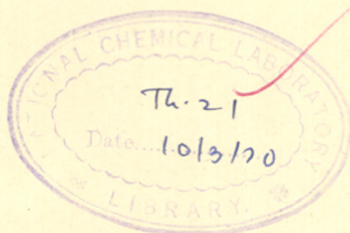


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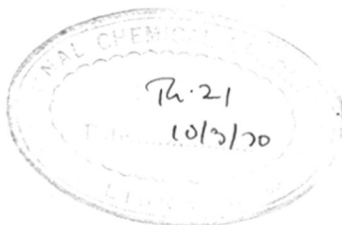


THE MÖSSBAUER SPECTRA
OF
SPINEL TYPE COMPOUNDS
CONTAINING IRON

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A Thesis
submitted to
The University of Poona
for
The Degree of
DOCTOR OF PHILOSOPHY
In Physics

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by
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1967

A C K N O W L E D G M E N T

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National Chemical Laboratory,
Poona-8.
July, 1967

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CHAPTER I

I N T R O D U C T I O N

INTRODUCTION

The discovery of recoil-free emission and absorption of gamma rays by Mössbauer¹ has led to a rapidly expanding new field of investigation which has produced a great deal of information during the last few years on several disciplines. This phenomenon which has now become known as the "Mössbauer Effect" has proved to be a powerful and unique tool for studies on diverse problems, such as measurement of gravitational red shift in an accelerated system², determination of nuclear moments^{3,4}, estimation of isomeric life times⁵ and of internal magnetic fields^{6,7}, study of chemical bonding⁸ and of quadrupole and Zeeman splittings^{9,10} and investigation of several other problems^{11,12}. The present thesis deals with the studies on the use of Mössbauer spectra to give information on the cation oxidation states and the site distribution in mixed oxide and sulphide systems containing iron with spinel structure where the cations can have a variable valency and can occupy more than one possible non-equivalent site.

As a background for the study the sections immediately following briefly discuss various theoretical and experimental aspects that are important for the understanding of the results represented in the thesis.

NUCLEAR RESONANCE ABSORPTION OF GAMMA RAYS

(The Mössbauer Effect)

There is a great unity in physics. The phenomenon of resonance which is familiar to us from many common accoustic and electrical phenomena has its analogy in optics and in the scattering and absorption of gamma rays. Accoustic resonance has been known since the times of Galileo; optical resonance was observed in 1904 by R. W. Wood; but it was not until the remarkable experiments of Mössbauer in 1958 that it was possible to observe gamma ray resonance with the same ease and clarity.

Several excellent accounts of the detailed theory of the Mössbauer Effect have been published elsewhere¹¹⁻¹⁴ and therefore, no attempt to reproduce this work will be made. However, a short description of the general principles of the phenomenon will be given together with some of its applications which will be useful in the later discussions.

When an isolated atom of mass m emits gamma radiation characteristic of its daughter atom, the atom recoils with the conservation of momentum. The recoil energy R , is given by the expression:

$$R = \frac{1}{2} mv^2 = \frac{p^2}{2m} = \frac{E_\gamma'^2}{2mc^2} \dots \dots \dots (1a)$$

where v is the velocity of the recoil and E_γ' is the energy of the emitted gamma ray. Since R is very small as compared to E_γ' and E_T

the transition energy, we can write the expression (1a) as

$$R = \frac{E_{\gamma}^2}{2mc^2} = \frac{E_T^2}{2mc^2} \dots \dots \dots (1b)$$

Conservation of energy demands that

$$E_T = E_{\gamma} + R \dots \dots \dots (2)$$

To have resonance absorption, the energy of the incident gamma ray must be greater than the resonance energy by the same amount R .

$$E_T = E_{\gamma} - R \dots \dots \dots (3)$$

The maxima for the emitter and the absorber are separated by $2R$.

If $2R \leq \Gamma$, where Γ is the natural line width, the two maxima overlap as happens in the optical transitions and hence resonance absorption takes place. Since R is proportional to the square of the transition energy in expression (1b), R increases by an extremely large amount in going from optical region (~ 1 ev) of the spectrum to the gamma radiation (~ 10 kev) no overlap takes place and hence there is no resonance absorption. The two cases are illustrated in Fig.1(a) and 1(b).

FIG. 1(a)

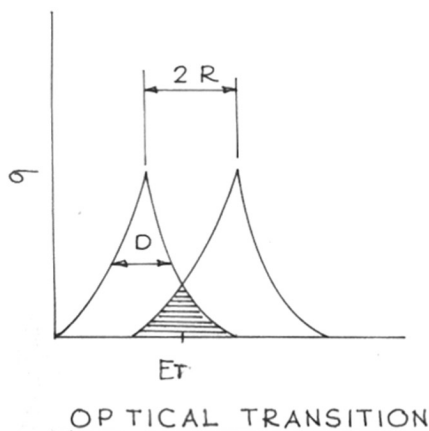


FIG. 1(b)

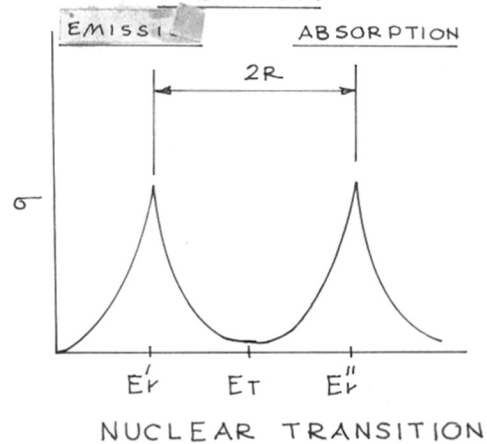


Table I gives the value of recoil energy as compared to the transition energy for the electromagnetic transition in the visible and the gamma ray regions.

Any excited state is characterized by excitation energy and by the natural width. The width Γ of the excited state or a resonance line is related to the life-time of the excited state by the Heisenberg's uncertainty principle.

$$\Gamma t = \frac{h}{2} = 1.05 \times 10^{-27} \text{ erg x sec} \dots (4)$$

where h is the Planck's constant, t , the life time (average life) of the excited state.

$$\text{for } t = 10^{-7} \text{ sec (Fe}^{57}\text{)}$$

$$\Gamma = 4.6 \times 10^{-9} \text{ e.v.} \dots (5)$$

If the resonance excitation probability is taken as unity, when the exact resonance energy (E_T) is given to the system, then the resonance excitation probability $W(E)$ at any energy E is given by the Breit-Wigner dispersion formula¹⁵.

$$W(E) = \frac{1}{1 + \left(\frac{E - E_T}{\Gamma/2} \right)^2} \dots (6)$$

The above equation also gives the energy dependence of the cross section σ for the resonance absorption of gamma rays

$$\sigma_a(E) = \sigma_0 W(E) \dots (7)$$

where σ_0 is the maximum resonance cross section given by,

$$\sigma_0 = \frac{2I_e + 1}{2I_g + 1} 2\pi \lambda^2 \frac{1}{1 + \alpha} \dots (8)$$

TABLE 1

	Visible Sodium D line	Isomeric Transition		Gamma ray emission Fe ⁵⁷
		Fe ⁵⁷	Sn ¹¹⁹	
λ (cm)	5.89×10^{-5}	-	-	-
Energy (e.v.)	2.1	14.4×10^3	23.8×10^3	137×10^3
E_R (e.v.)	1.13×10^{-8}	1.9×10^{-3}	2.6×10^{-3}	6.6×10^{-3}
Γ (e.v.)	6.6×10^{-8}	4.55×10^{-9}	2.4×10^{-8}	4.6×10^{-9}
$\frac{E_R}{\Gamma}$ (e.v.)	1.71×10^{-1}	4.2×10^6	2.8×10^6	1.4×10^6
$\frac{E_T}{\Gamma}$	3×10^8	3×10^{12}	8×10^{11}	-

where $2\pi/\lambda^2$ is the wavelength at the resonance, I_e and I_g are the spins of the excited state and ground state respectively, α is the internal conversion coefficient.

The nuclei, like atoms and molecules are not at rest but in constant thermal motion which has the effect of the broadening the emission or absorption lines due to the Doppler Effect. The Doppler broadening of the gamma radiation should be treated by taking into account the appropriate velocity distribution. In the case of a gas one can use Maxwell distribution¹⁶, then the spectrum assumes the Doppler width, $D = 2(RkT)^{\frac{1}{2}}$ where k is the Boltzmann constant and T is the absolute temperature. The energy distribution remains centered about the energy, $E = E_T \pm R$, but becomes Gaussian. This treatment holds only when $\Gamma \ll D$. In order to observe resonance, the condition now becomes $D \gg 2R$.

Before the Mössbauer's¹ discovery in 1958, several attempts were made to compensate the loss in energy of the gamma ray due to recoil. Gamma ray resonance scattering was observed by thermal excitation of the source¹⁷. Moon¹⁸ used ultracentrifuge to compensate for the recoil. Swann and Metzger¹⁹ attempted to make use of the recoil from a preceding decay to give an appropriate velocity to the source. Leamer and Hinman²⁰ considered the possibility of choosing a proper energy (and angle) in Compton scattering. Due to a large value of the Doppler width in these experiments, it was not possible to observe hyperfine splittings of the order of the natural line width Γ .

Mössbauer Discovery

In 1958, R. L. Mössbauer¹ reported his investigation of the nuclear resonance scattering of the 129 kev gamma ray from Ir^{191} , formed in the decay of Os^{191} . Even at the room temperature, the emission and absorption spectra overlap. In order to determine the background of his apparatus, he cooled both the source of Os^{191} and the Iridium foil absorber to liquid air temperature. He observed a decrease in the counting rate of the detector, when he expected an increase in the counting rate. He explained this apparently paradoxical result by referring to the paper of Lamb¹⁶, in which the effect of lattice binding on the capture cross section of slow neutrons has been discussed. When the emitting and the absorbing nuclei are embedded in a solid at low temperature, then there is a considerable probability that the recoil momentum of the gamma ray will be taken up by the crystal as a whole and therefore equation (1b) which has been derived for an isolated nucleus is no longer valid. The mass m of the nucleus should be replaced by the mass M of the whole crystal. The recoil energy then will be smaller by the order of the Avogadro's number, bringing about an overlap of the emission and absorption lines.

