.s. vs T. Experimental data
are given as points and the continuous
line reproduces the theoretical curve.

obtaining the crystal field parameters for the present case. The theoretical curve giving close agreement with experimental points thus obtained is also reproduced in Figure 7.4. A value of $\lambda = -80$ cm^{-1} was employed for spin-robit coupling constant [10]. The closest agreement is found to correspond to a tetragonal field (δ) of ~ 650 cm^{-1} and a rhombic field (ε) of ~ 190 cm^{-1} with an orbital singlet (d_{xy}) lying lowest. The theoretical prediction of a decrease in the quadrupole splitting at low temperature was substantiated by experiment. Any deviations between the theoretical curve and the experimental points may be attributed to the approximation employed by way of the crystal field approach.

A single crystal Mössbauer spectrum recorded at room temperature for an arbitrary orientation is reproduced in Figure 7.5 for a comparison with that of the powder spectrum. This shows significantly unequal intensities for the quadrupole split spectrum compared to the powder spectrum (Fig. 7.3) and arises due to the difference in the dependence of intensities for the lower and higher γ-rays to the angle between the direction of emission and the axis of symmetry [11-13]. Further Mössbauer and X-ray work to determine the e.f.g. tensor relative to the crystal axes are under progress.
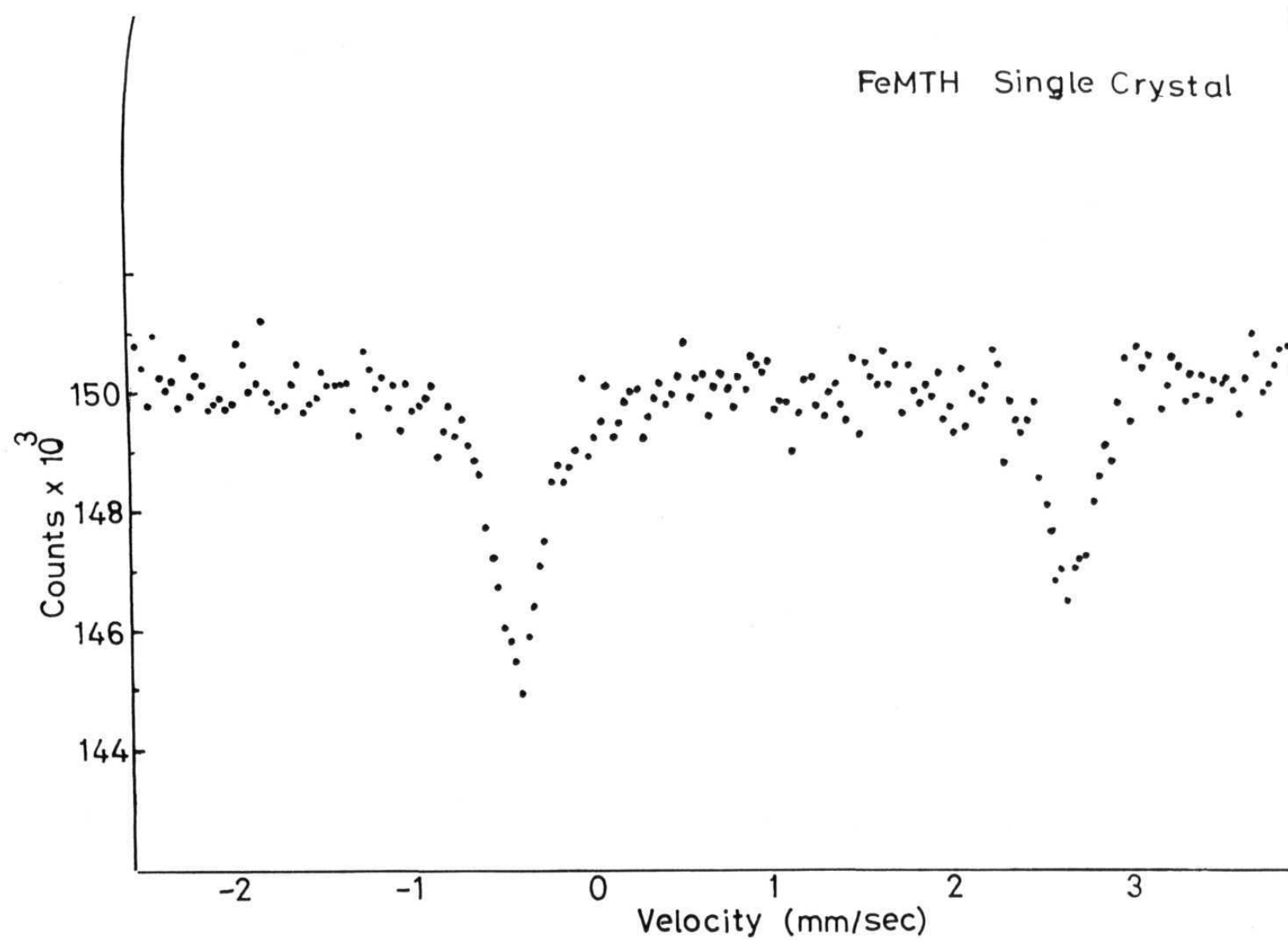
Fig.7.5 Single crystal Mössbauer spectrum of Ferrous Maleate Tetrahydrate at an arbitrary orientation.

7.3.3. Optical spectra

Optical spectra can give complementary information on
the lower ligand fields. The solution spectrum of FeMTH gives
a broad symmetric maximum around 10,000 cm^{-1} with an extinction
coefficient of 1.8 due to d-d transition (Fig. 7.6) [14]. The
photoacoustic spectrum (PAS) of solid FeMTH gives an asymmetric
band with shoulders, the centre of gravity of which was found
to be at 9800 cm^{-1} (Fig. 7.7). The band has a definite
doublet structure with a peak separation of 1400 cm^{-1}. The
optical spectrum is very similar to those reported for high-
spin Fe^{2+} and arises from the $^5T_{2g} \longrightarrow {}^5E_g$ transition [15].
The splitting of the band can be ascribed to the splitting
of the excited state in a permanently distorted ligand field
as in the case of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ or to dynamic Jahn-
Teller effects [15,16]. We prefer the former reason in the
present case in view of the large quadrupole splitting,
indicative of large distortion from cubic symmetry at the
iron site. A large distortion from cubic symmetry in this
case could arise both from the electronic and lattice
contributions. Evidence for a strongly distorted lattice
symmetry at the metal site was also obtained from the ESR
measurements on the manganese analogue [17].
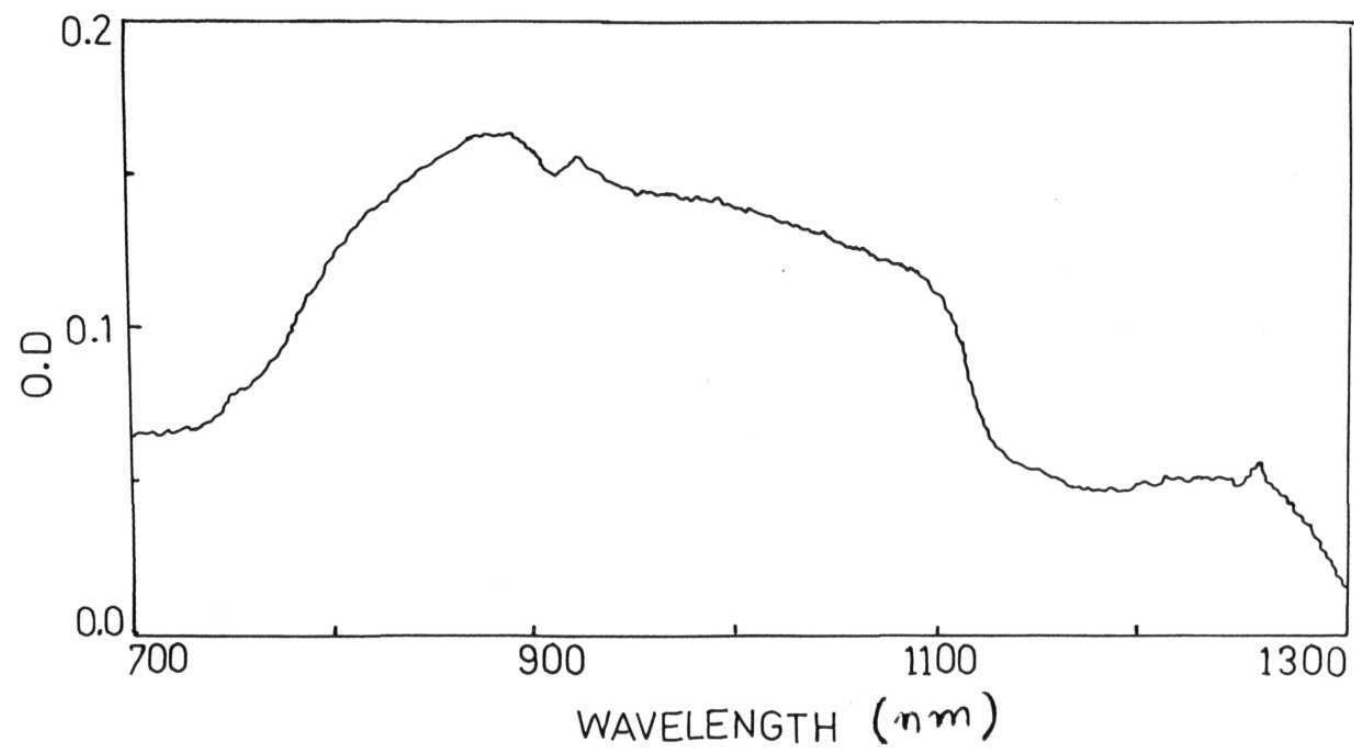
Fig.7.6 Optical spectrum of Ferrous Maleate Tetrahydrate.
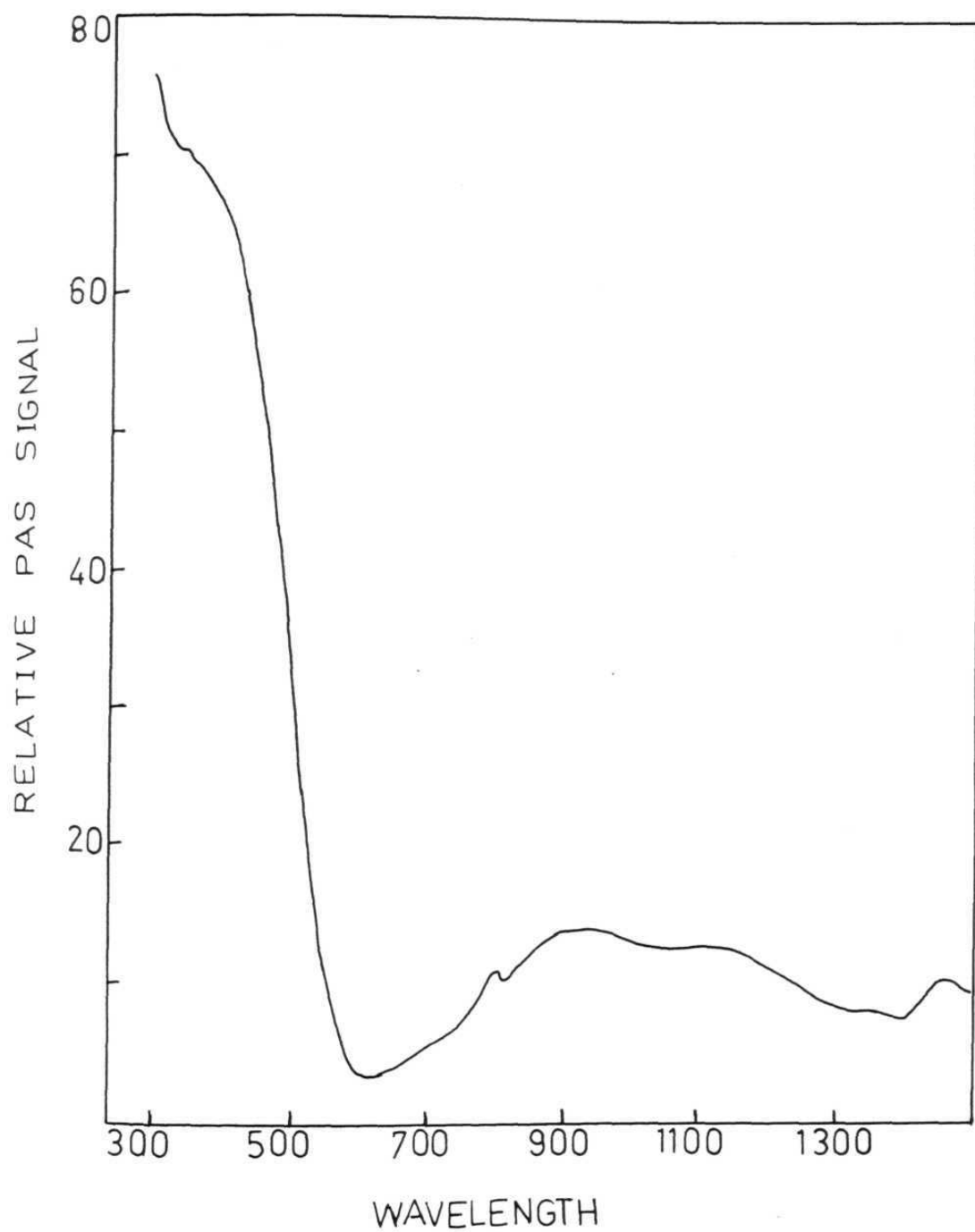
Fig.7.7 Photoacoustic spectrum of Ferrous Maleate Tetrahydrate (wavelength in nm).