In the Debye approximation, the fraction f of the gamma rays emitted or absorbed without energy loss is given¹² by

$$f = e^{-2W} \quad \dots \dots \dots (9)$$

where

$$W = 3 \frac{R}{k\theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx \right] \dots, (10)$$

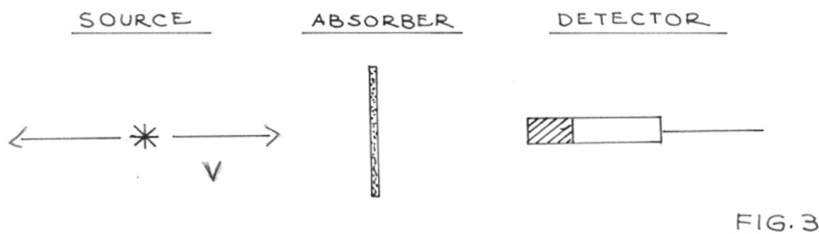
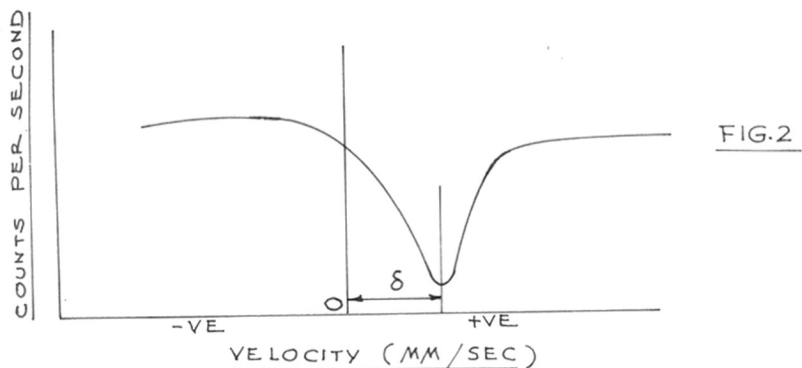
$$\text{where, recoil energy } R = \frac{E_\gamma^2}{2Mc^2}, \quad \theta_D \text{ is}$$

the Debye temperature.

It is clear from the equation (10) that the probability of recoilless process increases as the value of R and $\left(\frac{T}{\theta_D} \right)$ decreases.

Mössbauer further showed that the resonance can be destroyed by moving the source with respect to the absorber. This changes the energy of the emitted gamma ray which no longer matches with the transition energy of the excited level in the absorber. A plot of transmission intensity of the gamma ray versus the relative

velocity of the source or absorber is called the Mössbauer Spectrum (Fig. 2). The main parts of the equipment needed for studies on Mössbauer Effect are, the source of gamma ray, absorber containing Fe^{57} and the gamma ray detector (Fig.3).



Mössbauer Effect has been observed for 32 elements so far and it has been predicted for a further 17, approximately half the elements in the periodic table. Some of the isotopes on which studies of Mössbauer Effect have been conducted in greater detail are Au^{197} , Dy^{161} , Er^{166} , Eu^{153} , Fe^{57} , I^{127} , Ir^{191} , Sn^{119} , Te^{125} , Tm^{169} , W^{182} , Xe^{129} , Zn^{67} . Out of all these the largest amount of work has been done

on Fe^{57} and Sn^{119} . The present thesis deals with a Mössbauer study of the compounds containing Fe^{57} .

The Mössbauer Effect in Iron-57

The decay scheme of Co^{57} is shown below in Fig.(4).

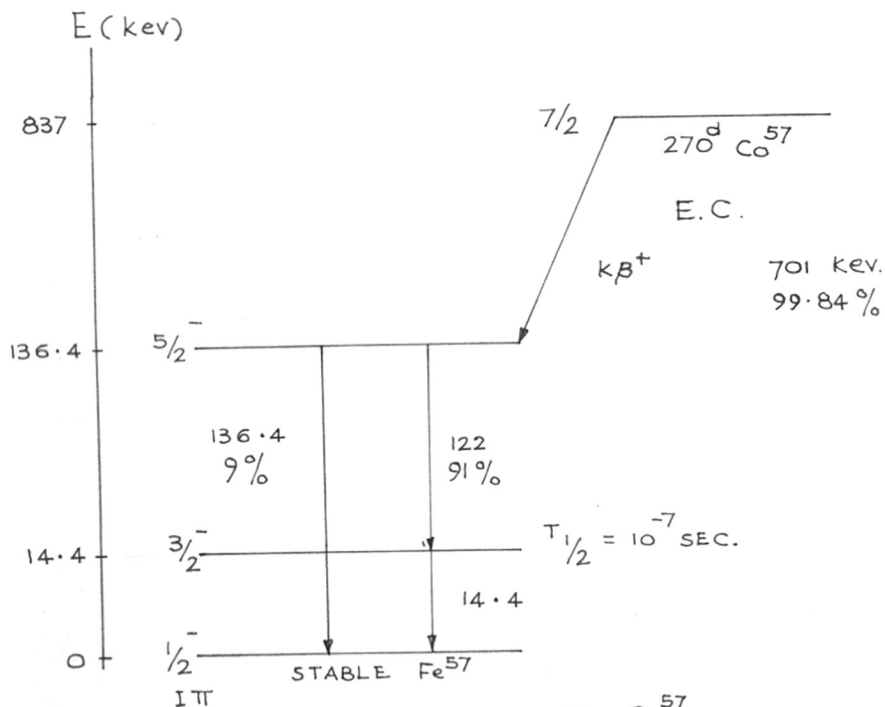


FIG. 4. THE DECAY SCHEME OF Co^{57}

Fe^{57} has many properties (Table 2) which make it very useful for Mössbauer Effect studies. Some of the properties of Fe^{57} of interest are:

- (1) The recoil energy for the 14.4 keV gamma transition is small, of the order of, $R \approx 1.9 \times 10^{-3}$ e.v.
- (2) A single line Co^{57} source can be prepared in a number of suitable host lattices.

TABLE II
 PROPERTIES OF Fe^{57}

	Ground state	First excited state	References
Energy (kev)	0	14.36	21
Spin and parity	$\frac{1}{2}^-$	$3/2^-$	21
Magnetic moment (nm)	0.0903	-0.1549	22
Quadrupole moment (barns)	0	0.29	23
		0.41	24
Recoil energy (e.v.)	0	1.9×10^{-3}	
Internal conversion coefficient	-	9.0 ± 0.4	25
Natural line-width (e.v.)	-	4.6×10^{-9}	
Radius of the nucleus (arb. units)	1.00	0.998	26

(3) The natural line-width is very narrow, permitting high resolution experiments, $\Gamma/E_0 \approx 10^{-12}$.

(4) The Debye temperature for iron is $400 \pm 30^\circ\text{K}$, so that $k\theta \approx 3.5 \times 10^{-2}$ e.v. Thus there is a substantial recoilless emission probability even at room temperature, $f = 0.8$.

(5) Co^{57} has comparatively long life time (270 days) so that one can use one source for a sufficiently long time.

(6) Since iron and its compounds are available in many different states, e.g. ferromagnetic, antiferromagnetic, paramagnetic, ferroelectric and antiferroelectric, the Mössbauer studies can be conducted under different conditions.

(7) Quadrupole interaction study is less complicated in iron compounds since its ground state has no quadrupole moment.

(8) It has a relatively high cross-section for resonant absorption, $\sigma_0 = 2.2 \times 10^{-18} \text{ cm}^2$.

Applications of the Mössbauer Effect

The importance of the Mössbauer Effect in solid-state studies is due to the hyperfine interactions between the nuclear energy levels in the Mössbauer nuclei and the extranuclear electrons, giving rise to isomer shift, δ , the quadrupole splitting, Q , and the hyperfine Zeeman splitting which are described in brief.

Isomer Shift

The shift of the centre of resonance spectrum from zero velocity of an arbitrarily chosen radiation source is known as the

isomer shift (Fig. 2). The isomer shift obtained with any one source can be converted with respect to any other source by a suitable correction factor. Table 3 prepared by Herber²⁷ gives the values of the correction factors for different sources. Similar tables have been prepared by other workers²⁸. However, it should be pointed out that two sources prepared by the same person and by the same method give slightly different values of the isomer shift and a person working in this field has to find out his own correction for his source by comparing the values of isomer shifts obtained by him for standard absorbers, like $K_4 Fe(CN)_6 \cdot 3H_2O$, $Na_2 [Fe(CN)_5 (NO)] \cdot 2H_2O$, 310 stainless steel absorber, etc.

TABLE 3
ISOMER SHIFTS OF SODIUM NITROPRUSSIDE WITH RESPECT
TO SEVERAL Co^{57} HOST MATRICES

Co^{57} source	Isomer shift mm/sec
Pt	-0.607
Cu	-0.483
Pd	-0.442
Fe	-0.348 -0.351
310 SS, Vacromium	-0.182
302 SS	-0.175
Cr	-0.075

The isomer shift arises because of the effect of chemical environment of the nucleus on the energy of the nuclear levels. The nucleus is not a point charge but has a finite volume which is different in the excited and the ground state. For a pair of resonant atoms, denoted by a given source-absorber pair, the isomer shift is given by the equations¹²,

$$\delta = \frac{2\pi}{5} Ze^2 \left[\left| \psi(0) \right|_{\text{absorber}}^2 - \left| \psi(0) \right|_{\text{source}}^2 \right] \left[r_{\text{ext}}^2 - r_{\text{grd}}^2 \right] \quad \dots\dots\dots (11)$$

$$= \text{Const} \frac{\partial F}{\partial r} \left[\left| \psi(0) \right|^2 \right] \quad \dots\dots\dots (12)$$

$$\text{where, } \partial r = r_{\text{ext}} - r_{\text{grd}} \quad \dots\dots\dots (13)$$

Ze is the charge and r is the radius of the nucleus, and $|\psi(0)|^2$ is the total electron density at the nucleus.

If the charge density in the excited state is smaller than that in the ground state, then the isomer-shift would decrease with an increase of electron density at the nucleus, as with the case of iron where the excited state is smaller than the ground state²⁶. In Sn^{119} , $\frac{\partial F}{\partial r}$ is positive²⁹, hence the isomer shift would increase with an increase in electron density at the nucleus. The importance of the sign of $\frac{\partial F}{\partial r}$ in the direction of isomer shift was clearly shown by the work of Debenedetti³⁰. Iodine has two Mössbauer nuclei, I^{127} for which $\frac{\partial F}{\partial r}$ is -ve and I^{129} for which the excited state is larger than the ground state $\frac{\partial F}{\partial r}$ +ve. In one and the same chemical compound of Iodine ($\text{Na}_3\text{H}_2\text{IO}_6$), the electron density at the nucleus is same, but

TABLE 4
ISOMER SHIFT VALUES FOR DIFFERENT OXIDATION STATES OF Fe⁵⁷

Outer electron configuration	Configuration	Nature	Isomer shift (mm/sec)	References
Fe ¹⁺	-	High spin	+ 2.1	33
Fe ²⁺ 3d ⁶	5T ₂	High spin	+ 1.3 to 1.5	31, 32
Fe ³⁺ 3d ⁵	6A ₁	High spin	+ 0.35 to 0.70	31, 32
Fe ⁴⁺	-	Ionic	+ 0.14 to 0.17	32
Fe ^{II} d ⁶ (d ⁴ s ² p ⁰)	1A ₁	Low spin	- 0.136 to + 1.464	34
Fe ^{III} d ⁵ (d ⁴ s ¹ p ⁰)	2T ₂	Low spin	+ 1.7 to 3.6	
Fe ^{VI} [FeO ₄] ⁻²	-	-	0.7 to -0.8	35, 36

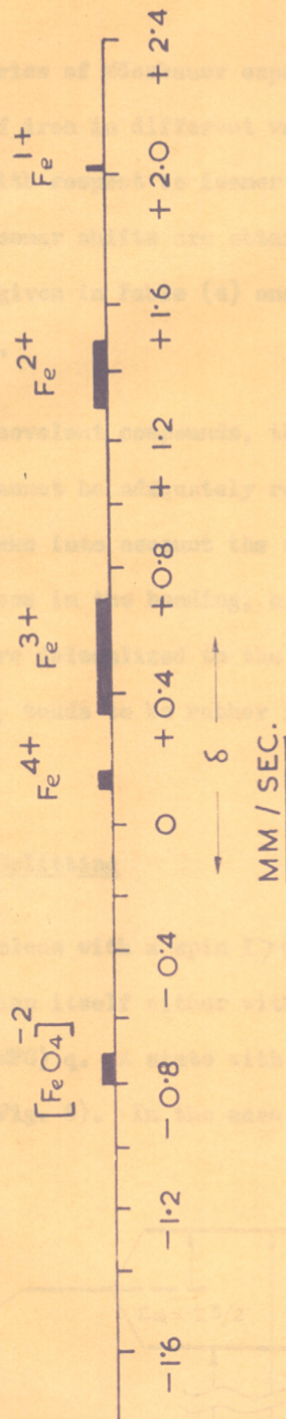


FIG. 5: ISOMER SHIFTS OF IRON COMPOUNDS WITH RESPECT TO ^{57}Co SOURCE IN STAINLESS STEEL 310

the isomer shifts have been found to be in opposite directions³⁰.

A series of Mössbauer experiments done with high spin compounds of iron in different valency states show a systematic behaviour with respect to isomer shift^{31,32,34}. Characteristic values of isomer shifts are obtained for different oxidation states, as given in Table (4) and illustrated graphically below in Fig. (5).

For covalent compounds, things are more complicated, since covalency cannot be adequately represented by a single parameter. We should take into account the relative importance of s, p and d, wave functions in the bonding, as well as, the extent to which the electrons are delocalized to the ligands. For low spin iron compounds, δ tends to be rather independent of the oxidation state.

Quadrupole Splitting

A nucleus with a spin $I > \frac{1}{2}$ has a quadrupole moment, Q , and this can align itself either with or across an electric field gradient, (EFG) q . A state with spin I would be split into $(I + \frac{1}{2})$ substates (Fig. 6). In the case of Fe^{57} and Sn^{119} , the excited

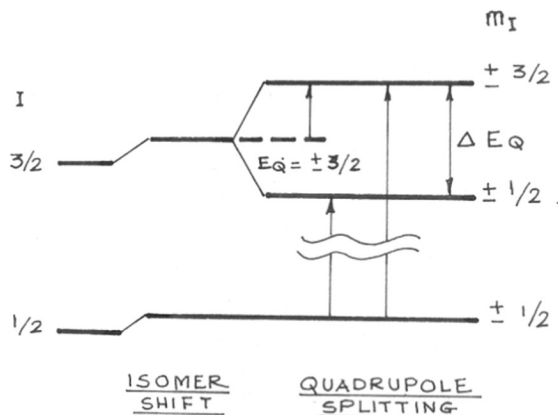


FIG. 6.

state with $I = 3/2$ would be split up into two sub-levels leading to a pair of lines instead of one line in the Mössbauer spectrum. The separation between these two lines Fig. (7) is termed as the quadrupole splitting, because it arises due to the interaction of quadrupole moment of the excited state with the EFG.

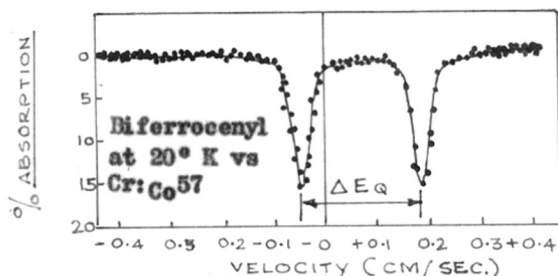


Fig. 7. Quadrupole splitting in Fe^{57} . Data on biferrocenyl from Wertheim (21).

The Hamiltonian describing the quadrupole coupling is derived by Abragam³⁷ and we shall simply quote the result.

$$H_Q = \frac{e^2 q Q}{4I(2I-1)} \left[3 I_z^2 - I(I+1) \right] + \eta \left(I_x^2 - I_y^2 \right) \dots (14)$$

where I_x and I_y are step-up and step-down operators³⁸, the electric field gradient $eq = \frac{\partial^2 V}{\partial z^2}$, asymmetry parameter

$$\eta = \left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2} \right) / \frac{\partial^2 V}{\partial z^2}, \text{ and } Q \text{ the quadrupole moment with spin } I.$$

For an axially symmetric field gradient, the energy shifts are given by

$$\Delta E_Q = \frac{e^2 q Q}{4I(2I-1)} \left[3 m_I^2 - I(I+1) \right] \dots (15)$$

No quadrupole splitting would be observed for nuclei with spin 0 or $\frac{1}{2}$, as the term $4I(2I-1)$ vanishes in the expression (15).

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In a chemical compound the (EFG) can be due to (i) incompletely filled (non-spherical symmetric) electron shells or (ii) asymmetric distribution of the charges on the ligand atoms.

In the case of ferric ion, (which is a spherical $3d^5$, $6s^0$ state is spherically symmetric, and therefore should not give rise to any quadrupole splitting. In many cases a small splitting may be observed due to factor (ii). In the calculation of field gradient for ferric ion one has to take into account the lattice sum. The first order distortion of ferric core by the lattice is given by Sternheimer³⁹ correction $(1 - \gamma_\infty)$, so that the field gradient for ferric substance is

$$q = (1 - \gamma_\infty) q_{\text{Lattice}} \dots\dots\dots (16)$$

In contrast the lower order state of ferrous ion is $(3d^6)$, $5D_4$, which may be pictured as the spherical ferric like core plus an unpaired 3d valence electron. The ionic contribution to field gradient is due to both the factors (i) and (ii). (i) Valence electron q_{val} and other due to lattice contribution q_{Lattice} . Therefore, the field gradient in the ferrous substances is approximately given by

$$q = (1 - \gamma_\infty) q_{\text{Lattice}} + (1 - R) q_{\text{val}} \dots\dots\dots (17)$$

where $(1 - R)$ is Sternheimer correction⁴⁰.

High spin Fe^{3+} ion shows a small quadrupole splitting upto 0.6 mm/sec^{41,42}. High spin Fe^{2+} salts show relatively large quadrupole splitting (from 1.7 mm/sec to 3.6 mm/sec) and these have relatively large temperature dependence due to the presence

of the sixth d electron which can occupy different levels in crystal field at different temperatures. Quadrupole splitting and related data for the Fe^{3+} and $\text{Fe}^{2+}_{10\%}$ are summarized in Table (5).

Hyperfine Magnetic Splitting

If a Mössbauer nucleus is placed in a magnetic field, which arises either internally (as in ferromagnetic material like Fe-metal) or is generated by an external device, the degeneracy of the level with spin I, is further lifted and it will be split into $(2I+1)$ levels.