7.3.4. Decomposition studies

The differential thermal analysis (DTA) and thermo-
gravimetric analysis (TGA) curves obtained for FeMTH are given
in Figure 7.8. The compound starts decomposing at $140^{\circ}C$ and
gives rise to an endothermic peak in the region $140-240^{\circ}C$.
Further decomposition of the resultant material occurs exo-
thermally at $270-500^{\circ}C$. Both the TGA results corresponding
to weight loss at $230^{\circ}C$ and independent decomposition studies
at this temperature showed weight loss corresponding to the
loss of 32.1% which is quite close to 32.4% corresponding to
the loss of one molecule of maleic acid. The TGA curve also
shows the decomposition product formed at $\sim 230^{\circ}C$ to be
fairly stable up to $\sim 260^{\circ}C$. The room temperature Mössbauer
spectra of the original compound and those of the decomposi-
tion products obtained at 235 and $275^{\circ}C$ are compared in
Figure 7.9. The product obtained by heating the complex at
$235^{\circ}C$ gave rise to a spectrum with an isomer shift of 1.20 $\pm$
0.02 mm/sec relative to iron and a quadrupole splitting of
2.5 $\pm$ 0.02 mm/sec providing evidence for Fe^{2+} in octahedral
symmetry. Further, the smaller quadrupole splitting of the
product compared to that in the parent material indicates a
structure with a significantly less distortion from cubic
symmetry. The iron(II) product thus obtained is also
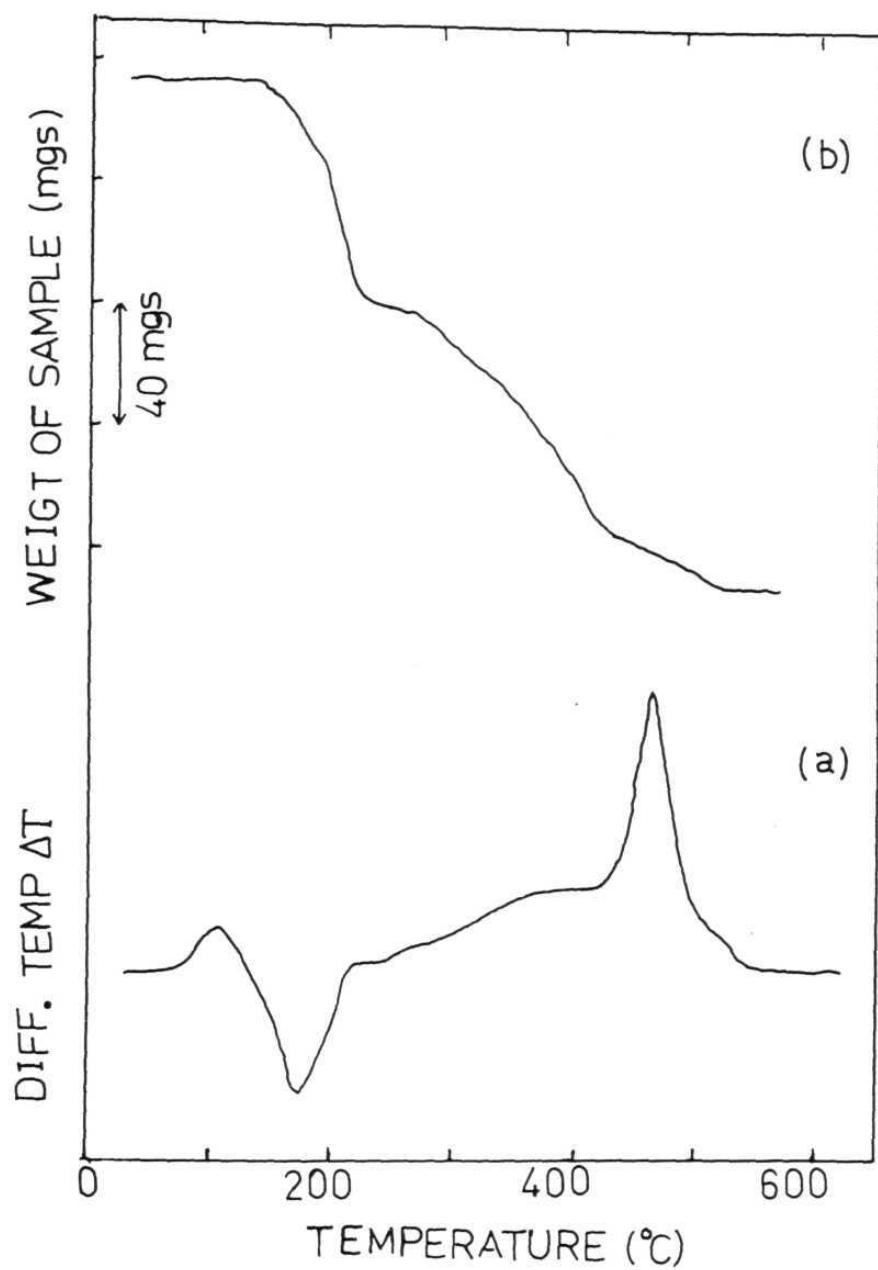
Fig.7.8 (a) DTA and (b) TGA curves for Ferrous Maleate
Tetrahydrate.
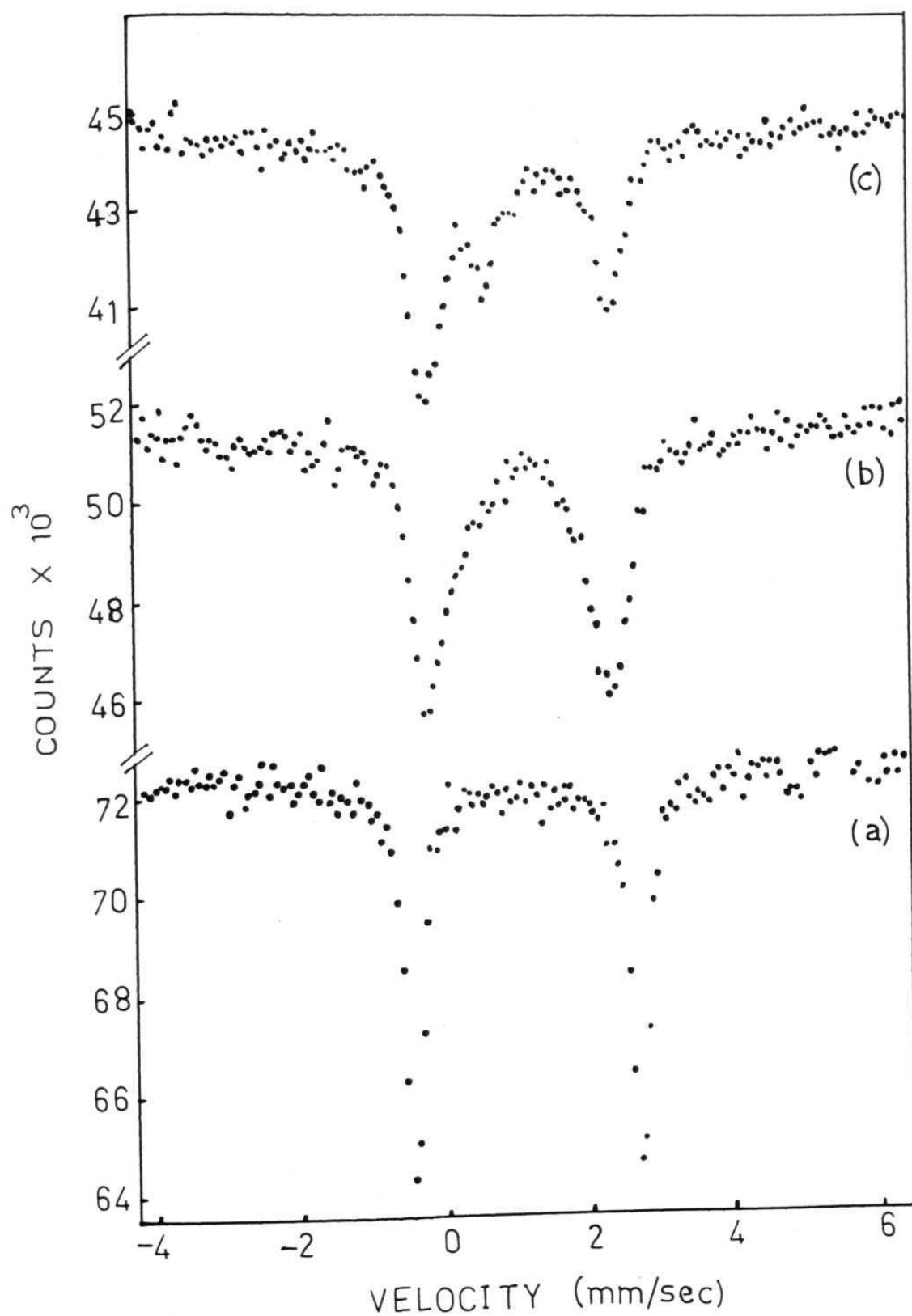
Fig.7.9 Room temperature Mössbauer spectra of (a) Ferrous Maleate Tetrahydrate (b) the product obtained after heating to 235°C and (c) after heating to 280°C.

resistant to air oxidation. Any heating carried out at higher temperatures give rise to products with Mössbauer spectra with components corresponding to iron(III) (Fig. 7.9c). The intermediate product is tentatively identified as an iron(II) maleate formed from the complex FeMTH by a reaction of the type shown

$$[Fe(H_2O)_4(LH)_2] \longrightarrow [Fe(H_2O)_4L] + LH_2$$
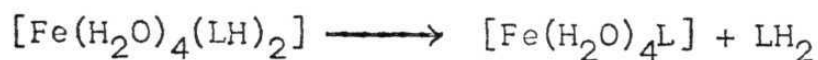
where LH_2 is maleic acid.

7.4. Conclusions

FeMTH contains maleate (1-) and is isomorphous with the manganese(II) analogue. Mössbauer studies show the structure to be highly distorted from cubic symmetry compared to the ferrous oxalate dihydrate and ferrous malonate dihydrate. The temperature dependence of quadrupole splitting in the range from 320 down to 15 K shows the absence of any metal-metal interactions. Mössbauer data and optical spectra allow estimates of 10 Dq, the tetragonal field, rhombic field and E_g level splitting to be~10,000, ~650, ~190 and ~1400 cm^{-1}, respectively. DTA and TGA studies indicate elimination of one molecule of maleic acid at 235°C. Mössbauer

studies of the decomposition products show formation of a stable compound with octahedral geometry and less distorted than the parent material. Further heating shows appearance of an iron (III) species which subsequently decomposes into oxide.

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ESR STUDY OF Cu^{2+} DOPED IN ZINC MALEATE TETRAHYDRATE[†]

Abstract

An ESR study of 1% Cu^{2+} doped in zinc maleate tetra-hydrate single crystal is found to give rise to $g_1 = 2.374$, $g_2 = 2.257$ and $g_3 = 2.043$. These values are quite different from the g values for the pure copper(II) compound, copper maleate tetrahydrate, viz., $g_{||} = 2.172$ and $g_{\perp} = 2.095$ indicating that in Cu^{2+}/ZnMTH, Cu^{2+} occupies a compressed octahedral, substitutional site. The ground state is determined to be $0.724|3Z^2-r^2> + 0.173|x^2-y^2>$. In this case Cu^{2+} is coordinated to two maleate groups and four water molecules unlike in the parent copper compound where coordination takes place only with water molecules. The photo-acoustic spectrum of copper maleate tetrahydrate gives rise to a charge-transfer band at $\sim 37,000$ cm^{-1} and d-d transition at $\sim 15,000$ cm^{-1} with a shoulder at $\sim 12,000$ cm^{-1}.

8.1. Introduction

An electron spin resonance (ESR) study of Cu^{2+} doped
in zinc maleate tetrahydrate (hereafter ZnMTH) is of interest
as the crystal structures of copper maleate tetrahydrate
(hereafter CuMTH) and ZnMTH are different and Cu^{2+} can retain
its original structure or it can assume a structure dictated
by the parent lattice [1-3]. In ZnMTH the metal ion is
coordinated to two maleate groups and four water molecules as
in the case of MnMTH, the structure of which is reproduced
in chapter 7 (Fig. 7.2). On the otherhand, in CuMTH the
maleate groups are not coordinated but only hydrogen bonded
to water molecules (Fig. 8.1). A third possibility is the
occupation of an interstitial site by Cu^{2+} as found in
cadmium maleate dihydrate [4]. In this chapter we present
the results of an ESR single crystal study of Cu^{2+}/ZnMTH.
The informations regarding the g and A tensors, the ground
state and the extent of mixing with higher orbitals are
obtained. A brief discussion of the powder ESR spectrum and
the photoacoustic spectrum giving the d-d transitions of the
parent copper compound, viz., CuMTH are also included to
bring out the differentiating features in the microsymmetries.
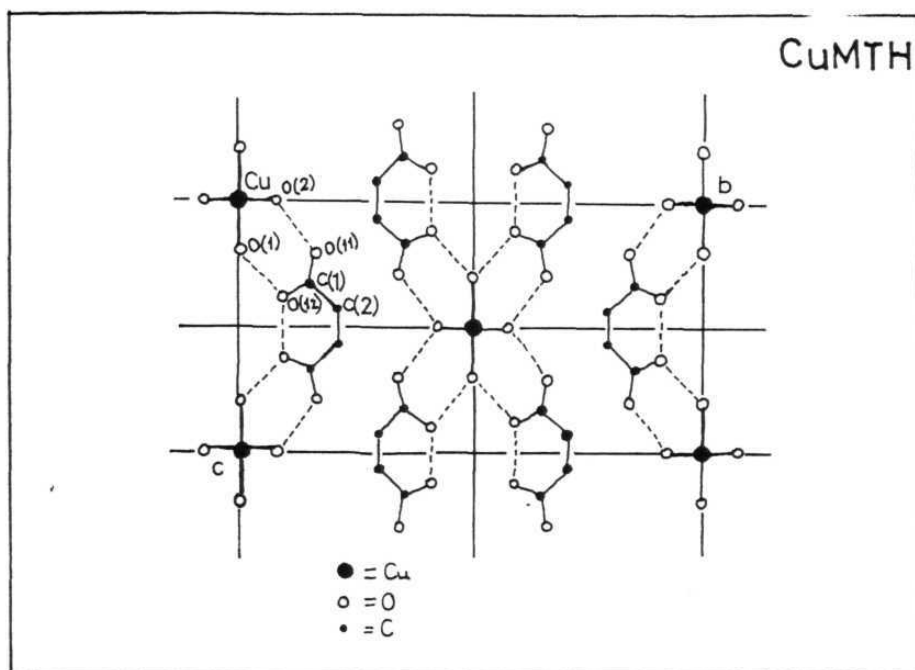
Fig.8.1 Crystal structure of Copper Maleate Tetrahydrate

8.2. Experimental

Stoichiometric amounts of Cu^{2+} or Zn^{2+} metal ions are taken in the form of sulphates (Analar. BDH) and precipitated as hydroxides using ammonium hydroxide. After eliminating excess ammonia by warming the solution the resultant hydroxide is treated with 100% excess hot maleic acid (SD chemical). Upon concentrating the solution deep blue crystals of CuMTH and colourless crystals of ZnMTH separated out. The ZnMTH crystals were doped with 1% Cu^{2+} at the starting point. Cu^{2+} and Zn^{2+} in the pure compounds were estimated as oxides. (Cald. for $C_8H_{14}O_{12}M^{II}$, (M = Cu^{2+}, Zn^{2+}): Cu^{2+} = 17.38%, Zn^{2+} = 17.79%, observed: Cu^{2+} = 17.05%, Zn^{2+} = 17.06%).

The ESR spectra have been recorded on three mutually perpendicular laboratory planes (hereafter plane $\acute{Y}Z$, $\acute{X}Z$ and $\acute{X}\acute{Y}$) at an interval of 10°.

The g values corresponding to equivalent positions achieved in rotating the crystal along the three mutually perpendicular axes were found to agree within experimental error confirming proper mounting of the crystal for different orientations. The values thus obtained for the equivalent positions are presented in Table 8.1.

Table 8.1. Comparison of g-values corresponding
            to identical orientations when the
            crystal in rotated in different planes.