The splitting of the excited state ($I = 3/2$) is given by the Hamiltonian²¹

$$\mathcal{H}_{\text{ex}} = -g_e \beta_n H I_z \dots\dots\dots (18)$$

and that of the ground state

$$\mathcal{H}_g = -g_g \beta_n H I_z \dots\dots\dots (19)$$

where H is the magnetic field, β_n is the nuclear magneton, g_g and g_e are the nuclear g factors for the ground and excited states respectively. The direction of spin alignment is taken to be Z axis. In the presence of EFG tensor, the equation (18) would be replaced by

$$\mathcal{H}_{\text{ex}} = -g_e \beta_n H I_z + \mathcal{H}_Q \dots\dots\dots (20)$$

The $3/2$ state in Fe^{57} will split into 4 levels and the ground state with spin $\frac{1}{2}$ will split into two levels. Transitions between these levels are governed by the selection rules. For a magnetic

dipole transitions (M_1) $\Delta m = 0, \pm 1$, there would be six possible transitions Fig. (8) (see also Fig. 15).

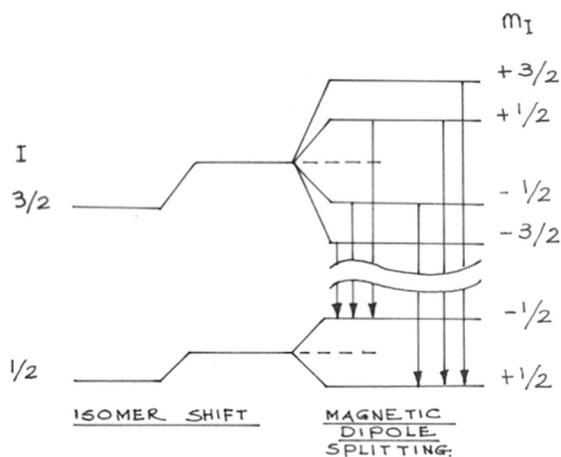


FIG. 8 : MAGNETIC HYPERFINE SPLITTING OF THE GROUND AND FIRST EXCITED STATE OF Fe^{57}

In the case of an axially symmetric EFG tensor with the symmetry axis at an angle θ with respect to magnetic axis, the energy levels in Fe^{57} of an excited state, with quadrupole moment Q are given by²¹

$$E = -g\beta_n H m_I + (-1)^{|m_I|} + \frac{1}{2} \frac{e^2 q Q}{4} \frac{3 \cos^2 \theta - 1}{2} \dots (21)$$

if $eqQ/\mu H \ll 1$.

The quadrupole splitting, in such a case may be expressed

as¹²

$$\epsilon_m = \frac{e^2 q Q}{8I(2I-1)} [3m^2 - I(I+1)] (3\cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi) \dots (22)$$

where Θ and ϕ are the polar angles defining the direction of magnetic field H with the crystal axes.

If $I = 3/2$ and $\eta = 0$, then

$$C_{\pm 3/2} = C = \frac{e^2 q Q}{8} (3 \cos^2 \Theta - 1) \dots\dots\dots (23)$$

The Mössbauer parameters, δ , C and H can be determined experimentally from the following relationships^{45,46}.

The isomer shift δ , in the hyperfine split spectrum is given by,

$$\delta = \frac{S_1 + S_2 + S_5 + S_6}{4} \dots\dots\dots (24)$$

The quadrupole splitting C , can be determined from the relation,

$$C = \frac{1}{4} e^2 q Q = \frac{S_1 + S_6 - S_2 - S_5}{4} \dots\dots\dots (25)$$

and the effective magnetic field H , can be determined from

$$H = - \frac{S_6 - S_1}{5.43} \times \frac{1}{\mu_0} \dots\dots\dots (26)$$

$$H = \frac{(S_6 - S_5) + (S_2 - S_1)}{2g_e \beta_n} \dots\dots\dots (27)$$

and

$$H = \frac{S_4 - S_2}{g_g \beta_n} = \frac{S_5 - S_3}{g_g \beta_n} \dots\dots\dots (28)$$

where, S_1 , S_2 , S_3 , S_4 , S_5 and S_6 are the positions of the six maxima in the Mössbauer spectrum shown in Fig. (15), β_n is the Bohr magneton, μ_0 is the magnetic moment of the ground state, and g_e and g_g are the g factors for the excited and ground states respectively.

Mössbauer Effect studies have, therefore, been used to study magnetic parameters, the magnitude^{47,48,49} and direction⁵⁰ of the

effective magnetic field at the nucleus, as well as the direction of the EFG^{43,51}.

HISTORICAL ACCOUNT OF SPINELS

Spinel the name originally given to the mineral magnesium-aluminate MgAl_2O_4 , has now come to represent a class of compounds isomorphous with MgAl_2O_4 . The detailed study on this structure was carried out by Bragg⁵² and Nishikawa⁵³.

The general formula of a spinel can be written as, AB_2X_4 , where X is an anion, A and B are cations. Many compounds with spinel structure have been reported in literature⁵⁴, most of them are oxidic spinels ($\text{X}=\text{O}^{2-}$), but a few non-oxidic spinels with $\text{X} = \text{F}^{55-}$, Cl^{56-} , CN^{57-} , S^{2-58} , Se^{2-58} and Te^{2-58} have also been reported.

In an ideal spinel structure the anions form a cubic close packing Fig. (9) in which the cations partly occupy the tetrahedral and octahedral interstices. In a unit cell there are 32 octahedral and 64 tetrahedral interstices, of which 16 octahedral and 8 tetrahedral interstices are occupied by the metal ions. The tetrahedral and octahedral positions in the spinel structure are called the A sites and B sites respectively. It is a common practice to denote the octahedrally surrounded cations within the brackets, as:



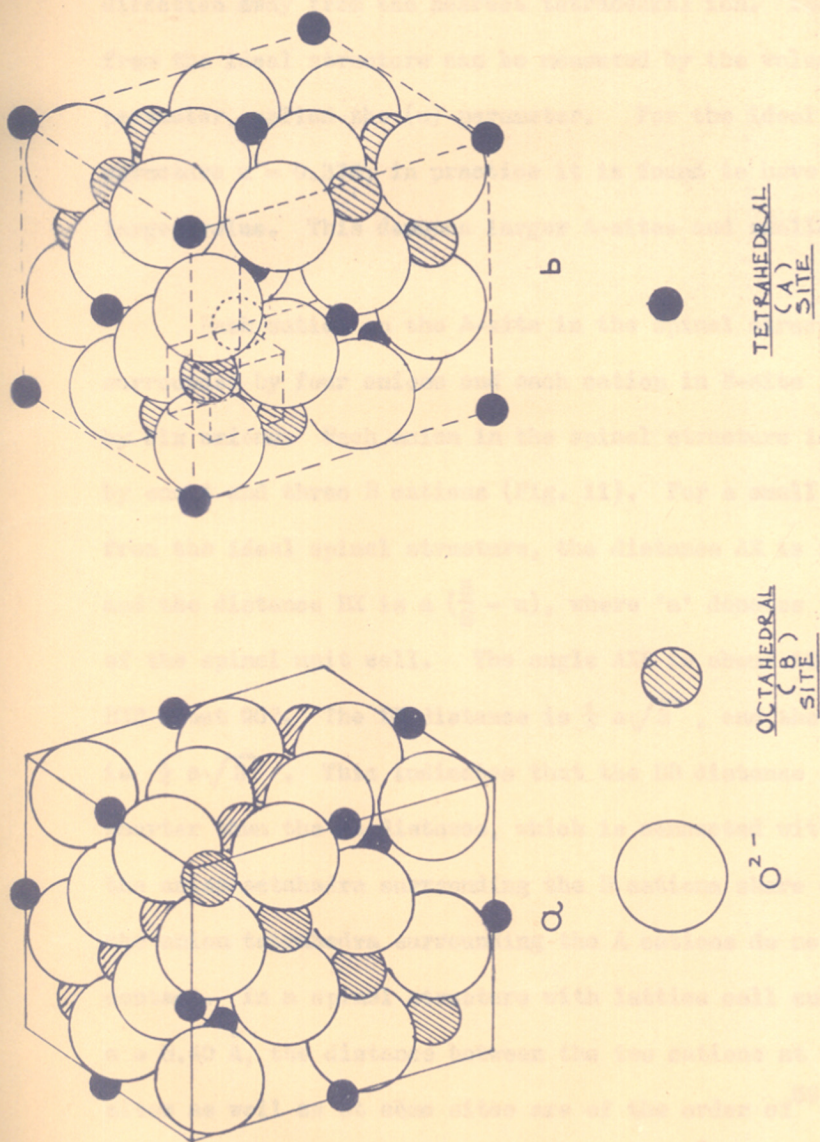


FIG. 9

a. ARRANGEMENT AND PACKING OF ATOMS IN UNIT CELL OF AN IDEAL SPINEL

b. UNIT CELL SHIFTED BY ONE-HALF A CUBE EDGE

The unit cell of an ideal spinel structure is shown in Fig. (10). The non-ideal spinel structure is derived by moving the four anions around the tetrahedral site in a $[111]$ direction away from the nearest tetrahedral ion. The deviation from the ideal structure can be measured by the value of anion parameter, called the (u) parameter. For the ideal spinel structure $u = 0.375$; in practice it is found to have a slightly larger value. This denotes larger A-sites and smaller B-sites.