Plane $\parallel$ H	g ($\pm$0.003)		
	X'	Y'	Z
X'Y'	2.270	2.176	–
Y'Z	–	2.172	2.168
X'Z	2.262	–	2.167

8.3. Results and Discussion

The ESR spectra Cu^{2+}/ZnMTH consists of four lines for an arbitrary orientation of the crystal in the static magnetic field with adjacent lines seperated by ⌐40 gauss (Fig. 8.2). The linewidth of the individual lines is found to be ⌐ 40 gauss. The results of an angular variation study carried out for crystal rotations in three mutually perpendicular planes are reproduced as g^2 <u>vs</u> Θ and g^2A^2 <u>vs</u> Θ plots in Figures 8.3 and 8.4, where Θ is the angle between the dc magnetic field and the reference axis. These plots were analysed according to the method of Schonland [5] by least square fitting the experimental data to the expression

$$g(\Theta) \;=\; U + VCos2\Theta + WSin2\Theta \qquad \ldots (6.7)$$

as discussed in section 6.2.4. The solid lines in the figure correspond to the least square fit expression of the experimental points. Using the g^2_{max}, g^2_{min}, $g^2A^2_{max}$ and $g^2A^2_{min}$ the g and A matrices were set up and diagonalised to give the g and A values in the principal axes system. The values thus obtained are given in Table 8.2. Figures 8.5 and 8.6 show the powder ESR spectra of CuMTH and Cu^{2+}/ZnMTH respectively. The g values evaluated from these powder spectra are also included in Table 8.2.

Fig.8.2 Room temperature ESR spectrum of Cu-doped ZnMTH for crystal rotation about Y' axis.
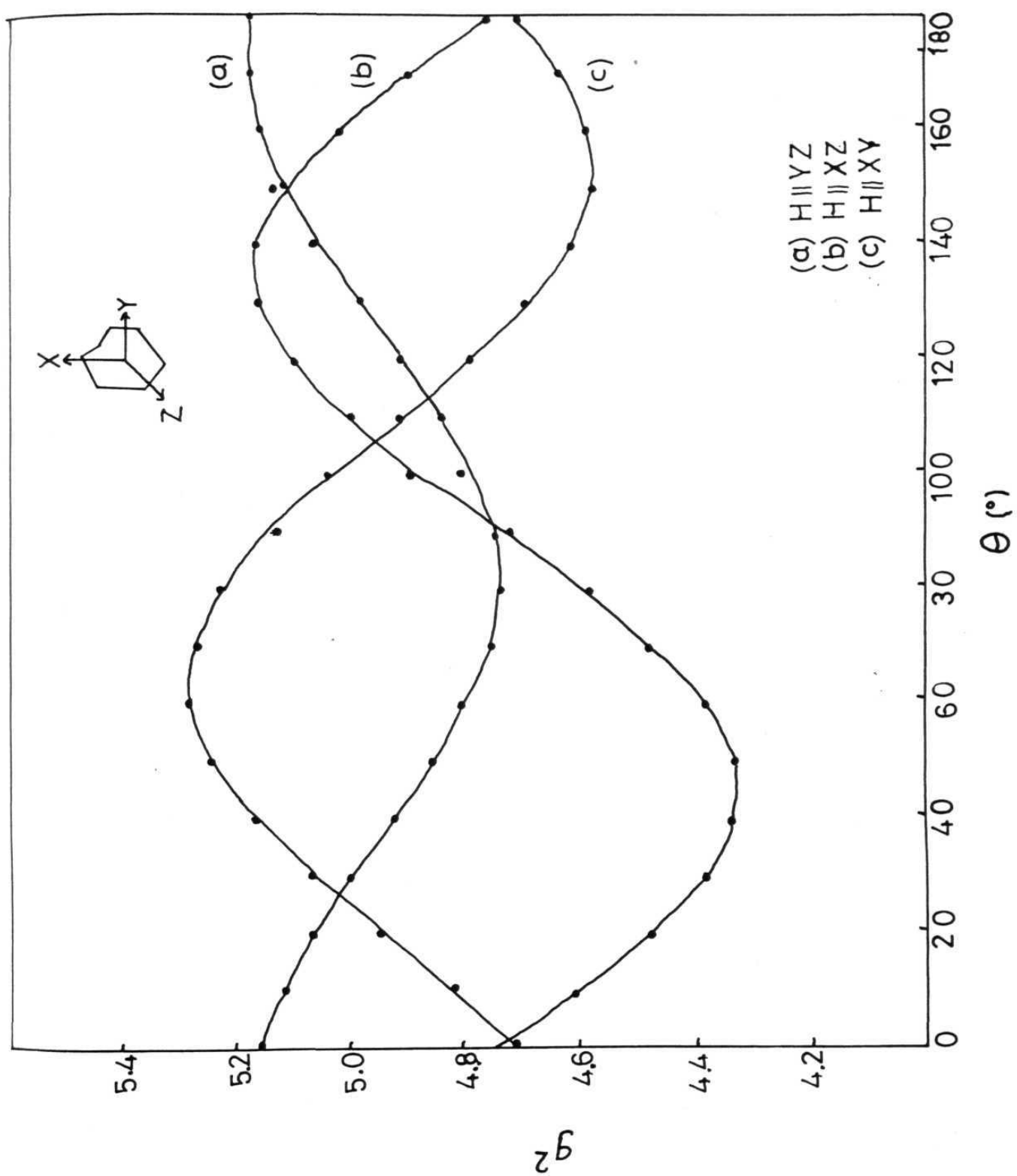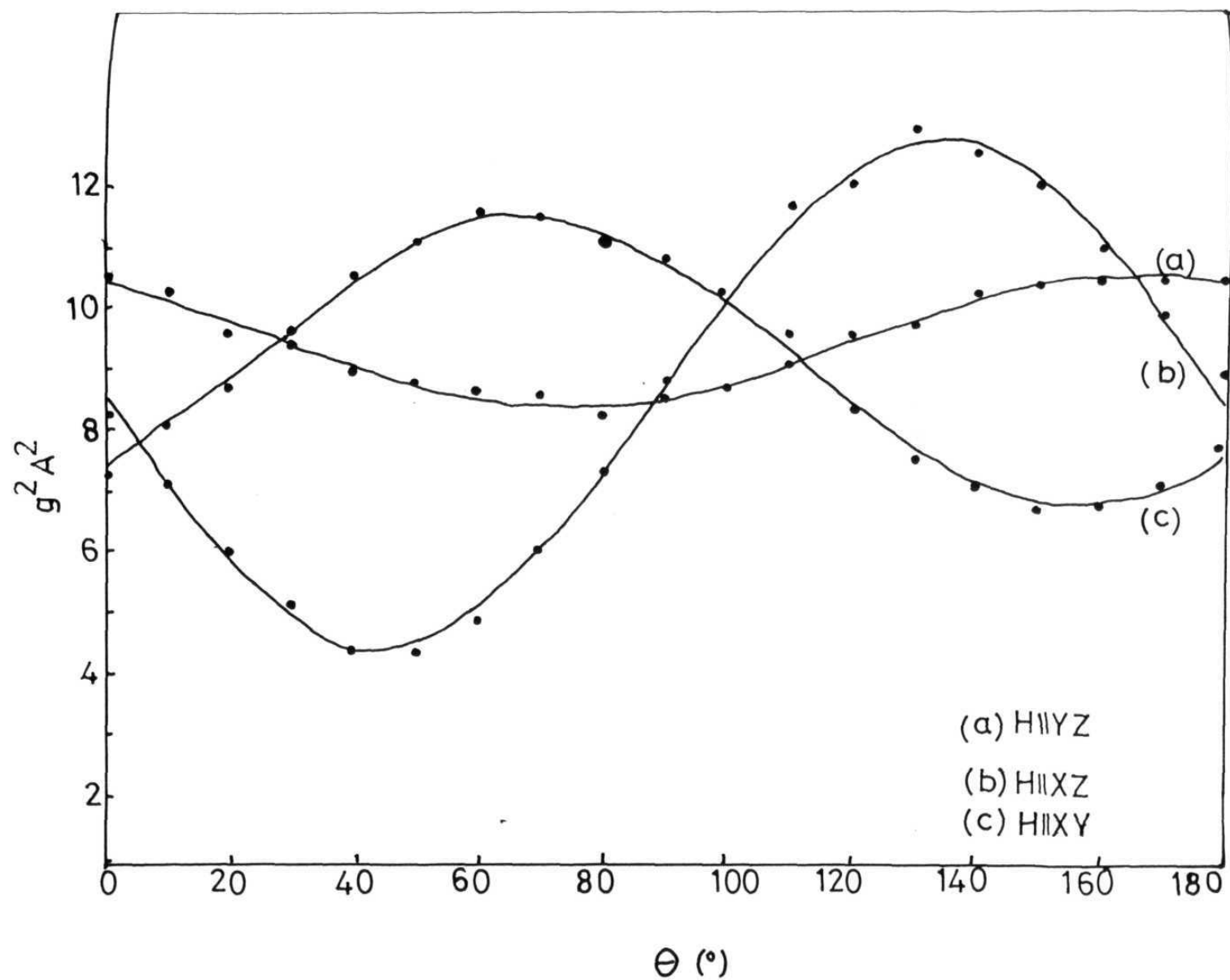
Fig.8.4 Angular variation of Cu-hyperfine structure (g^2A^2) in the ESR spectra of Cu-doped ZnMTH for crystal rotations about (a) X' axis, (b) Y' axis and (c) Z axis.

Table 8.2. Comparison of g, A, α, β values in Cu-doped ZnMTH and related systems (A values are in units of 10^{-4} cm^{-1}).

Host lattice	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	α	β	ground state	Remarks	Ref.
$Zn(HCOO)_2 \cdot 2H_2O$	2.077	2.077	2.416	23	23	124			$d_{x^2-y^2}$	2 sites Substitutional	13
ZnMTH* (Single crystal)	2.374	2.207	2.043	46.8	39.7	29.5	0.724	0.173	d_{z^2}	Substitution	Present work
ZnMTH (powder)	2.33	2.21	2.06	-	-	-	-	-	-	-	Present work
CuMTH (powder)	2.095	2.095	2.172	-	-	-	-	-	-	-	Present work
Cadmium maleate dihydrate	2.091	2.091	2.409	11	11	126	0.895	0.104	$d_{x^2-y^2}$	Interstitial	4
Zn(II) (pyridine-3-sulphonate)	2.283	2.221	2.055	63	42	77	-	-	d_{z^2}	Substitutional	10

*g values are accurate to ± 0.003.
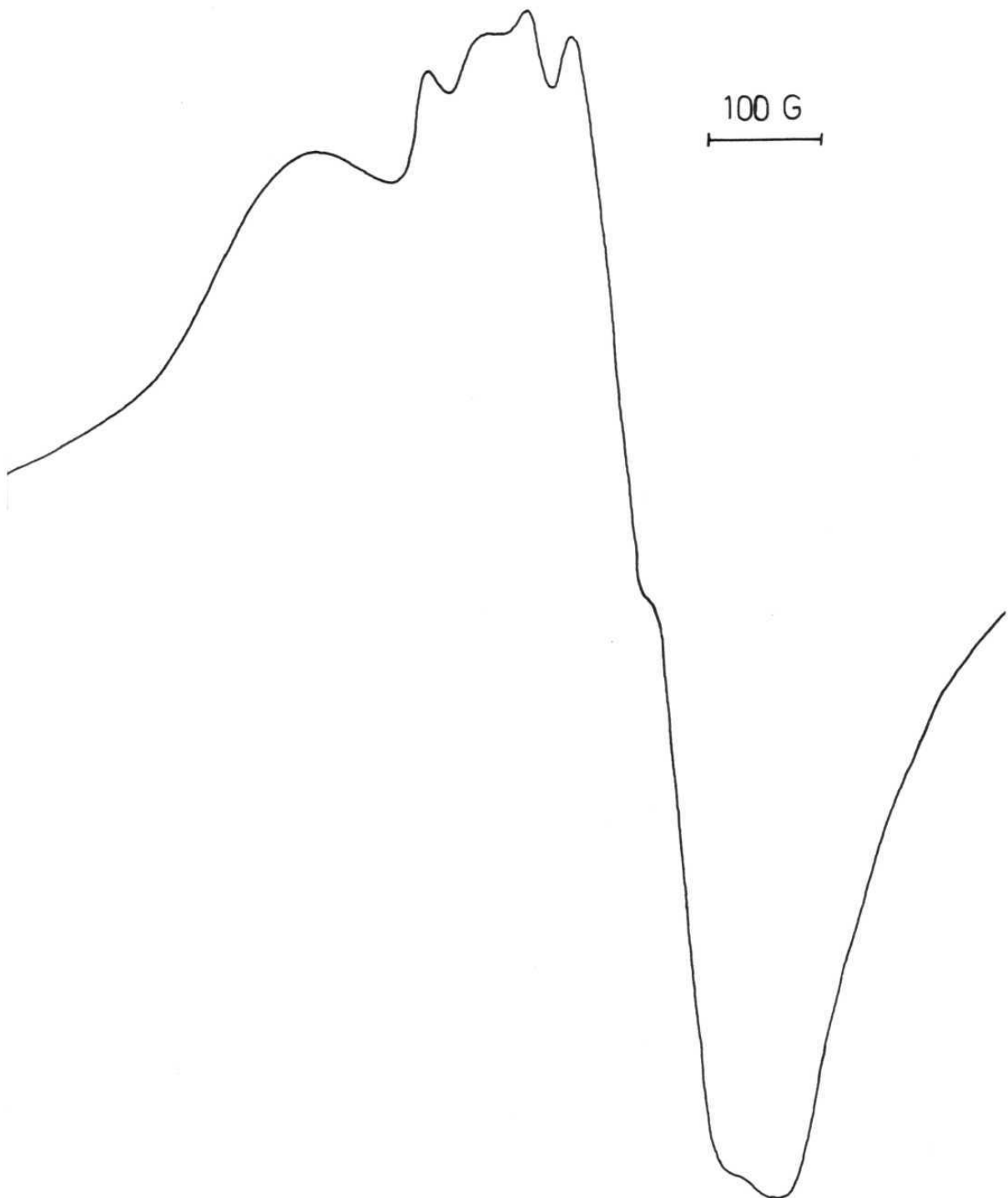
Fig.8.5 Room temperature powder ESR spectrum of Copper Maleate Tetrahydrate.
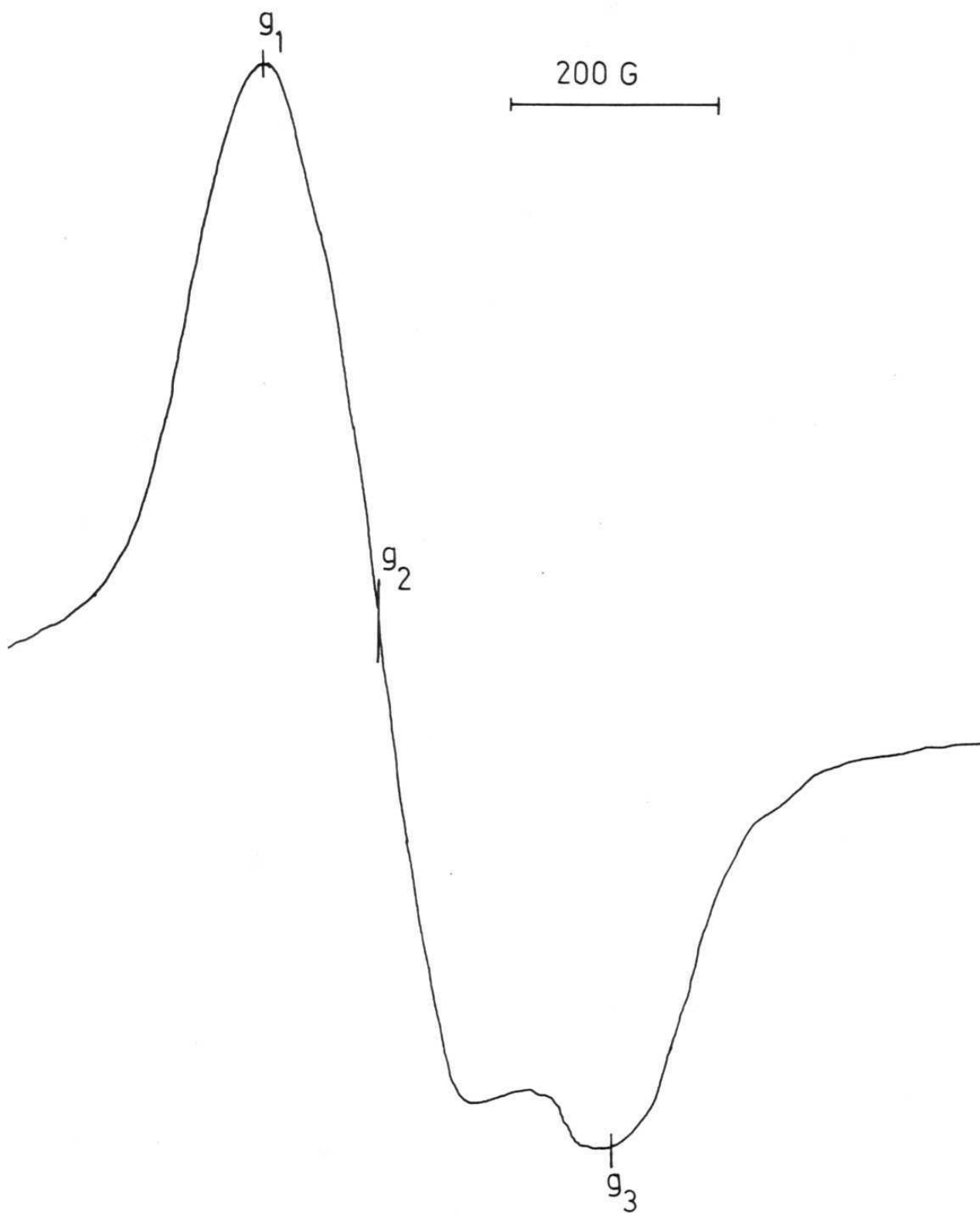
Fig.8.6 Room temperature powder ESR spectrum of Cu-doped ZnMTH.