Each cation on the A-site in the spinel structure is surrounded by four anions and each cation in B-site is surrounded by six anions. Each anion in the spinel structure is surrounded by one A and three B cations (Fig. 11). For a small deviation from the ideal spinel structure, the distance AX is a $(u - \frac{1}{4})\sqrt{3}$ and the distance BX is a $(\frac{5}{8} - u)$, where 'a' denotes the cell edge of the spinel unit cell. The angle AXB is about 125° and the BXB about 90° . The BB distance is $\frac{1}{4} a\sqrt{2}$, and the AA distance is $\frac{1}{4} a\sqrt{3}$. This indicates that the BB distance is considerably shorter than the AA distance, which is connected with the fact that the anion octahedra surrounding the B cations share edges, whereas the anion tetrahedra surrounding the A cations do not have any contact. In a spinel structure with lattice cell cube edge of $a = 8.40 \text{ \AA}$, the distance between the two cations at different sites as well as at same sites are of the order of⁵⁹

$$\overset{\circ}{\text{A-A separation}} = 3.65 \overset{\circ}{\text{\AA}}$$

$$\overset{\circ}{\text{A-B separation}} = 3.48 \overset{\circ}{\text{\AA}}$$

$$\overset{\circ}{\text{B-B separation}} = 2.97 \overset{\circ}{\text{\AA}}$$

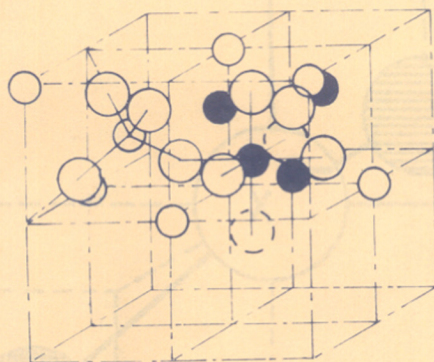


FIG. 10

UNIT CELL OF AN IDEAL SPINEL
SHOWING ONLY TWO OCTANTS.



FIG. 11: THE NEIGHBOURS OF AN ANION IN THE SPINEL
STRUCTURE



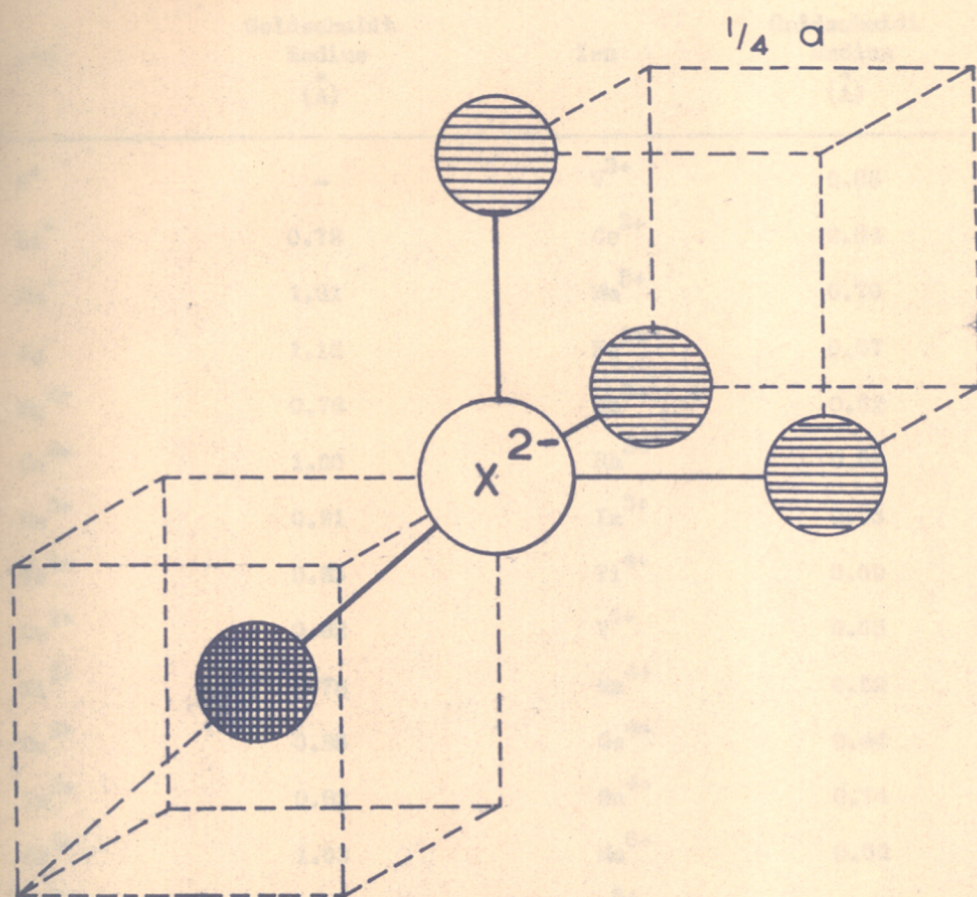
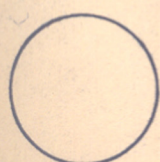


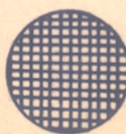
FIG. II : THE NEIGHBOURS OF AN ANION IN THE SPINEL STRUCTURE



ANION.



B-SITE CATION.



A-SITE CATION.

a

CELL EDGE.

TABLE 6

THE GOLDSCHMIDT RADII FOR METALLIC IONS FOUND TO OCCUR IN OXIDIC SPINELS

Ion	Goldschmidt Radius ($\text{\AA}$)	Ion	Goldschmidt Radius ($\text{\AA}$)
H ⁺	-	V ³⁺	0.65
Li ⁺	0.78	Cr ³⁺	0.64
Cu ⁺	1.01	Mn ³⁺	0.70
Ag ⁺	1.13	Fe ³⁺	0.67
Mg ²⁺	0.78	Ga ³⁺	0.62
Ca ²⁺	1.06	Rh ³⁺	0.68
Mn ²⁺	0.91	In ³⁺	0.93
Fe ²⁺	0.83	Ti ⁴⁺	0.69
Co ²⁺	0.82	V ⁴⁺	0.65
Ni ²⁺	0.78	Mn ⁴⁺	0.52
Cu ²⁺	0.85	Ge ⁴⁺	0.44
Zn ²⁺	0.82	Sn ⁴⁺	0.74
Cd ²⁺	1.03	Mo ⁶⁺	0.62
Al ³⁺	0.57	W ⁶⁺	0.63
Ti ³⁺	0.69		

These distances are of the nearest neighbours in each case. The distances between the anions and the A and B sites are,

$$\text{X-A separation} = 1.9 \text{ \AA}$$

$$\text{X-B separation} = 2.1 \text{ \AA}$$

A large number of cations have been found experimentally in the spinel structure. A table of such cations prepared by Gorter⁶⁰ is reproduced in Table (6). It will be observed that the radii of all these ions lie between 0.44 and approximately 1.04 Å, with the exception of Ag¹⁺.

Several ions with the radii between the above limits were not found originally in the oxidic spinels, among which were all pentavalent ions. As a result of more recent investigations, Gorter's list is no longer complete because a number of pentavalent ions, e.g. V⁵⁺⁶¹, Sb⁵⁺⁶² and Nb⁵⁺⁶³ have already been established to occur in the spinel structure.

Some compounds have a structure which can be described as a tetragonal or orthorhombic distortion of spinel structure. This has been attributed to two causes⁵⁴. (1) The Jahn-Teller effect⁶⁴ and (2) The superstructure formation^{65,66}.

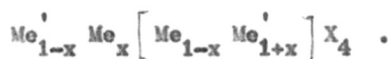
Cation Distribution

The most interesting property of the spinel type compounds is the distribution of cations among the two possible sites, viz., tetrahedral and octahedral ones. The distribution of the cations, e.g. for a 2-3 spinels $\text{Me Me}_2' \text{X}_4$ may be

(i) "Normal" $\text{Me} \left[\overset{\cdot}{\text{Me}}_2 \right] \text{X}_4$ i.e., one Me ion in the tetrahedral site and two Me ions in the octahedral sites. e.g. $\text{Zn Fe}_2 \text{O}_4$, is normal: $\text{Zn} \left[\text{Fe}_2 \right] \text{O}_4$.

(ii) "Inverse" $\text{Me} \left[\text{Me} \overset{\cdot}{\text{Me}} \right] \text{X}_4$ i.e., one Me ion in the octahedral position and the other Me ion in the tetrahedral position. e.g. in $\text{NiFe}_2 \text{O}_4$ the distribution is inverse: $\text{Fe} \left[\text{NiFe} \right] \text{O}_4$.

(iii) Intermediate, the distribution of cations between normal and inverse, which may be denoted by the general formula



e.g. In $\text{MnFe}_2 \text{O}_4$ and $\text{MgFe}_2 \text{O}_4$ the distributions are intermediate, $\text{Mn}_{0.8} \text{Fe}_{0.2} \left[\text{Mn}_{0.2} \text{Fe}_{1.8} \right] \text{O}_4$ and $\text{Mg}_{0.1} \text{Fe}_{0.9} \left[\text{Mg}_{0.9} \text{Fe}_{1.1} \right] \text{O}_4$ respectively.

It is known that some cations have pronounced preference for certain coordination numbers and this influences the cation distribution in the spinel structure. Verwey⁶⁷, Heilmann⁶⁸ and Romeijn made a systematic study of cation distribution and deduced a site preference sequence of the ions for the tetrahedral or octahedral sites viz.

a) Zn^{2+} , Cd^{2+} , Ga^{3+} , In^{3+} , Ge^{4+} ions have strong preference for the tetrahedral site.

b) Cr^{3+} , Ni^{2+} , Ti^{4+} , Sn^{4+} , Mn^{3+} , ions have strong preference for the octahedral site.

c) Mg^{2+} , Fe^{2+} , Co^{2+} , Mn^{2+} , Fe^{3+} , Al^{3+} ions do not show any strong preference for either the tetrahedral or the octahedral sites in the spinel structure.