The observed four line spectra (Fig. 8.2) is typical of Cu^{2+} resonance arising from single site. The linewidth of the individual lines which is $\smile$40 gauss is of the order of hyperfine coupling constant. The present system being paramagnetically dilute, the observed linewidth could arise from (i) spin lattice relaxation (ii) unresolved isotopic resonances (^{63}Cu and ^{65}Cu) and (iii) possible unresolved super hyperfine interaction with nearby protons. Furthermore, the lines are fairly symmetric and there are only four peaks for all crystal orientations. The crystal structure of the host lattice being of such low symmetry, any physical or chemical inequivalence in the occupancy of Cu^{2+} would easily manifest in the ESR spectra [6]. Interstitial insertion may also be ruled out in view of the fact that in analogous systems it is found to give rise to poorly resolved broad lines in all orientations in the room temperature measurements [4]. A comparison of the unit-cell dimensions of the isomorphous triclinic systems M'MTH(M' = Co^{2+}, Ni^{2+} and Zn^{2+}) with the reported detailed crystal structure data for MnMTH, according to which Mn^{2+} ions occupy special positions (OOO) in the triclinic unit cell, and our own observation by ESR that Mn^{2+} goes into substitutional site in ZnMTH, support the view that the transition metal ion in ZnMTH and MnMTH have closely similar micro-symmetry with only type of site occupancy [1,2,7,8]. In

such a case, Cu^{2+} occupying only one type of site substitutionally, should also give rise to ESR spectrum due to only one type of Cu^{2+} ion as observed.

The ^2D (d^9) ground state of Cu^{2+} splits into five non-degenerate orbitals if the symmetry of the crystalline electric field is lower than axial. Taking d_z2 as the ground state for reasons discussed later, and $d_x2_{-y}2$ as the close by, higher state, the ground state wavefunction may be written as $\alpha|3z^2-r^2> + \beta|x^2-y^2>$ where α and β are the mixing coefficients arising from spin-orbit interaction. The departure (Δg_i) of each of the three principal g-values, g_i from the free spin value 2.0023, and the principal A values are substituted in the simultaneous equations developed by Sroubeck and Zdansky [9] and solved to obtain the values of α and β. As the signs of A_1, A_2 and A_3 are not known, trial combinations were used in the above equations. Only when A_1 and A_2 were chosen positive and A_3 negative, the conditions $\alpha \approx 1$ and $\beta << 1$ could be met and the values were found to be $\alpha = 0.724$ and $\beta = 0.173$. The other parameters obtained are $P_{exptl} = \alpha^2$ $P_{freeion} = \alpha^2$ $g\beta g_N\beta_N < r^{-3}> = 0.019$ cm^{-1} using the value 0.036 cm^{-1} for $P_{freeion}$ in the case of Cu^{2+} and $k = 0.353$ which represents the admixture of configurations with s electrons caused by spin exchange polarisation.

To facilitate discussion we have included the g and A values of related systems along with those of Cu^{2+}/ZnMTH in Table 8.2. The lowest g value obtained for Cu^{2+}/ZnMTH viz., 2.043 is rather high to correspond to a pure d_z2 ground state and suggests extensive mixing of the d_z2 and the $d_x2_{-y}2$ in the ground state [10]. This is well in accord with the α and β values obtained. Two other noteworthy features are (i) the comparable magnitude of the A values and (ii) the association of the largest g-value with the largest A-value. Attempts to explain these features pointing out the importance of temperature dependence of the hyperfine parameters in such cases have been made by Walsh and Hathaway [10].

A comparison of the g-value for the Cu^{2+}/ZnMTH in single crystal and powder form of Cu^{2+}/ZnMTH and that of pure copper compound in the powder form show that Cu^{2+} is in different microsymmetries in ZnMTH and CuMTH. The g-values for the Cu^{2+} doped ZnMTH powder are close to those obtained for the single crystal (Table 8.2). On the other hand the pure copper compound, gives $g_{\parallel}$ = 2.172 $\pm$ 0.002, $g_{\perp}$ = 2.095 $\pm$ 0.002 indicating axial symmetry with Cu^{2+} in elongated octahedron ($g_{\parallel} > g_{\perp}$) with $d_x2_{-y}2$ as the ground state [1]. For the doped system $g_3 > g_2 > g_1 > 2.0$ signifies a distorted octahedron [11]. A survey of literature shows that in

parent zinc host lattices Cu^{2+} invariably goes into Zn^{2+} site, unlike in the case of Cd^{2+}, Sr^{2+} host lattices, where Cu^{2+} can also occupy interstitial sites. This may be attributed to comparable ionic radii for Cu^{2+} and Zn^{2+} (Cu^{2+} = 0.73 Å, Zn^{2+} = 0.75 Å) unlike in the case of Cu^{2+} and Cd^{2+} or Sr^{2+} (Cd^{2+} = 0.95 Å, Sr^{2+} = 1.16 Å). This is found to be true in the case of complexes of organic acids as well [4,12,13]. It is therefore reasonable to attribute the above g-values as due to substituted Cu^{2+}. The space group, unit cell dimensions and coordinations reported for the host lattice suggest a close similarity with that of manganese maleate tetrahydrate [2,3,7]. Assuming similar microsymmetry for the Cu^{2+} environment would imply that the g-values correspond to a compressed octahedron with d_z2 ground state. Such a conclusion would mean that Zn-lattice dictates both coordination and microsymmetry to the Cu^{2+} ion. Similar situations have been reported in cases like Zn(II) bis(pyridine-3-Sulphonate) [10,14]. Thus unlike in the CuMTH where copper ion is coordinated to six water molecules, in 1% Cu^{2+}/ZnMTH it will be bound to two maleate groups and four water molecules. Further confirmation of this conclusion can be obtained by determining the direction cosines provided the detailed crystal structure data for ZnMTH are available.

The photoacoustic spectrum of CuMTH is reproduced in Figure 8.7. An intense band at $\sim$ 37,000 cm^{-1} and a relatively less intense and broad band at $\sim$15,000 cm^{-1} with a shoulder at $\sim$12,000 cm^{-1} are observed. The intense band at $\sim$37,000 cm^{-1} arises due to charge transfer [15]. The broad bands at $\sim$ 15,000 cm^{-1} arise from d-d transitions. For the present case where Cu^{2+} is situated in an octahedron with four oxygen atoms in the plane at 1.95 Å and two oxygen atoms at 2.68 Å with $d_{x^2-y^2}$ as the ground state, the transitions would correspond to $d_{z^2} \longrightarrow d_{x^2-y^2}$, $d_{xy} \longrightarrow d_{x^2-y^2}$ and $d_{xz,yz} \longrightarrow d_{x^2-y^2}$. However, only two bands are observed due to poor resolution in a powder spectrum [15,16].

8.4. Conclusions

An ESR study of 1% Cu^{2+} doped in ZnMTH single crystal gives rise to g_1 = 2.374, g_2 = 2.257 and g_3 = 2.043. These values are quite different from the g-values for the pure copper compound viz., $g_{||}$ = 2.172 and $g_{\perp}$ = 2.095, indicating that in Cu^{2+}/ZnMTH, Cu^{2+} occupies a compressed octahedral, substitutional site with the ground state $0.724|3z^2-r^2> + 0.173|x^2-y^2>$, coordinated to two maleate groups and four water molecules, the microsymmetry being dictated by the host lattice, unlike in the copper compound
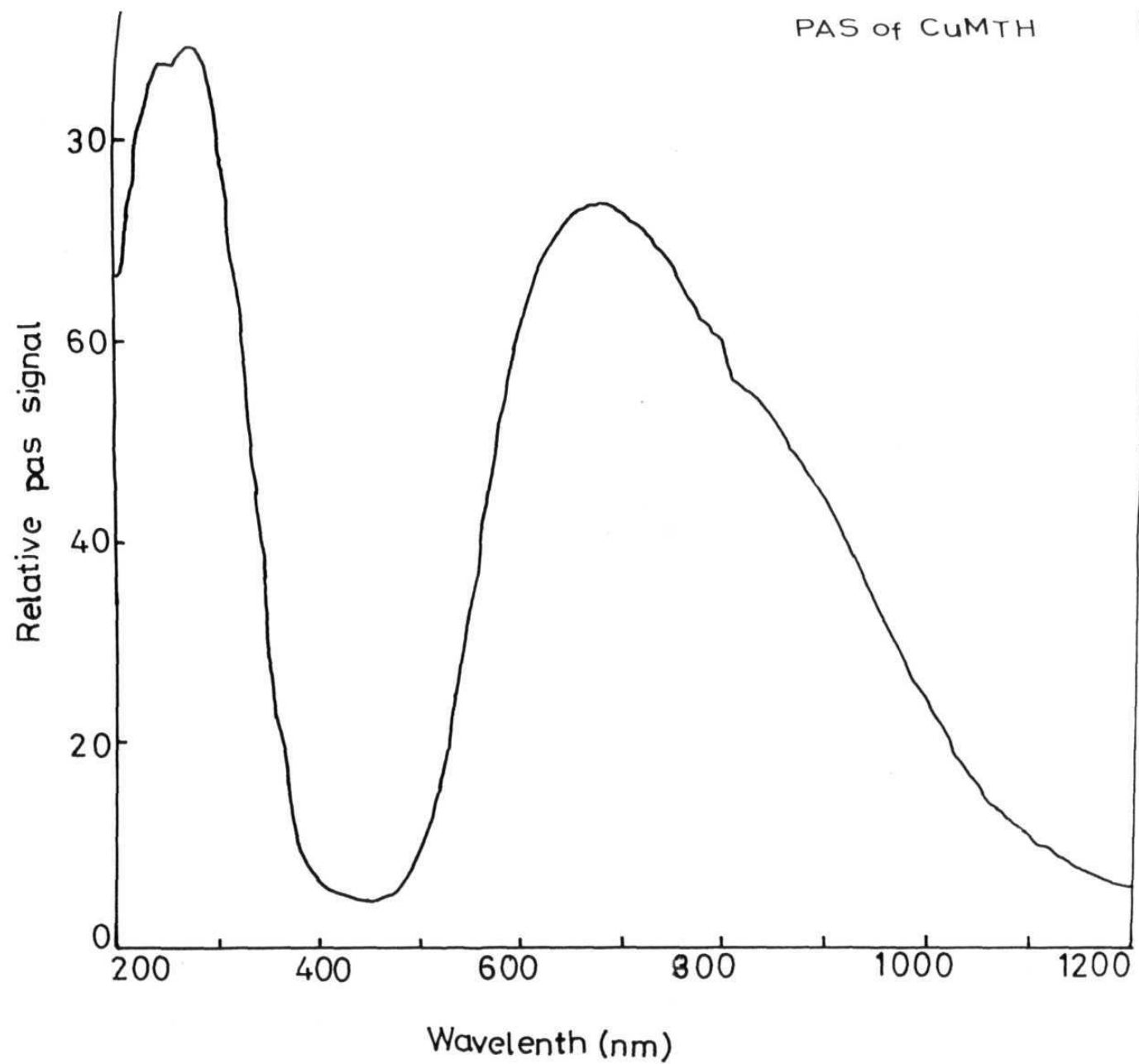
Fig.8.7 Photoacoustic spectrum of solid Copper Maleate Tetrahydrate.

where coordination takes place only with water molecules. The photoacoustic spectrum of CuMTH gives rise to a charge transfer band at $\sim$ 37,000 cm^{-1} and d–d transitions at $\sim$ 15,000 cm^{-1} with a shoulder at $\sim$ 12,000 cm^{-1}.

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CHAPTER 9

AN ESR STUDY OF Mn^{2+} DOPED ZINC
MALEATE TETRAHYDRATE

Abstract

The ESR study of 1% Mn^{2+} doped in ZnMTH single
crystal gives rise to the spin-Hamiltomian parameters
$D = 385.6$, $E = 71.5$, $a = -9.5$ and $A = -93$ gauss from an
analysis of the allowed hyperfine transitions corresponding
to the orientation of the principal axis parallel to the
magnetic field as shown by the absence of forbidden transi-
tions. The large g value viz., 2.035 observed for this
system has been attributed to a highly distorted cubic environ-
ment. An ionicity of 96.5% is deduced for the metal-ligand
bonding from a plot of A vs the Pauling's covalency parameter.
The analysis of forbidden hyperfine transitions is shown to
lead to $Q' = 1.69$ and $Q'' = 0.304$ for the axial and rhombic
componants of the quadrupole coupling constants respectively
of the ^{55}Mn nucleus.