CRYSTAL FIELD THEORY DATA FOR TRANSITION METAL IONS

No. of d- elec- trons	Ion	Free ion ground state	Octahedral field ground state	Tetrahedral field ground state	Dq cm ⁻¹		Stabilization kcal		Octa.site preference energy/ kcal/mole
					Oct.	Tetr.	Oct.	Tetr.	
1	Ti ⁺⁺⁺	2D	2T _{2g}	2E _g	2030	900	23.1	15.4	7.7
2	V ⁺⁺⁺	3F	3T _{1g}	3A _{2g}	1800	840	30.7	28.7	2.0
3	V ⁺⁺	4F	4A _{2g}	4T _{1g}	1180	520	40.2	8.7	31.5
		4F	4A _{2g}	4T _{1g}	1760	780	60.0	13.3	46.7
4	Cr ⁺⁺	5D	5E _g	5T _{2g}	1400	620	24.0	7.0	17.0
		5D	5E _g	5T _{2g}	2100	930	35.9	10.6	25.3
5	Mn ⁺⁺	6S	6A _{1g}	6A _{1g}	750	330	0	0	0
		6S	6A _{1g}	6A _{1g}	1400	620	0	0	0
6	Fe ⁺⁺	5D	5T _{2g}	5E _g	1000	440	11.4	7.5	3.9
		5D	1A _{1g}	5E _g	780	780	45.0	26.0	19.0
7	Co ⁺⁺	4F	4T _{1g}	4A _{2g}	1000	440	17.1	15.0	2.1
		3F	3A _{2g}	3T _{1g}	860	380	29.3	6.5	22.8
9	Cu ⁺⁺	2D	2F _g	2T _{2g}	1300	580	22.2	6.6	15.6
10	Zn ⁺⁺	1S	1A _{1g}	1A _{1g}	0	0	0	0	0

* Note: It is probably more accurate to use the strong field theory for the +3 ions. This changes the site preference energy of V⁺⁺⁺ to 12.3 kcal.

McClure⁷⁰ and Dunitz and Orgel⁷¹ made use of the crystal field theory to obtain the quantitative information on the relative stability of the "Normal" and "Inverse" spinels. On the basis of purely electrostatic arguments of the crystal field theory, they calculated the stabilization energy for the tetrahedral and octahedral coordination in terms of the crystal field stabilization parameter Dq (The crystal field splitting is denoted by $10 Dq$). Covalent bonding is undoubtedly significant in these compounds, and part of the stabilization would be due to the covalent effects in addition to the crystal field effects. But this can be automatically taken into account in the calculation of stabilization energy if the value of $10 Dq$ is derived from the spectroscopic data. The cation distribution can then be predicted depending only on the value of this parameter and not on its origin. Both Dunitz and Orgel as well as McClure have calculated the value of the stabilization energies in terms of $10 Dq$ for the transition metal ions in a crystal field. We reproduce the table due to McClure⁷⁰ where in the last column are given the values of octahedral site preference energies - Table (7).

The theoretical results based on the crystal field theory have been found to predict the correct cation distribution in many cases but there have been also a few notable disagreement between the predictions and the experimental results. Miller⁷² extended the concept of the octahedral site preference energy in a spinel structure to include the Madelung and short-ranged terms in addition to the crystal field terms. The value of octahedral site preference energy for different ions as given by Miller are reproduced in Table 8.

TABLE 8

OCTAHEDRAL SITE PREFERENCE ENERGIES FOR CATIONS

values of P are in k cal/g atomic weight

Ion	P	Ion	P
Li ⁺	-3.6	Zn ⁺⁺	-31.6
Cu ⁺	-8.6	Cd ⁺⁺	-29.1
Ag ⁺	-19.6	Al ³⁺	-2.5
Mg ⁺⁺	-5.0	Ti ³⁺	-21.9
Ca ⁺⁺	-30.7	V ³⁺	-11.6
Mn ⁺⁺	-14.7	Cr ³⁺	+16.6
Fe ⁺⁺	-9.9	Mn ³⁺	+ 3.1
Co ⁺⁺	-10.5	Fe ³⁺	-13.3
Ni ⁺⁺	9.0	Ga ³⁺	-15.4
Cu ⁺⁺	-0.1	In ³⁺	-40.2

Miller obtained a reasonably good correlation between the experimental and the theoretical values.

REVIEW OF THE LITERATURE ON THE MÖSSBAUER SPECTRA OF SPINEL TYPE COMPOUNDS

Bauminger et al.⁴⁷ were among the earliest investigators who used the Mössbauer Effect for studies on cation distribution. In the hyperfine split spectra of Yttrium iron and dysprosium iron garnets, they observed a series of doublets and explained these results as due to two hyperfine split spectra of Fe^{3+} ions at the tetrahedral and the octahedral sites in the garnet structure. From the distances between the position of the peaks, they determined the values of effective magnetic fields at the iron nuclei on the tetrahedral and octahedral sites in the Yttrium iron and dysprosium garnets to be 3.9×10^5 Oe and 4.85×10^5 Oe respectively at 25°C.

Yamadaya et al.⁷³ studied the Mössbauer spectra of CuFe_2O_4 in both the tetragonal and the cubic phases. A quadrupole split spectrum was observed in both cases. An abrupt change in the magnitude of quadrupole splitting at 90°C was explained due to the transition from tetragonal to cubic phase. Mizoguchi and Tanaka⁷⁴ studied the crystal distortion in the germanium substituted copper ferrite by Mössbauer Effect. No difference in quadrupole splitting was observed in tetragonal and cubic phases in contrast to the observation of Yamadaya et al. in CuFe_2O_4 . Mössbauer spectra of the system $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ were studied by same workers⁷⁵. They deduced an effective magnetic field of 425 kOe and an isomer shift

of 0.49 mm/sec with respect to stainless steel from the hyperfine split Mössbauer spectrum of MnFe_2O_4 . The observed isomer shift is characteristic of Fe^{3+} ion indicating that manganese is present in the 2+ state. In the paramagnetic state the specimens exhibited quadrupole splitting. There was no difference in the quadrupole splitting in tetragonal and cubic phases. The same authors⁷⁶ further investigated the spinel type oxides, ZnFe_2O_4 , FeCrNiO_4 , FeNiAlO_4 and FeAl_2O_4 in their paramagnetic state. A quadrupole splitting was observed in all the cases with the exception of FeAl_2O_4 . The observed quadrupole splitting in ZnFe_2O_4 was explained due to a trigonal field at the octahedral site in the spinel structure. The quadrupole splitting in FeNiAlO_4 and FeCrNiO_4 was attributed to the heterogeneous nature of the neighbouring sites. The Mössbauer spectrum of FeAl_2O_4 showed a single resonance peak with $\delta = 0.98$ mm/sec with respect to stainless steel at 25°C which is characteristic of spin free Fe^{2+} compounds. Rossiter⁷⁷ studied the spectra of FeCr_2O_4 , FeAl_2O_4 and $\text{Fe}_{1+x}\text{V}_{2-x}\text{O}_4$ ($0 \leq x \leq 1$) system. He observed a single line spectrum for FeV_2O_4 but a hyperfine spectrum for Fe_2VO_4 . A single line Mössbauer spectrum with a large line width (~ 1 mm/sec) was observed for FeCr_2O_4 at 295°K, while a quadrupole split spectrum was observed for FeAl_2O_4 in contrast to the results of Mizoguchi and Tanaka⁷⁶. Mathur *et al.*^{78,79} reported a single line spectrum with a large line width for FeCr_2O_4 and a quadrupole split spectrum for GeFe_2O_4 , ZnFe_2O_4 and CdFe_2O_4 . The large line width in the spectrum of FeCr_2O_4 was attributed to a local distortion at the A sites. This was confirmed later by the detailed work of Tanaka *et al.*⁸⁰. The quadrupole splitting in

GeFe_2O_4 , ZnFe_2O_4 and CdFe_2O_4 observed by Mathur et al was attributed to the non-cubic B sites in the spinel structure. Rossiter^{81,82} studied the Mössbauer spectra of the inverse spinels $\text{Fe}[\text{TiFe}]_4\text{O}_4$ and $\text{Ga}[\text{FeGa}]_4\text{O}_4$ and the normal spinel $\text{Ge}[\text{Fe}_2]_4\text{O}_4$ and found a quadrupole splitting in all the three cases. The Mössbauer studies of Fe^{2+} in FeAl_2O_4 and $\text{Mg}_{0.98}\text{Fe}_{0.2}\text{AlO}_4$ were undertaken by Ono et al.⁸³. The observed quadrupole splitting is in agreement with the results of Rossiter⁷⁷ but in disagreement with the results of Mizoguchi and Tanaka⁷⁶. Ono and his coworkers⁸⁴ also studied the Mössbauer spectrum of natural spinel MgAl_2O_4 containing 2.4% Fe^{2+} ions. The observed quadrupole splitting was attributed to the field of symmetry lower than cubic. Shtrikman et al.⁸⁵ studied the Mössbauer spectra of GeFe_2O_4 at different temperatures and calculated the value of trigonal field at B sites in GeFe_2O_4 .

Bauminger et al.⁴⁸ and Ito et al.⁸⁶ and Ono et al.⁸⁷ studied the low temperature order-disorder transition in magnetite (Fe_3O_4). The effective magnetic fields (H_{eff}) at B sites due to Fe^{3+} and Fe^{2+} ions were found to be 510 koe and 450 koe respectively. The values of H_{eff} due to Fe^{3+} ions at A and B sites were 495 ± 20 koe and 470 ± 20 koe and the value of e^2qQ to be 0.2 mm/sec and 0.1 mm/sec respectively. Several workers^{48,88,89,90} have studied the Mössbauer spectrum of NiFe_2O_4 . H_{eff} was found to be 475 ± 20 koe at liquid air temperature by Bauminger et al.⁴⁸ and Wertheim⁸⁸ and 532 ± 20 koe at 0°K by Hryniewicz et al.⁹⁰. The isomer shift of 0.50 mm/sec with respect to stainless steel indicates that the iron is present in trivalent state. The absence of quadrupole splitting was attributed to the cubic symmetry of the Fe^{3+} ion in NiFe_2O_4 by Hryniewicz et al.⁹⁰

Kelly et al.⁴⁹ studied the Mössbauer spectra of lithium ferrite ($\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$) in the ordered and disordered states. The effective magnetic fields at Fe^{57} nucleus in the two states were found to be 508 ± 20 kOe and 510 ± 20 kOe respectively. Ritter⁹¹ found H_{eff} at A and B sites in $\text{Li}_{0.5}^{1+}$, $\text{Fe}_{1.3}^{3+}$, $\text{Cr}_{1.2}^{3+} \text{O}_4$ to have the same value of 504 ± 4 kOe at 88°K. The work of Hryniewicz et al.⁹⁰ and Dezsai et al.⁹² and Schuele et al.⁹³ showed that the Mössbauer parameters for CoFe_2O_4 in its ferrimagnetic state are similar to those of NiFe_2O_4 . In the paramagnetic state, a well defined doublet was observed in the Mössbauer spectrum, indicating the presence of quadrupole interaction, while in the ferrimagnetic state, the symmetric hyperfine splitting indicated the absence of quadrupole interaction. Hryniewicz et al.⁹⁰ and Tanaka et al.⁷⁵ studied the Mössbauer spectrum of MnFe_2O_4 in the ferrimagnetic state and found an effective magnetic field of 516 ± 20 kOe at 0°K with no quadrupole splitting. Tanaka et al.⁷⁵ studied the Mössbauer spectrum of MnFe_2O_4 in the paramagnetic state and observed a quadrupole splitting. Belov et al.⁹⁴ studied the Mössbauer effect in Mn- and Mg-Mn-ferrites. It was shown that the s electrons density at the nucleus is same in all the compounds studied by them. Evans and Hafner⁹⁵ studied the Mössbauer spectrum of CuFe_2O_4 in tetragonal and cubic phases. The effective magnetic fields at A and B sites were found to be 478 ± 5 kOe and 514 ± 5 kOe respectively in the tetragonal phase. In the cubic phase the hyperfine spectra due to A and B sites were not resolvable.

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CHAPTER II

EXPERIMENTAL PROCEDURE

MÖSSBAUER SPECTROMETER

Different types of velocity drives may be used to provide a well defined relative velocity between the source and the absorber. These may be divided into two main classes.

(i) A purely mechanical drive in which the moving part follows the motion of the revolving cam which is shaped to give a desired linear displacement.

(ii) An electromechanical drive in which a transducer, frequently consisting of a loudspeaker system, is fed with a suitable driving voltage. It picks up a signal proportional to the velocity. The Mössbauer spectrum is directly read on a multi-channel pulse height analyser.

The results reported in this thesis have been taken on a velocity drive of type (i).

The main components of the Mössbauer spectrometer are

- 1) A velocity drive to provide a relative velocity between the source and the absorber.
- 2) A radioactive source emitting the gamma rays.
- 3) An absorber containing the isotope under study.
- 4) A gamma ray detecting system.

Velocity Spectrometer

Fig. (12) shows the schematic diagram of the apparatus. A 15 W synchronous motor with reduction gear system can give any of the three speeds of 3, 30 and 300 r.p.m. It was mounted on a vibration-proof separate table. The cam with its follower and the

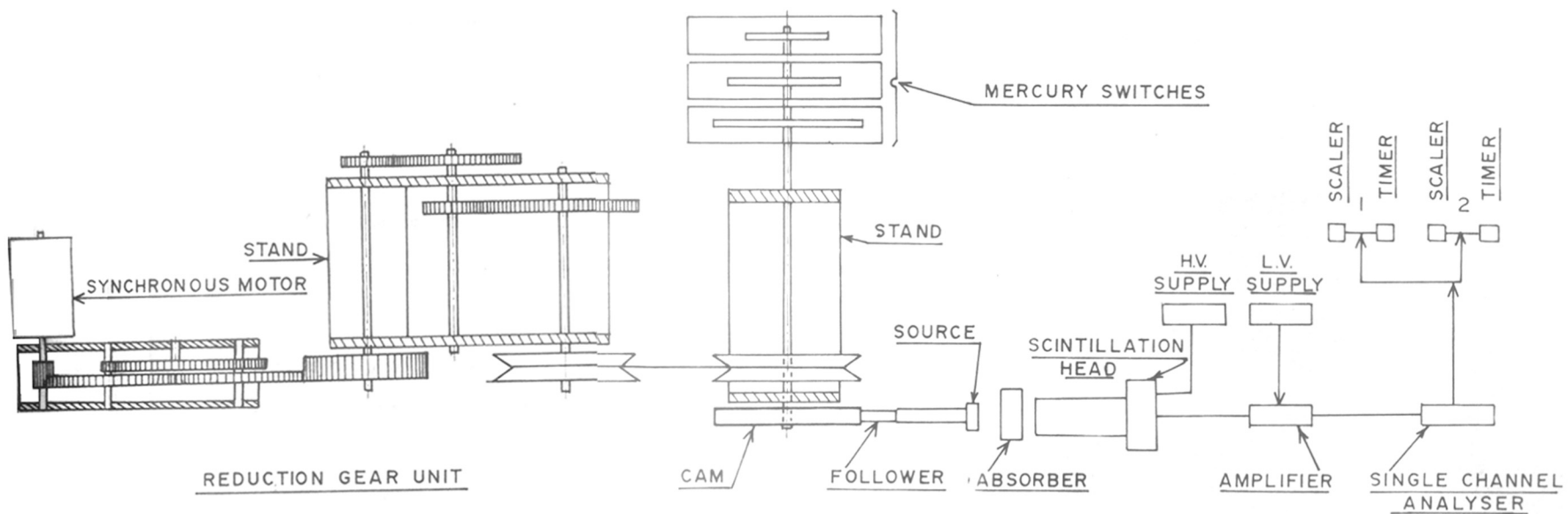


Fig. 12: SCHEMATIC DIAGRAM OF THE MÖSSBAUER APPARATUS

gamma ray detector were fixed on another vibration-proof table in order to avoid the vibrations from the motor. The motor is connected by means of a belt pulley arrangement to a spindle carrying a cam at one end and a set of mercury switches on the other end. Co^{57} source is mounted on the cam follower. The source can be moved with respect to the absorber with velocities up to 3.6 cm/sec, in steps of 0.0036 cm/sec or its multiples, by a suitable change of the combination of the gears.

The gamma rays from Co^{57} are detected by means of a 1 mm thick NaI (Tl activated) crystal coupled to a RCA-6810- A photo-multiplier tube. The output from the detector is fed into a single channel pulse height selector whose window is set on the 14.4 kev photopeak.

The mercury switches are so synchronised that when the source is moving towards the absorber (+ve velocity) or when it is moving away from the absorber (-ve velocity), the output from the pulse-height selector is fed into two different scalers. Two other scalers connected in parallels with the first two and running on a 50-cycles pulse determine the time for which the output is measured. The absorber is mounted between the source and the gamma ray detector.

If it is desired to keep the source stationary and move only the absorber, then absorber is mounted on the cam follower and placed between the source and detector, shown in Fig. (13).

Preparation of the source and absorbers

The source used was Co^{57} on copper backing, 1 mg carrier-free Co^{57} was electroplated onto a spectroscopically pure copper foil 0.001 in thick. It was then annealed in nitrogen atmosphere at 500°C for 1 hour and then in vacuum of 10^{-6} mm Hg at 500°C for another hour. The source was then mounted in a pyrex holder which can be fixed to the cam follower.

The absorbers were prepared by extending the powder

DETECTOR

ABSORBER

* SOURCE

PERSPEX

CAM FOLLOWER

FIG. 13. DIAGRAM FOR THE MOVING ABSORBER

Preparation of the source and absorbers

The source used was Co^{57} on copper backing. 1 mc carrier-free Co^{57} was electroplated onto a spectroscopically pure copper foil 0.05 mm thick. It was then annealed in hydrogen atmosphere at 800°C for 1 hour and then in vacuum of 10^{-6} mm Hg at 800°C for another hour. The source was then mounted in a perspex holder which can be fixed to the cam follower.

The absorbers were prepared by spreading the powder material between two thin aluminium or mica sheets of 1 cm radius sandwiched between two brass rings. The thickness of the absorber was so adjusted that it contained $\approx 8 \text{ mg/cm}^2$ of natural iron or 0.18 mg/cm^2 of Fe^{57} .

Preparation of the CoMnFeO_4 source

200 μc of carrier-free Co^{57} solution in the form of CoCl_2 was added to a powdered sample of CoMnFeO_4 . It was then annealed in air at 950°C for 1 hour, so that Co^{57} forms a part of the lattice of CoMnFeO_4 by diffusion. This sample was then mounted in a brass-holder and used as such as source of Co^{57} .

Preparation of the Enriched $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$

5 mgs of enriched iron ($\approx 92\% \text{ Fe}^{57}$) was dissolved into minimum quantity of concentrated HCl, in an atmosphere of nitrogen gas which was purified free from oxygen. This solution was evaporated to dryness in a paraffin bath maintained at 120°C in order to remove the excess HCl. It was then dissolved in water and then a freshly prepared potassium-cyanide solution was added to it drop by drop

TABLE 9

MÖSSBAUER DATA FOR POTASSIUM FERROCYANIDE ABSORBER AND 310 STAINLESS STEEL FOIL

 ^{57}Co /Cu source at 25°C

Absorber at 25°C	Displacement of the centroid from zero velocity relative to copper backing mm/sec		Displacement of the centroid from zero velocity, relative to stainless steel mm/sec		Line width with respect to copper backing mm/sec.	
	Experi- mental	Litera- ture	Experi- mental	Litera- ture	Experi- mental	Litera- ture
Potassium ferrocyanide powder (64 mg/cm ²)	-0.26±0.04	-0.27 ¹	+0.08±0.04	+0.083 ^{2,3}	0.36±0.04	0.29 ⁴
310-Stainless steel foil (0.002")	-0.32±0.04	-0.34 ⁵	+0.02±0.04	-	0.44±0.04	-

until the precipitate which was formed dissolved in excess of KCN solution. Potassium ferrocyanide was separated from the solution by the addition of excess of absolute alcohol and centrifuging. The residue was dissolved in a minimum quantity of water then reprecipitated by the addition of alcohol. It was dried in a vacuum oven at room temperature.