9.1. Introduction

Electron spin resonance studies in organic acid complexes show that the dopant can go into substitutional or interstitial sites [1-5]. In addition, ESR studies throw light on the nature of the microsymmetry of the dopant [6]. A more interesting feature in such studies in the case of Mn^{2+} systems is the observation of forbidden transitions which arise due to the admixture of the off diagonal terms of the type,

$$(S_z \, S_+) \, (S_- \, I_+), \, (S_z \, S_-) \, (S_+ \, I_-)$$

in the spin Hamiltonian [section 6.2.3]. However in most cases, where such forbidden transitions are observed, detailed analysis are precluded due to large line widths or presence of more than one inequivalent site. Consequently analyses of forbidden transitions have been reported only in few cases [7-9]. Wherever the analysis is possible one gets the Spin-Hamiltonian subjected to a more extensive analysis of the ESR spectra and additional hyperfine parameters relating to the quadrupole moment. In this chapter we present the results of a single crystal ESR study of Mn^{2+} ions doped in zinc maleate tetrahydrate (hereafter ZnMTH). Rotation of the

single crystal along mutually perependicular axes is shown
to lead to variations in the intensities of allowed and
forbidden transitions as predicted by theory including total
absence of the forbidden transitions corresponding to $H||Z$.
The line positions in the case of $H||Z$ have been analysed to
give the spin Hamiltonian parameters. From the zero field
splitting, information on the microsymmetry of Mn^{2+} is
obtained. From the value of A, the percentage ionicity in the
metal-ligand bodning is estimated. Using the spin-Hamiltonian
parameters, the line positions of the forbidden transitions
also have been analysed as discussed in section 6.2.5, and
the values of Q' and Q'' , the axial and rhombic components of
the quadrupole coupling moment of ^{55}Mn respectively, are
derived.

9.2. Experimental section

Stoichiometric amount of Zn^{2+} is taken in the form of
sulphate (Analar. BDH) and precipitated as hydroxides using
ammonium hydroxide. After eliminating excess ammonia by
warming the solution, the resultant hydroxide is treated with
100% excess hot maleic acid (SD Chemical). Upon concentrating
the solution colourless crystals seperated out. The ZnMTH
was doped with 1% Mn^{2+} at the starting point. Zn^{2+} in the

pure compound <u>viz</u>., ZnMTH was estimated as oxide. (Cald. for $C_8H_{14}O_{12}Zn$, Zn^{2+} = 17.79%, observed: Zn^{2+} = 17.14%).

The detailed crystal structure of ZnMTH is not yet available. However, as per the preliminary reports, ZnMTH forms a triclinic system with space group Pl. There is slight difference in the unit-cell dimensions reported by the two groups. Antsyshkina <u>et</u> <u>al</u> have reported a = 7.30, b = 9.82 and c = 5.28 Å and α = 110.2°, β = 77.1° and γ = 117.0° which may be compared with a = 7.29, b = 9.73, c = 5.36 Å and α = 110.° 48' β = 63°.18' and γ = 63°.18' reported by Saroja and Raman [10,11]. There is one molecule of ZnMTH per unit cell. Experimentally the principal axis is located by observing the spectra at different orientations and achieving that orientation which gives rise to only allowed transitions with intensities free from forbidden transitions which corresponds to H||Z. Figure 9.1(inset) shows the morphology of the crystal and the plane (marked with crosses) which gives rise to 30 ESR transitions free from forbidden lines. The spectra were subsequently recorded by rotating in two other axes choosing these axes such that they form a mutually perpendicular system with respect to the principal axis. The spectra have been recorded at an interval of 10°. Other details of ESR measurements are already given in 2.1.
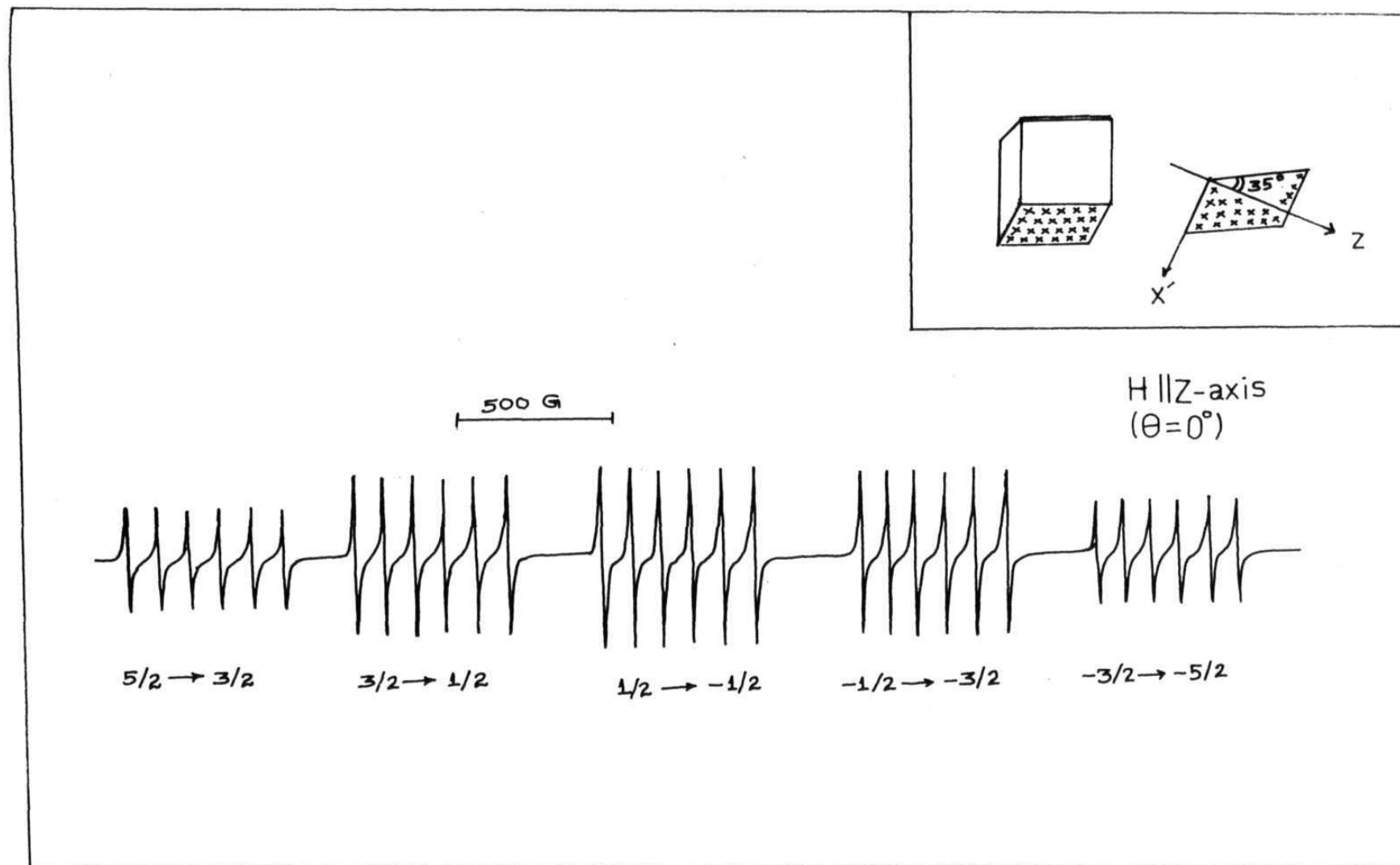
Fig.9.1 Room temperature ESR spectrum of Mn^{2+}/ZnMTH in the X'Z plane at $\Theta = 0°$

9.3. Results and discussion

A thirty line spectra is typically observed for ESR
of Mn^{2+} in orthorhombic symmetry when no forbidden lines are
present as shown in Figure 9.1. The ground state of Mn^{2+}
with d^5 configuration is unique among d^n configurations in that
there is only one state with maximum spin multiplicity ($^6S_{5/2}$).
This state splits into three Kramers doublets ($\pm 5/2$, $\pm 3/2$
and $\pm 1/2$) in an orthorhombic crystalline field which are
further split in the presence of applied magnetic field.
These six levels will give rise to five fine structure transi-
tions. Each fine structure transition will be further split
into six hyperfine components due to nuclear spin of 5/2 of
^{55}Mn isotope. Figure 9.2 shows the ESR spectra recorded in
the X'Z-plane making an angle of 5° and 7° with Z-axis
respectively. A neat thirty line spectrum indicates that
there is only one type of site in the lattice. Even a small
rotation of about 5° around the principal axis makes the
presence of forbidden transitions conspicuous as shown in
Figure 9.2 compared to Figure 9.1. When the principal axis
is parallel to the magnetic field the separation in energy
levels and hence the seperation between the M = $5/2 \longrightarrow -3/2$
and M = $+3/2 \longrightarrow +5/2$ will be maximum [12]. The ratio of the
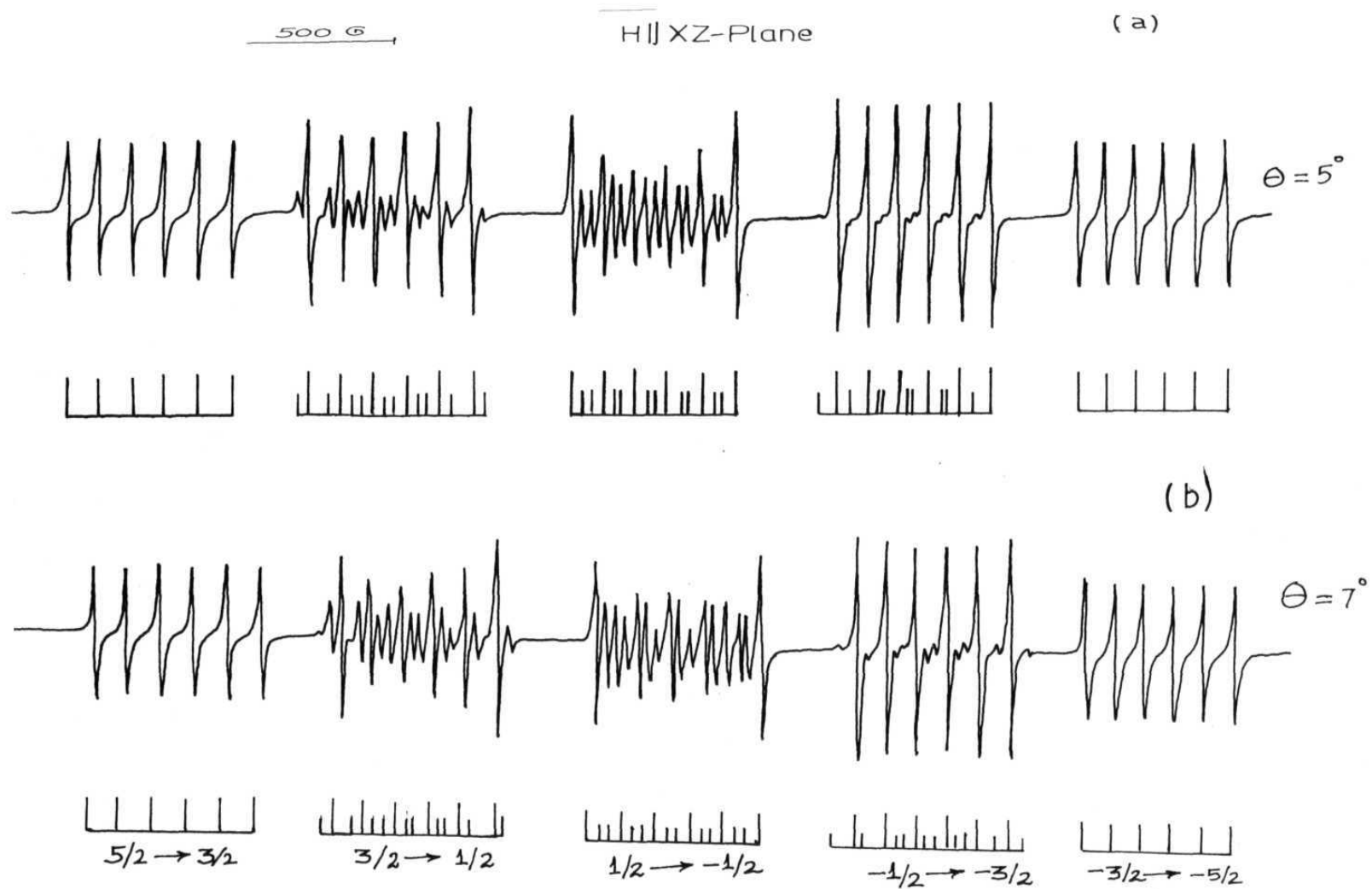
Fig.9.2 Room temperature ESR spectra of Mn^{2+}/ZnMTH in the X'Z plane at (a) O = 5° and (b) O = 7°; longer vertical lines correspond to $\Delta m = O$ transitions and small vertical lines corresponding to $\Delta m = \pm 1$ transitions.

relative intensities are proportional to (J+M) (J-M+1). These therefore occur in the ratios 5:8:9:8:5 as observed.

The angular variation of the fine structure transitions corresponding to M $\longrightarrow$ M$\pm$1, depends on the term $(3\cos^2\theta - 1)$, when the higher order terms are neglected [13]. The field for all the sextets will be same at the magic angle. However, if the higher order terms are also included, all the five curves corresponding to the five sextets may not meet at the same point. Figure 9.3 shows the angular variations of these transitions in the X'Z plane. The theoretical curves corresponding to each sextet is found to overlap closely with experimental points.

The line positions of the spectrum corresponding to H$||$Z are given by a set of five simultaneous equations in terms of spin Hamiltonian parameters, as discussed in section 6.2.5. The spin-Hamiltonian parameters D, E, 'a' whose significances have been discussed earlier (Section 6.2.3, p.162) are obtained using a computer programme based on these equations (appendix IV). The value of A is then calculated from the line positions in each sextet and the error given viz., $\pm$1 G corresponds to the A value obtained from the different sextets. Expression 6.14 provides a check on the value of A obtained. The calculated field position of the sextets,

Fig.9.3 Angular variation in X'Z plane of the allowed transitions in the ESR spectrum of Mn^{2+}/ZnMTH at RT. Full curves: theoretical; circles: experimental.
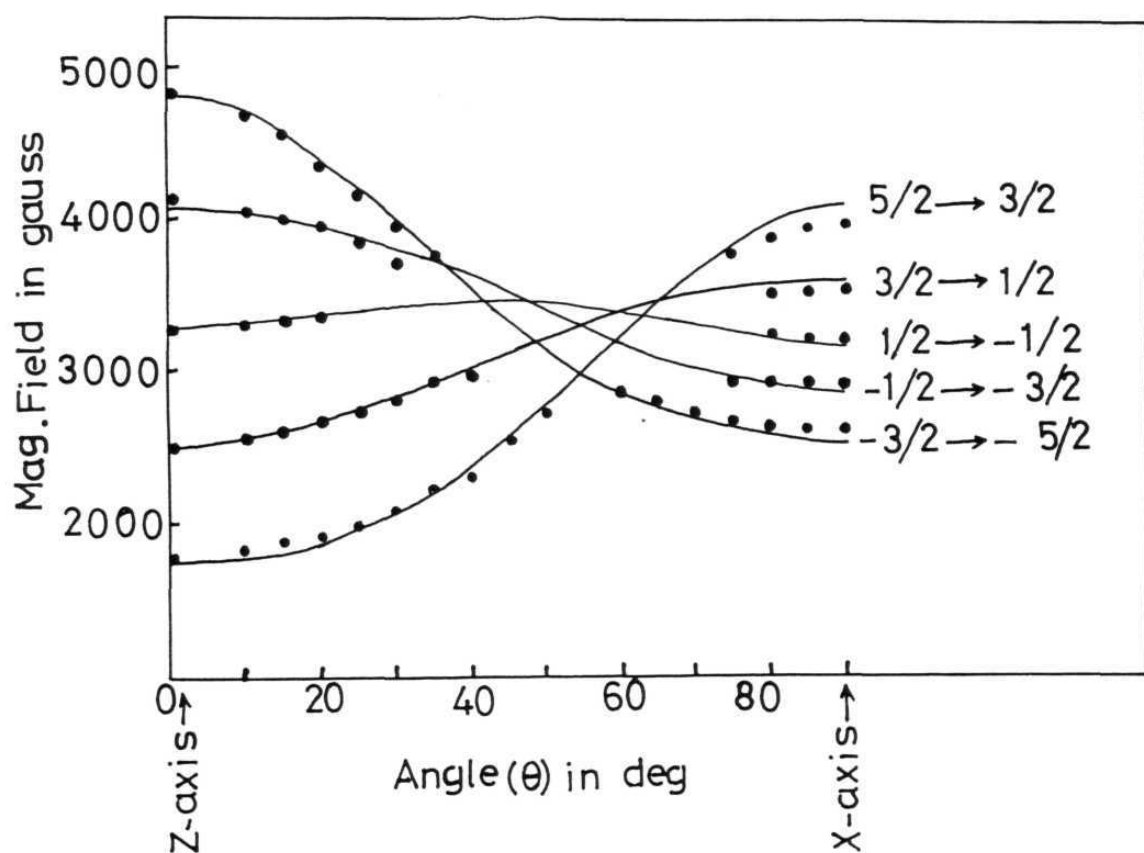
H_i, and the experimental H values are given in Table 9.1. along with the D,E,'a' and A values. An indirect check on the relative sign of D is as follows. If the seperations of these sextets decreases on the high field side when the direction of the magnetic field is parallel to Z-axis, D/A will be positive. In all the systems so far studied A is negative [14]. In the present case the separation of the sextets increase towards the high field side and hence D/A is negative which implies D is positive if we take a negative sign for A for the present system as well. The sign and magnitude of D gives information regarding the microsymmetry of the metal ion. A positive D is associated with a tetragonal compression or trigonal elongation [15]. In the present case the positive **D** corresponds to tetragonal compression. Such a conclusion is in accordance with the known crystal structure of MnMTH if we assume that a similar symmetry is obtained when Mn^{2+} goes substitutionally into ZnMTH. A comparison of the unit cell dimensions of MnMTH and ZnMTH suggests that these two systems are likely to be closely similar if not isomorphous, facilitating the above described situation [10,11,16]. However a definite conclusion regarding whether the microsymmetry is governed purely by the guest ion or dictated both by the guest ion as well as the parent diamagnetic zinc lattice can be drawn only when

Table 9.1. Observed and calculated H_i values for H||Z axis in Mn^{2+}/ZnMTH along with D, E, a and A values.

	Cald.	Obs (±3 gauss)	D (±1 gauss)	E (±1 gauss)	a (±1 gauss)	A (±1 gauss)
H_1	1785	1780	385.6	71.5	-9.5	-93
H_2	2493	2495				
H_3	3290	3275				
H_4	4070	4075				
H_5	4815	4818				

a knowledge of a detailed crystal structure for the ZnMTH becomes available.

The g value (viz., 2.035) shows large anisotropy. Most of the Mn^{2+} systems reported in literature show g values close to free spin value of 2.0023. However deviation from this value has been observed in highly distorted systems such as Mn^{2+} doped tris ethylene diamine Zinc(II), Mn^{2+} doped lithium ammonium tartrate monohydrate [17,18]. Two mechanisms have been suggested for the enhancement of g-value. The spin-orbit coupling produces a slight breakdown of LS coupling introducing an admixture of the excited state $^4P_{1/2}$ but the expected deviation in this case is small. A more dominant contribution comes due to covalent bonding excited states of symmetry $^6T_{1g}$ whose single electron states will tend to be full or empty depending upon the nature of the metal-ligand bondings [19,20]. The D value of 0.0358 cm^{-1} does indicate a significantly large distortion from cubic symmetry for Mn^{2+}/ZnMTH [15]. An estimate of the covalency in the present case may be obtained from the hyperfine splitting constant A. The relation between A and the local bonding of the Mn^{2+} and the nearest neighbour ligands has been derived phenomenologically on a more quantitative basis by plotting A versus the Pauling covalency parameter [21,22].

From this curve we obtain, for A = -93 gauss, an ionicity of 96.5% for Mn^{2+}/ZnMTH. Similar values have been found for Mn^{2+} doped $(NH_4)_2(COO)_2H_2O$[23]; $K_2(COO)_2 \cdot H_2O$[24] and $Cd(COO)_2 \cdot 3H_2O$[9] single crystals.

Figure 9.2 shows the appearance of forbidden transitions when the crystal is rotated by 5 and 7° respectively, the intensities becoming larger with increasing rotation. The increase in intensity with angular variation is illustrated for the first sextet in Figure 9.4. Theoretically intensities for forbidden transitions vary as Sin 2θ (eq. 6.19) and the observed spectral behaviour is in agreement with the expected trend. These forbidden transitions occur in pairs correspond-ing to $\Delta m_I = \pm 1$ (see section 6.2.5). The relationship for the positions of the different forbidden transitions and the hyperfine parameters are presented in section 6.2.5 and the computer programmes based on these expressions are given in appendices Va and Vb. Using these programmes the line positions for the forbidden transitions have been analysed. For all the sextets the doublet separations have been calcu-lated and are given in Table 9.2 along with the experimental doublet separations. A good fit is obtained for $Q' = 1.69$ and $Q'' = 0.304$, which are the axial and rhombic components of the quadrupole coupling constant of the ^{55}Mn nucleus
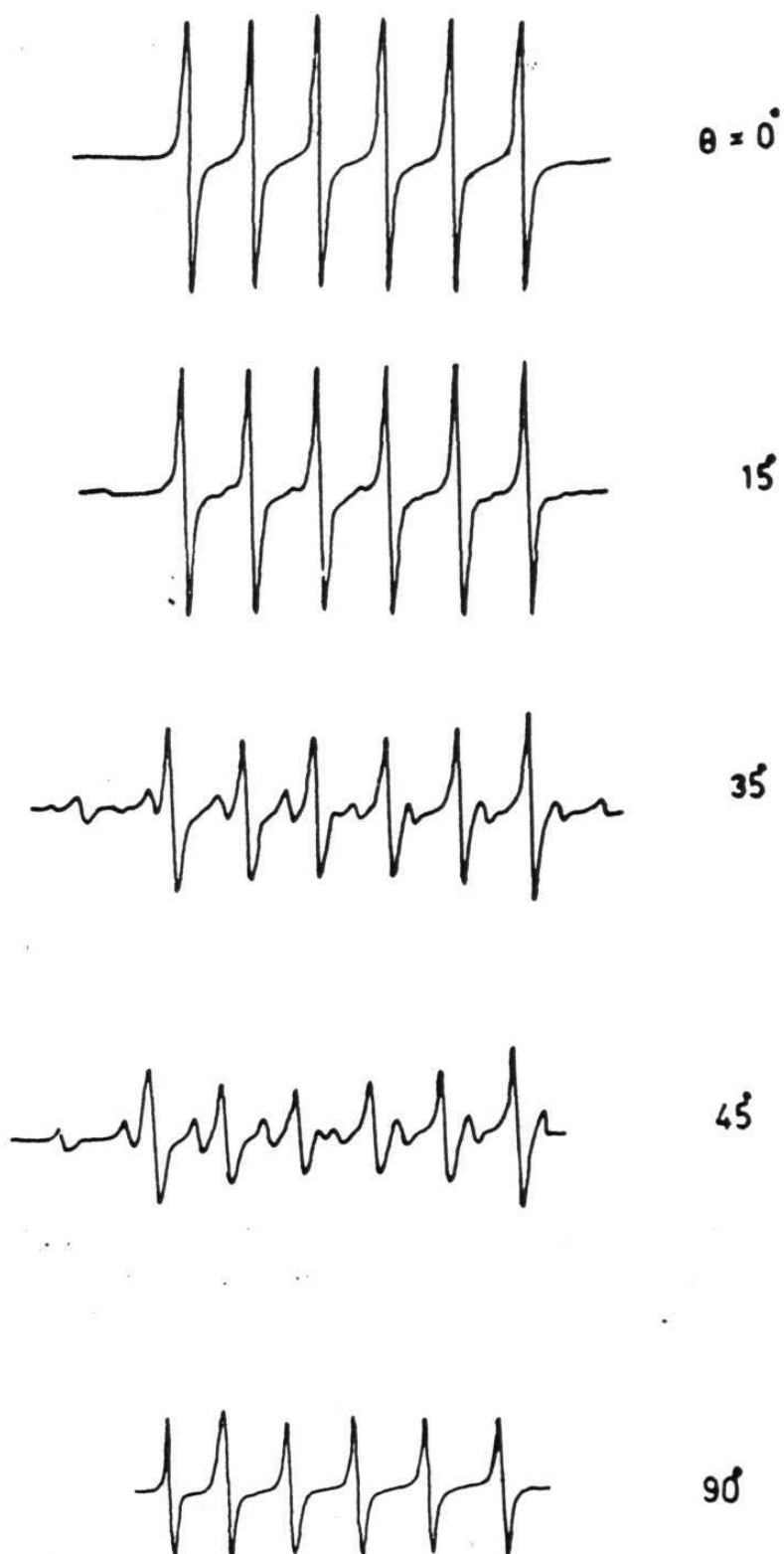
Fig.9.4 Angular variation of ESR spectra of Mn^{2+}/ZnMTH in
X'Z plane. The first sextet is given to illustrate the
variation of intensities of forbidden transitions.

Table 9.2. Observed and calculated doublet separations ΔH(in G) of the forbidden hyperfine transitions ($\Delta m = \pm 1$) for various transitions ($\Delta M = \pm 1$) in the X'Z-plane ($\phi = 0^{o}$, $\Theta = $ Variable) of the complex Mn^{2+}/zinc maleate tetrahydrate single crystals at 298 K.

m	Doublet separation (H)									
	$M = \frac{1}{2} - -\frac{1}{2}$ $m = \pm 1$ $\Theta = 5^{o}$		$M = \frac{3}{2} - \frac{1}{2}$ $m = \pm 1$ $\Theta = 10^{o}$		$M = -\frac{1}{2} - - -\frac{3}{2}$ $m = \pm 1$ $\Theta = 5^{o}$		$M = -\frac{5}{2} - \frac{3}{2}$ $m = \pm 1$ $\Theta = 15^{o}$		$M = -\frac{3}{2} - - -\frac{5}{2}$ $m = \pm 1$ $\Theta = 25^{o}$	
	obs	cal	obs	cal	obs	cal	obs	cal	obs	cal
- 5/2	23.8	24.7	201.6	202.8	149.2	152.5	369.2	377.0	330.1	339.4
- 3/2	24.5	25.0	205.8	207.1	155.8	158.5	372.3	383.2	341.3	350.2
- 1/2	24.9	25.3	210.8	211.5	163.1	164.8	379.2	389.7	350.9	362.4
+ 1/2	25.0	25.5	215.8	216.0	168.3	171.2	388.3	396.4	362.3	374.4
+ 3/2	25.1	25.8	217.5	220.8	174.2	177.7	395.5	403.5	377.0	386.7

respectively. The relatively large deviation between the observed and calculated doublet separations in M = +5/2 ⟶ +3/2 and M = -5/2 ⟶ -3/2 sextets may be attributed to the large angle (θ = 15 and 25) at which the comparison is made. The perturbation theory gives quantitatively unsatisfactory results at large angles and a considerable deviation of the direction of the nuclear magnetic moment from that of H has to be taken into account [25]. For these sextets the forbidden transitions were observable only at large angles i.e., away from the principal axis and hence a comparison at smaller angles was not possible.

9.4. Conclusions.

Mn^{2+} when doped in zinc maleate tetrahydrate is found to occupy a compressed octahedral site, substitutionally replacing the Zn^{2+} ion. The spin-Hamiltonian parameters have been determined to be D = 385.6, E = 71.5, a = -9.5 and A = -93 gauss, where D, E, a and A are the axial component of zero field splitting, the rhombic component of zero field splitting, the cubic field term and the hyperfine coupling constant respectively. The unusually large anisotropy in the g value viz., 2.035 has been ascribed to a highly distorted cubic environment. An ionicity of 96.5% is deduced for the

metal-ligand bonding from a plot of A $\underline{vs}$ the Pauling's covalency parameter [22]. The analysis of forbidden ESR transitions which give good agreement between calculated and observed $\triangle$H, the splitting of the lines leading to $Q = 1.69$ and $Q'' = 0.304$ which are the axial and rhombic components of the quadrupole coupling constants of the ^{55}Mn nucleus respectively.

References:

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Computer programme for simulation of relaxation spectra
employing Eq.2.23:

The following computer programme is written in
HI-BASIC to evaluate the Mössbauer spectrum based on the
relaxation model due to Blume and Tjon discussed in
Chapter 2. To evaluate the expression

$$F(\omega) = \sum_{i=1}^{6} \frac{(\frac{\Gamma}{2} + 2\lambda)\,[\frac{\Gamma^2}{4} + \lambda\Gamma - (\alpha-\omega)^2 + \beta^2] + (\alpha-\omega)^2(\Gamma + 2\lambda)}{(\frac{\Gamma^2}{4} + \Gamma\lambda - (\alpha-\omega)^2 + \beta^2)^2 + (\alpha-\omega)^2(2\lambda + \Gamma)^2}$$

$$\dots (2.23)$$

λ and Γ (mm/sec) are given as input parameters. In addition
'HZERO' and 'HONE' which define line positions are also
given as input parameters. The output 'SUM' plotted against
W (JA) gives the required spectrum. The representative
spectra simulated using the above equation are reproduced
in Figure 2.5 for different values of λ.

```
LPRINTER WIDTH 130

REM THIS PROGRAMME CALCULATES THE LINE PROFILES USING

REM D. DATTAGUPTA'S EXPRESSION FOR VALUES OF LAMDA, THE

REM RELAXATION RATE 'NLW' IS LINE WIDTH, 'QUAD' IS QUADRUPOLE

REM SPLITTING, 'GNOT' AND 'GONE' ARE THE 'g' VALUES FOR

REM GROUND AND EXCITED STATE OF $^{57}$Fe NUCLEUS.  HZERO AND HONE

REM ARE THE INPUT PARAMETERS.  'CGRC' IS CLEBSH - GORDON

REM COEFFICIENT.

DIM BETA(8), MEX(4), MGR(2), ALP(8), CGRC(8), W(300)

PP = 10.657/160

PPA = (256*PP)/2

PP1 = (20*PP)-PPA

PP2 = (40*PP)-PPA

PP3 = (60*PP)-PPA

PP4 = (80*PP)-PPA

PP5 = (100*PP)-PPA

PRINT TAB(10); PP; TAB(25); PP1; TAB(40); PP2; TAB(55); PP3;
      TAB(70); PP4; TAB(85); PP5.

PAP = 0.1*PP

INPUT 'HZERO ='; HZERO

INPUT 'HONE ='; HONE

INPUT 'NLW = '; NLW
```

```
GNOT = 0.181208
GONE = -0.1036
INPUT 'LAMDA = '; LAMDA
INPUT 'QUAD = '; QUAD
FOR I = 1 TO 4
INPUT 'MEX(I) = '; MEX(I)
NEXT I
FOR JP = 1 TO 8
INPUT 'CGRC(JP)= '; CGRC(JP)
NEXT JP
INPUT AMGR1, AMGR2
FOR IA = 1 TO 4
BETA(IA) = ((AMGR1*HZERO) - (MEX(IA)*HONE))
NEXT IA
FOR IB = 1 TO 4
BETA(9-IB) = -BETA(IB)
NEXT IB
FOR IC = 1 TO 8
PRINT 'BETA(IC) = ', BETA(IC)
NEXT IC
FOR IA = 1 TO 4
ALP(IA) = QUAD*(3*MEX(IA)*MEX(IA) - 3.75)
PRINT 'ALP(IA) = ', ALP(IA)
NEXT IA
```

```
FOR ID = 1 TO 4
ALP(ID+4) = ALP(ID)
NEXT ID
INCRM = PP
INPUT 'W(1) = '; W(1)
PRINT TAB(15);'SUM'; TAB(35); 'W'; TAB(70); 'CHA'
FOR JA = 1 TO 300
SUM = 0.0
FOR JB = 1 TO 8
ALPS = ALP(JB)*ALP(JB)
BETAS = BETA(JB)*BETA(JB)
AA = (NLW*0.5) + (2*LAMDA)
ALPOME = (ALP(JB) -W(JA))*(ALP(JB)-W(JA))
BB = (NLW*NLW*0.25) + (NLW*LAMDA)-ALPOME +BETAS
BBB = BB * BB
CC = NLW+(2*LAMDA)
CCS = CC*CC
DD = ALPOME*CC
ANUME = (AA*BB)+DD
ADENOM = BBS+(ALPOME*CCS)
EQAV = (ANUME)/(ADENOM)
MASTEQ = EQAV*CGRC(JB)
SUM = SUM+MASTEQ
NEXT JB
```

```
CHA = W(JA)/PP
PRINT TAB(10); SUM; TAB(25); W(JA); TAB(JO); CHA
W(JA + 1) = W(JA) + INCRM
NEXT JA
STOP
END
```

Computer programme for the simulation of relaxation spectra employing Eq. 2.26:

The following computer programme is written in FORTRAN IV to evaluate the Mössbauer spectrum based on the relaxation model due to van der Woude and Dekker discussed in Chapter 2. To evaluate the expression

$$I(\omega) = \sum_{i=1}^{6} \frac{\frac{2\Omega_s}{(1-\eta)} \delta_i^2(\eta^2-1) - \Gamma[\delta_i^2 + \omega^2 + \frac{\Omega_s}{(1-\eta)^2} - 2\omega\delta_i\eta]}{(\delta_i^2 - \omega^2)^2 + \frac{4\Omega_s}{(1-\eta)^2}(\omega+\eta\delta_i)^2 + \frac{4\Omega_s}{(1-\eta)}\Gamma(\omega^2+\delta_i^2+2\omega\delta_i\eta)}$$

$$\dots (2.26)$$

Ω, δ_i and η are given as input parameters. The output 'ANINTE' plotted against 'CHA(J)' gives the required spectrum. The representative spectra simulated using the above equation are reproduced in Figure 2.6.

```
C       THIS IS A MODIFIED EXP. OF VANDER WOUDE  INCLUDING NATURAL

C       LINE WIDTH.NLW SHOULD BE IN UNITS OF DELTA. 'DELTA' IS LINE

C       POSITION. 'N' IS NO. OF LORENTZIANS.

C       PCVEL IS PER CHANNEL VELOCITY

        DIMENSION WATT(8),DELTA(8),OMEGA(8),SOME(256),AKONST(8),

        CHA(250)

        READ 9,NSET

    9   FORMAT(13)

        DO 16 IB=1,NSET

        N=6

        ANLW=0.064

        ETA=0.4

        PRINT 20,N,ANLW,NSET

   20   FORMAT(10X,'N=',13,5X,'ANLW=',F6.4,'NSET=',13)

        YSCAL=5.0

        YSCAL1=6.0

        YSCAL2=7.0

        WAIT(1)=3.0

        WAIT(2)=3.0

        WAIT(3)=1.0

        WAIT(4)=1.0

        WAIT(5)=3.0
```

```
      WAIT(6)=3.0
      DELTA(1)= -1.00
      DELTA(2)= -0.58
      DELTA(3)= -0.16
      DELTA(4)= 0.16
      DELTA(5)= 0.58
      DELTA(6)= 1.00
      READ 21,(OMEGA(I),I=1,N)
21    FORMAT(F5.3)
      PRINT 25, (DELTA(I),OMEGA(I),WAIT(I),I=1,N)
25    FORMAT(3F6.3)
      PCVEL =0.0166666
      AAB=(130*PCVEL)/2
      AAC=45*PCVEL
      AAD= -(AAB+AAC)
      PRINT 30, AAD
30    FORMAT(10X,'AAD=',F10.6)
      PRINT 26,PCVEL
26    FORMAT('PCVEL=',F10.7)
      PRINT 40,ETA,YSCAL
40    FORMAT(5X,'ETA=',F10.2,5X,'YSCAL=',F10.2)
      DO 45 IA=1,N
      PRINT 41,OMEGA(IA)
41    FORMAT('OMEGA(IA)=',F10.6)
```

```
45    CONTINUE
      ETASQ=ETA*ETA
      AA=(ETASQ-1)
      AB=(1-ETA)
      AC=AB*AB
      SOME(1)=(-1.333332)
      DO 55 J=1.200
      AINTE=0.0
      DO 60 I=1,N
      DEL=DELTA(I)*DELTA(I)
      ETADE=ETA*DELTA(I)
      AD=(4*OMEGA(1)*OMEGA(I))/AC
      SOMESQ=SOME(J)*SOME(J)
      ETSOD=2*SOME(J)*DELTA(I)*ETA
      ANUM. (AA*DEL*2*OMEGA(I))/AB
      BNUM=(DEL+SOMESQ+AD-ETSOD)
      CNUM=ANLW*BNUM
      ANUMER=(ANUM-CNUM)
      ADENOM=(DEL-SOMESQ)*(DEL-SOMESQ)
      BDENOM=(SOME(J)+ETADE)*(SOME(J)+ETADE)
      CDENOM=AD*BDENOM
      DDENOM=(SUMESQ+DEL+ETSOD)
      EDENOM=(DDENOM*4*OMEGA(I)*ANLW)/AB
      DENOM=(ADENOM+CDENOM+EDENOM)
```

```
      SIME=(ANUMER/DENOM)*WAIT(I)

      AINTE=AINTE+SIME

60    CONTINUE

      ANEWY=AINTE/YSCAL

      BNEWY=AINTE/YSCAL1

      CNEWY=AINTE/YSCAL2

      CHA(J)=SOME(J)/PCVEL

      PRINT 65,SOME(J),CHA(J),AINTE,ANEWY,BNEWY,CNEWY

65    FORMAT(5X,2F12.6,10X,2F10.6,10X,2F10.6)

      SOME(J+1)=SOME(J)+0.0166666

55    CONTINUE

16    CONTINUE

      STOP

      END
```

Computer programme for the least square fit of angular variation data of Cu^{2+} ESR spectra:

$$g^2 (\theta) = U + V \cos 2\theta + W \sin 2\theta \qquad \ldots (6.7)$$

The experimental $g^2 (\theta)$ and $g^2A^2(\theta)$ values for the three laboratory crystal planes were fitted to the above equation. Experimental values of g^2, g^2A^2 and θ are given as input parameters and the values of U, V and W are evaluated by setting up the appropriate minimisation conditions viz.,

$$\Sigma (g^2(cal)-g^2(obs))^2 = minimum$$

and $\quad \Sigma ((g^2A^2)(cal) - (g^2A^2)(obs))^2 = minimum$

are satisfied.

```
LPRINTER WIDTH 130
REM CALCULATION OF U,V,W IN THE EQ. Y = U+V COS 2X + W SIN X
REM BY THE METHOD OF LEAST SQUARES
DIM Y(100), X(100), C(100), S(100), YCAL(100), TIT(5)
INPUT 'NAME='; NAME
100 INPUT 'N='; N
INPUT 'YFILNAME='; A $
INPUT 'K,L='; K,L
PRINT TAB(10); NAME; TAB(20); N; TAB(35); K; TAB(60); L
IF N=0 THEN 1200
IF END ## 1 THEN 25
IF END ## 2 THEN 26
OPEN 'X.FIL' AS 1
OPEN A $ AS 2
PRINT TAB(40); 'X(I)'; TAB(80); 'Y(I)'
FOR I = 1 TO N
READ ## 1; X(I)
READ ## 2; Y(I)
PRINT TAB(40); X(I); TAB(80); Y(I)
NEXT I
25 CLOSE 1
26 CLOSE 2
```

```
SUMY = 0.0

SUMX = 0.0

SUMCC = 0.0

SUMS = 0.0; SUMSS = 0.0; SUMCS = 0.0

SUMYC = 0.0; SUMYS = 0.0

FOR I = 1 TO N

C(I) = COS(X(I)*3.1416/90)

S(I) = SIN(X(I)*3.1416/90)

CC = C(I)*C(I); SS = S(I)*S(I)

CS = C(I)*S(I); YC = Y(I)*C(I)

YS = Y(I)*S(I)

SUMY = SUMY+Y(I)

SUMC = SUMC+C(I)

SUMCC = SUMCC + CC

SUMS = SUMS + S(I)

SUMSS = SUMSS + SS; SUMCS = SUMCS + CS

SUMYC = SUMYC + YC; SUMYS = SUMYS + YS

NEXT I

E = SUMC*SUMC -N*SUMCC

G = SUMS*SUMS-N*SUMSS

H = SUMC*SUMY-N*SUMYC

T = SUMS*SUMY-N*SUMYS

F = SUMC*SUMS-N*SUMCS

D = F*F-E*G
```

```
W = (H*F-T*E)/D

V = (T*F-H*G)/D

U = (SUMY-(SUMC*V+SUMS*W))/N

PRINT TAB(10); 'W='; W; TAB(40); 'V='; V; TAB(70); 'U='; U

TRUDY = W/V

TANIA = ATN(TRUDY)

THETA1 = TANIA/2

THETA2 = (TENIA/2.0)+1.5/08

YTETA1 = U+V*COS(2.*THETA1)+W*SIN(2.*THETA1)

YTETA2 = U+V*COS(2.*THETA2)+W*SIN(2.*THETA2)

TD1 = THETA1*180.0/3.1416

TD2 = THETA2*180.0/3.1416

YEX1 = (YTETA1)  0.5

YEX2 = (YTETA2)  0.5

PRINT TAB(10); 'TD1=';TD1

PRINT TAB(10); 'TD2='; TD2 ; TAB(30); 'YEX1='; YEX1; TAB(55);
      'YEX2='; YEX2

PRINT TAB(10); 'X(I)'; TAB(30); 'Y(I); TAB(50):, 'YCAL(I)'

FOR I = 1 TO N

YCAL(I) = U+V*C(I)+W*S(I)

PRINT TAB(10); X(I); TAB(30); Y(I); TAB(50); YCAL(I)

NEXT I

IF N = 19 THEN 100

PRINT TAB(10); 'J'; TAB(30); 'X(J)'; TAB(50); 'YCAL(J)'
```

```
FOR J = N TO K
IF K = N THEN 1150
YCAL(J) = U+V*COS(X(J)*3.1416/90)+W*SIN(X(J)*3.1416/90
PRINT TAB(10); J; TAB(30); X(J): TAB(50); YCAL(J)
1100 X(J+1) = X(J)+L
NEXT J
1150 GO TO 100
1200 STOP
END
```

Evaluation of spin-Hamiltonian parameters D, E. a and A
using Eqs. 6.13 and 6.14:

      A computer programme is written in HI-BASIC to
evaluate the spin-Hamiltonian parameters viz., D, E, a and
A based on the simultaneous equations 6.13 and 6.14. Experi-
mental positions of the five sextets (H_i) and the trial D
value are given as input parameters. The calculation is
carried out self-consistently till a good match between
$H_i(cal)$ and $H_i(obs)$ is obtained.

```
LPRINTER WIDTH 130
REM THIS PROGRAMME CALCULATES, 'A', 'E', 'D' AND H(ZERO)USING
REM P.VENKATESHWARLU'S EXPRESSIONS KON1 IS '(H1+H5) -(H2-H4)'
REM KON2 IS '[(H1-H5)*5] + [(H2-H4)*4]'
INPUT 'D = '; D
INPUT 'KON2 = '; KON2
INPUT 'KON1 = '; KON1
INPUT 'H1 = '; H1
INPUT 'H2 = '; H2
INPUT 'H4 = '; H4
INPUT 'H5 = '; H5
100 X1 = 9/(H1+D)
X2 = 5/(H1+(3*D))
X3 = 9/(H5-D)
X4 = 5/(H5-(%*D))
X5 = 9/(H2+D)
X6 = 9/(H2-D)
X7 = 5/(H2+(3*D))
X8 = 9/(H4+D)
X9 = 9/(H4-D)
X10 = 5/(H4-(3*D))
XX = (X1 - X2 + X3 - X4 + X5 - X6 + X7 - X8 + X9 + X10)
```

```
PRINT 'XY = '; XX
EE = KON1/XX
EEE = (EE)  (0.5)
PRINT 'EEE = '; EEE
Y1 = 45/(H1+D)
Y2 = 25/(H1+(3*D))
Y3 = 45/(H5 -D)
Y4 = 25/(H5-(3*D))
Y5 = 36/(H2+D)
Y6 = 36/(H2-D)
Y7 = 2C/(H2+(3*D)
Y8 = 36/(H4+D)
Y9 = 36/(H4-D)
Y10 = 20/(H4-(3*D)
YY = (Y1-Y2-Y3+Y4-Y5+Y6-Y7-Y8+Y9+Y10)
YYY = YY*EEE*EEE
PRINT 'YYY = '; YYY
SUM = YYY-(56*D)
PRINT 'SUM = '; SUM
PRINT
PRINT 'D = '; D
DIF = (SUM-KON2)
IF(ABS(DIF)< = 1) THEN 10
IF((DIF)<0.01) THEN 20
```

```
IF((DIF)>0.01) THEN 30

20 D = D-0.01

GO TO 100

30 D = D+0.01

GO TO 100

10 PRINT TAB(10); 'D'; TAB(40); 'EEE'; TAB(60); 'KON1';
   TAB (80); 'KON2'; TAB(100); 'SUM

PRINT

PRINT TAB(10); D; TAB(40); EEE; TAB(60); KON1; TAB(80);
      KON2; TAB(100); SUM

TWOHO = H1+H5-(9*EE)/H1+D)+(5*EE)/(H1+(3*D))-(9*EE)/(H5-D)
        +(5*EE)/(H5-(3*D))

HO = TWOHO/2

PRINT

PRINT TAB(10); 'HO = '; HO

TWOAA = HO-4*D+(9*EE)/(H1+D) - (5*EE/(H1+(3*D))-H1

AA = TWOAA/2

PRINT

PRINT TAB(10); 'AA ='; AA

H1CAL = HO-4*D+(9*EE/(H1+D))-(5*EE/(H1+(3*D)))

H5CAL = HO+4*D+(9*EE/(H5-D))-(5*EE/(H5-(3*D)))+2*AA

H2CAL = HO-2*D-(9*EE/(H2+D))+(9*EE/(H2-D))-(5*EE/(H2+(3*D)))
        +2.5*AA
```

```
H4CAL = HO+2*D+(9*EE/(H4+D))-(9*EE/(H4-D))-(5*EE/(H4-(3*D)))
        -2.5*A.
PRINT TAB(10); 'H1 ='; H1; TAB(50); 'H1CAL ='; H1CAL
PRINT TAB (10); 'H2='; H2; TAB(50); 'H2CAL='; H2CAL
PRINT TAB(10); 'H4='; H4; TAB(50); 'H4CAL='; H4CAL
PRINT TAB(10); 'H5='; H5; TAB(50); 'H5CAL='; H5CAL
STOP
END
```

(a)   Evaluation of Q' and Q''

A computer programme is written in HI-BASIC to evaluate Q' and Q'' based on the equation

$$M = +1/2 \longrightarrow -1/2$$

$$\Delta m = \pm 1 \text{ transition}$$

$$H = H_{|1/2,m+1\rangle \longrightarrow |-1/2,m\rangle} - H_{|1/2,m\rangle \longrightarrow |-1/2,m+1\rangle}$$

$$= (17\ A^2/2\ H_o) + (2\ \gamma\beta_N H_o/g\beta) - (2m+1)[2P-(8A^2\sigma/H_o^2) +$$

$$(25A^3/2H_o^2) + (\gamma\beta_N A/g\beta)] \qquad \ldots (6.18)$$

Two sets of experimental $\Delta H(obs)$ values corresponding to two different θ values are given as input parameters to evaluate two P values, where P is a function of θ of the form

$$P = \frac{1}{2} [Q'(3\cos^2\theta - 1) + 3Q'' \sin^2\theta \cos^2\phi].$$

Using the values of $P(\theta)$ two simultaneous equations are set up and solved for Q' and Q''. The programme used is reproduced here.

```
LPRINTER WIDTH 130
REM THIS PROGRAMME IS TO CALCULATE Q' AND Q'' USING THIRD
REM SEXTET AT TWO DIFFERENT ANGLES.  SM(I) IS SMALL M. (DH(I)
REM IS DELTA H(OBSERVED).
DIM  DH(10), DHCAL(10), SM(10)
INPUT 'A='; A
INPUT 'HZERO='; HZERO
GBNGB = 0.00037
INPUT 'SIG='; SIG
FOR I = 1 TO 5
INPUT 'DH(I)='; DH(I)
NEXT I
INPUT 'P='; P
PRINT
PRINT TAB(10); 'A'; TAB(20); 'HZERO'; TAB(30); 'GBNGB';
     TAB(50); 'SIG'; TAB(60); 'P'
PRINT
PRINT TAB(10); A; TAB(20); HZERO; TAB(30); GBNGB; TAB(50);SIG;
     TAB(60); P
FOR I = 1 TO 5
PRINT 'DH(I)='; DH(I)
NEXT I
```

```
HZEROS=HZERO*HZERO
100 SM(1)= -2.5
SUM = 0.0
FOR I = 1 TO 5
BB = (17*A*A)/(2*HZERO)
CC = (2*GBNGB*HZERO)
DD = (8*A*A*SIG)/HZEROS
EE = (A*A*A*12.5)/HZEROS
FF = (GBNGB*A)
GG = ((2*P)-DD+EE+FF)
MM = (2*SM(I))+1
NN = (MM*GG)
DHCAL(I) = (BB+CC-NN)
DIFF = DH(I)-DHCAL(I)
DIFFS = DIFF*DIFF
SUM = SUM+DIFFS
SM(I+1) = SM(I)+1.0
NEXT I
PRINT 'SUM='; SUM
PRINT
PRINT TAB(10); 'A='; TAB(20); 'P='; P
IF SUM < = 20.0 THEN GO TO 200 ELSE
    GO TO 300
200 FOR I = 1 TO 5
```

```
PRINT TAB(10); DH(I); TAB(30); DHCAL(I); TAB(50); SM(I);
      TAB(70); SUM; TAB(90); A
NEXT I
GO TO 500
300 P = P+0.01
GO TO 100
500 STOP
END.
```

APPENDIX V

(b) Evaluation of ΔH_{cal} for the transitions $|M, m_I \rangle \longrightarrow |M \pm 1, m_I \rangle$:

A computer programme is written in HI-BASIC language to calculate the ΔH values for the analysis of forbidden transitions in pairs based on the equations 6.18. The Q' and Q'' values obtained in the previous output (Appendix Va) along with the D, E, a and A spin-Hamiltonian parameters obtained from Appendix IV are given as input parameters for these equations to calculate ΔH, and compare with the experimental values.

```
REM THIS PROGRAMME CALCULATES THE DISTANCE BETWEEN TWO
REM FORBIDDEN TRANSITIONS. REF. UPRETI, J. MAG. RES. 13,
REM 339 (1974). 'A' IS HYPERFINE COUPLING CONSTANT AND 'Q'
REM IS Q-PRIME AND 'QQ' IS Q-DOUBLE PRIME 'SM' IS SMALL M.
REM 'ABC' IS GAMMA * BETA(N)/G * BETA. 'DH' IS DELTA H FOR
REM ± 1 FORBIDDEN TRANSITIONS. 'D', 'HZERO' AND 'E' VALUES
REM ARE CALCULATED FROM PUTCHA'S EXPRESSIONS. 'THES' AND
REM 'PHYS' ARE ANGLES IN DEGREES. 'LAM' IS LAMDA
DIM SM(10), DH(10), DHH(10)
ABC = 0.00037
20 INPUT 'A='; A
INPUT 'D='; D
INPUT 'E='; E
INPUT 'THES='; THES
INPUT 'PHYS='; PHYS
55 INPUT 'HZERO='; HZERO
INPUT 'Q='; Q
INPUT 'QQ='; QQ
320 PRINT TAB(10); 'D'; TAB(20); 'E'; TAB(30); 'THES'; TAB(40)
        'PHYS'; TAB(50); 'A'; TAB(60); 'Q'; TAB(70); 'QQ'
PRINT TAB(10); D; TAB(20); E; TAB(30); THES; TAB(40); PHYS;
        TAB(50); A; TAB(60); Q; TAB(70); QQ
```

```
THE =(THES*22)/(180*7)

PHY = (PHYS*22)/(180*7)

PRINT TAB(10); 'THE='; THE ; TAB(30); 'PHY'=; PHY

AA = COS(THE)

BB = (3*AA*AA)-1

CC = SIN(THE)

DD = CC*CC

TPHY = (2*PHY)

EE = COS(PHY)

FF = SIN(PHY)

P = 0.5*((Q*BB)+(3*QQ*DD*EE))

LAM = CC*((D-(E*EE))*AA)

ROW = 0.25*((D*DD)+(E*((AA*AA*EE) - (FF*FF))))

SIG = 0.5*((D*BB)+(3*E*DD*EE))

PRINT TAB(10); 'P'; TAB(40); 'LAM'; TAB(70); 'ROW'; TAB(110);
      'SIG'

PRINT TAB(10); P; TAB(40); LAM; TAB(70); ROW; TAB(110); SIG.

PRINT 'M=+1/2 TO -1/2 SEXTET, DELTA-M = ±1 TRANSITIONS

AAA = (17*A*A)/HZERO

HZEROS = HZERO*HZERO

BBB = (2*ABC*HZERO)

CCC = (8*A*A*SIG)/HZEROS

DDD = (12.5*A*A*A)/HZEROS

EEE = A*ABC
```

```
PRINT TAB(15); 'SM(I)'; TAB(30); 'DH(I)'
SM(1) = -2.5
FOR I = 1 TO 5
DH(I) = (AAA/2)+BBB - ((2*SM(I))+1)*((2*P) -CCC+DDD+(ABC*A)
PRINT TAB(15); SM(I); TAB(30); DH(I)
IF SM(I) = 2.5 THEN GO TO 100
SM(I+1) = SM(I)+1.0
NEXT I
100 SM(I)  = -1.5
PRINT TAB(10); 'SM(I)'; TAB(25); 'DHH(I)'
FOR I = 1 TO 4
DHH(I) = AAA*(2*BBB)-(2*SM(I))*((4*P)+(2*CCC)+(2*DDD)+(2*ABC*A))
PRINT TAB(10);SM(I); TAB(25); DHH(I)
IF SM(I) = 2.5 THEN GO TO 200
SM(I+1) = SM(I)+1.0
NEXT I
200 PRINT TAB(50); 'M= +3/2 TO +1/2 TRANSITIONS'
SM(1) = -2.5
PRINT TAB(30); 'SM(I)'; TAB(50); 'DH(I)'
FOR I = 1 TO 5
155 GGG = 2*P*((2*SM(I))+1)
KKK = ((ABS(LAM*LAM))*A*256)/(HZEROS*3)
LLL = ((ABS(ROW*ROW))*52*A)/HZEROS
MMM = ((A*A)/HZERO)*((2*SM(I))+8.5
```

```
NNN = ((A*A*SIG)/(HZEROS))*((14*SM(I))+9)
OOO = ((A*A*A)/(HZEROS))*((SM(I)*SM(I))+(19*SM(I)) -(51/4)
DH(I) = (-(2*A)+BBB-GGG-KKK+LLL+MMM+NNN-OOO)
PRINT TAB(20); SM(I); TAB(50); DH(I)
IF SM(I) = 2.5 THEN GO TO 300
SM(I+1) = SM(I)+1.0
NEXT I
300 PRINT TAB(40); 'M = -3/2 TO -1/2 TRANSITIONS'
SM(1) = -2.5
PRINT TAB(20); 'SM(I)'; TAB(50); 'DH(I)'
FOR I = 1 TO 5
GGG = 2*P*((2*SM(I))+1)
KKK = ((ABS(LAM*LAM))*A*256)/(HZEROS*3)
LLL = ((ABS(ROW*ROW))*52*A)/HZEROS
MMM = ((A*A)/HZERO)*((2*SM(I)) - 6.5)
NNN = ((A*A*SIG)/(HZEROS))*((14*SM(I))+5)
OOO = ((A*A*A)/(HZEROS)*((SM(I)*SM(I) -(17*SM(I)) - (123/4)))
DH(I) = (-(2*A) - BBB + GGG - KKK + LLL + MMM - NNN -OOO)
PRINT TAB(20); SM(I); TAB(50); DH(I)
IF SM(I) = 2.5 THEN GO TO 400
SM(I+1) = SM(I)+1.0
NEXT I
400 PRINT TAB(40); 'M = +5/2 TO +3/2 TRANSITIONS'
SM(1) = -2.5
```

```
PRINT TAB(30); 'SM(I)'; TAB(60); 'DH(I)'
FOR I = 1 TO 5
PP = 2*ABC*HZERO
QQQ = ((2*SM(I))+1)*(2*P)
RR = (ABS(LAM*LAM)*A*40)/(HZEROS*3)
SS = (ABS(ROW*ROW)*56*A)/HZEROS
TT = ((4*SM(I))+6.5)*((A*A)/HZERO)
UU = ((8*SM(I))+8)*((A*A*SIG)/HZEROS)
VV = ((2*SM(I)*SM(I)) - SM(I) - 33)*((A*A*A)/HZEROS)
DH(I) = ((-(4*A))+PP-QQQ-RR+SS+TT+UU-VV)
PRINT TAB(30); SM(I); TAB(60); DH(I)
IF SM(I) = 2.5 THEN GO TO 500
SM(I+1) = SM(I)+1.0
NEXT I
500 PRINT TAB(40); 'M = -5/2 TO  -3/2 TRANSITIONS
SM(1) = -2.5
PRINT TAB(30); 'SM(I)'; TAB(60); 'DH(I)'
FOR I = 1 TO 5
WW = 2*ABC*HZERO
XX = ((2*SM(I))+1)*(2*P)
YY = (ABS(LAM*LAM)*A*40)/(HZEROS*3)
ZZ = (ABS(ROW*ROW)*56*A)/HZEROS
PPP = ((4*SM(I)) - 2.5)*((A*A)/HZERO)
QQQ = (18*SM(I)*SIG*A*A)/HZEROS
```

```
RRR = ((2*SM(I)*SM(I))+(5*SM(I))-30)*((A*A*A)/HZEROS)
DH(I) = ((-(4*A)) - WW + XX - YY + ZZ + PPP - QQQ -RRR)
PRINT TAB(30); SM(I); TAB(60); DH(I)
IF SM(I) = 2.5 THEN GO TO 600
SM(I+1) = SM(I) + 1.0
NEXT I
STOP
END
```

VITAE

Born on 15th July 1957 at Adilabad, A.P., the author had his early education at Govt. High School, Adilabad, A.P. and then joined Govt. College, Adilabad from where he received his B.Sc., Degree (First class) from Osmania University in 1977. Later he studied at Kakatiya University and obtained his Master's Degree in Chemistry (First class) in 1979. He then joined University of Hyderabad and obtained M.Phil. Degree in Chemistry (First class) in 1980. Subsequently he continued for Ph.D. degree in 1980. He was a Junior Research Fellow (UGC) from August 1980 to September 1983 and a Senior Research Fellow (CSIR) from October 1983 to February 1985. At present he is working as Scientist in the Regional Research Laboratory, Hyderabad.