An absorber of $K_4Fe(CN)_6 \cdot 3H_2O$ was prepared from the above sample so that Fe^{57} thickness was 0.8 mg/cm^2 .

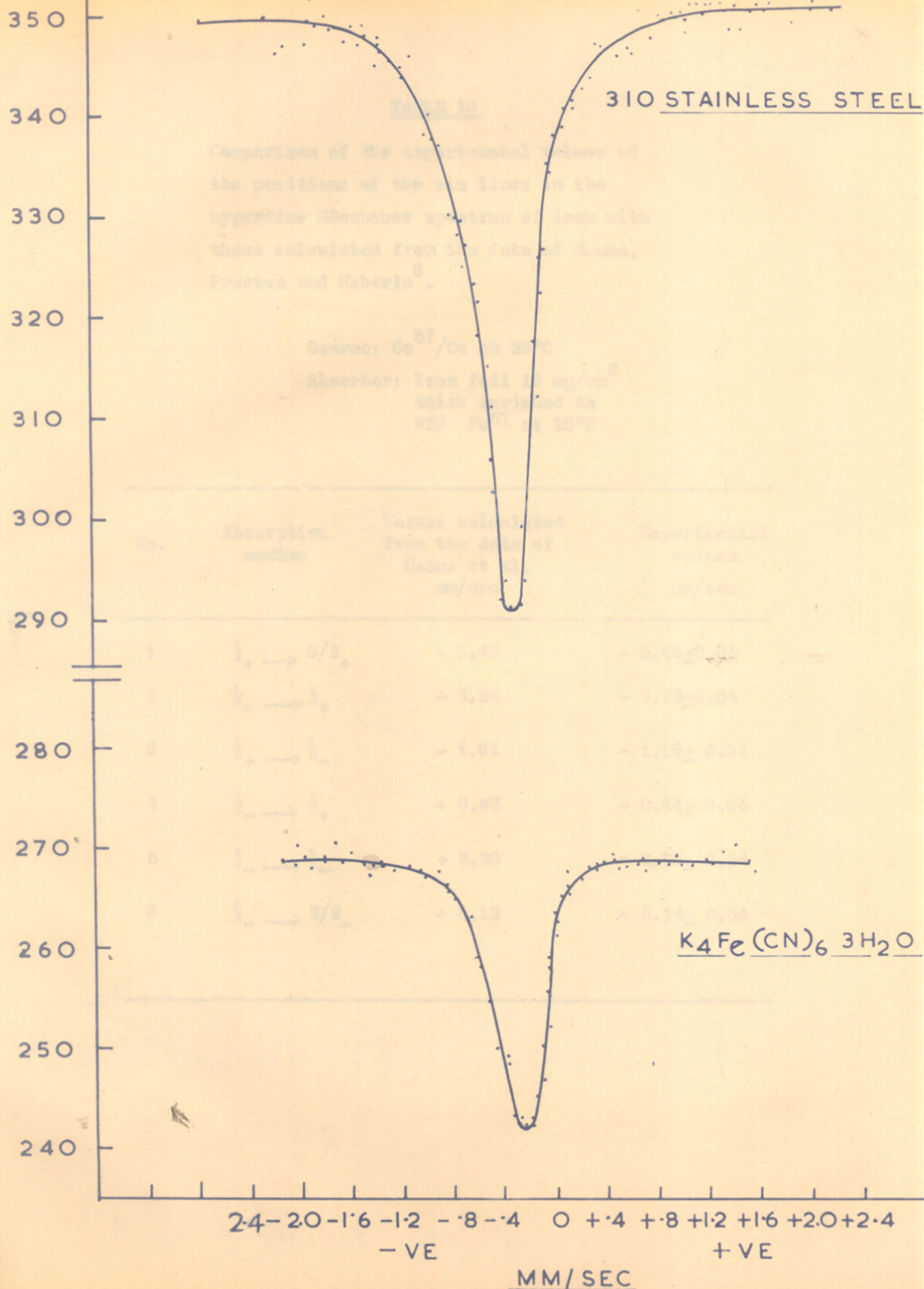
Calibration of the spectrometer

All the gears used in the gear box were calibrated and found to give the experimental value of the speed of rotation within 0.4% of the expected value in every case.

The equipment was standardized by taking the Mössbauer spectra of absorbers made of powdered potassium ferrocyanide and 310-stainless steel foil.

The Mössbauer spectra for these two absorbers were obtained with Co^{57} source on Cu backing. This source gave single line resonance spectra for $K_4Fe(CN)_6 \cdot 3H_2O$ and 310-stainless steel with the centroid shifted to $-0.26 \pm 0.04 \text{ mm/sec}$ and $-0.32 \pm 0.04 \text{ mm/sec}$ respectively, from zero velocity (Fig. 14). These experimental values of the isomer shifts (in Table 9) are in agreement with the available data in literature on potassium ferrocyanide and stainless steel¹ absorbers. The line width for $K_4Fe(CN)_6 \cdot 3H_2O$ absorber (64 mg/cm^2 thick) and stainless steel foil (0.002" thick) was found

COUNTS PER SECOND



MÖSSBAUER SPECTRA OF 310 STAINLESS STEEL FOIL AND $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$
ABSORBER AT 25°C

TABLE 10

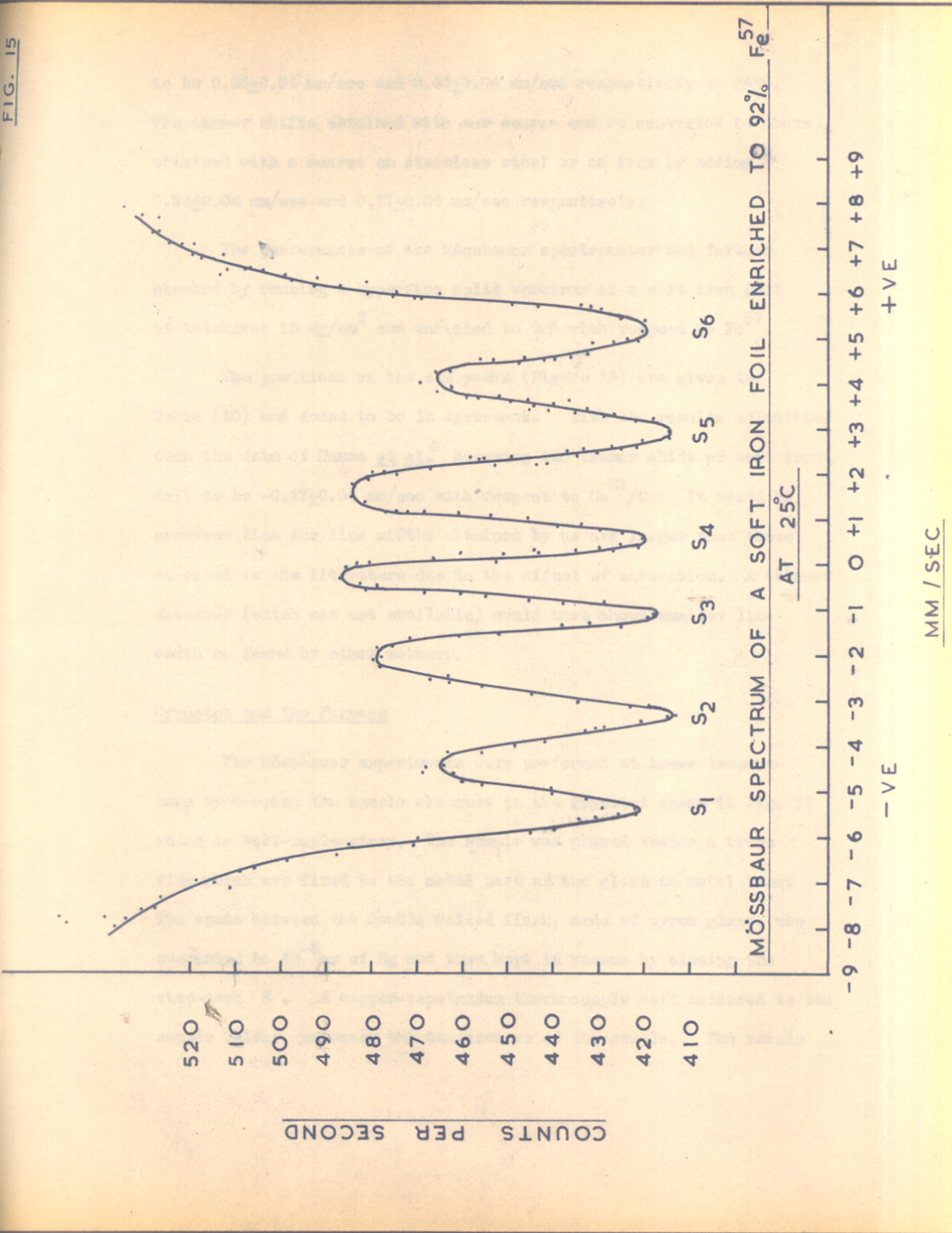
Comparison of the experimental values of the positions of the six lines in the hyperfine Mössbauer spectrum of iron with those calculated from the data of Hanna, Preston and Heberle⁶.

Source: Co⁵⁷/Cu at 25°C

Absorber: Iron foil 19 mg/cm²
thick enriched to
92% Fe⁵⁷ at 25°C

No.	Absorption maxima	Values calculated from the data of Hanna et al. mm/sec	Experimental values mm/sec
1	$\frac{1}{2}_+ \rightarrow 3/2_+$	- 5.47	- 5.46 $\pm$ 0.04
2	$\frac{1}{2}_+ \rightarrow \frac{1}{2}_+$	- 3.24	- 3.26 $\pm$ 0.04
3	$\frac{1}{2}_+ \rightarrow \frac{1}{2}_-$	- 1.01	- 1.06 $\pm$ 0.04
4	$\frac{1}{2}_- \rightarrow \frac{1}{2}_+$	+ 0.67	+ 0.64 $\pm$ 0.04
5	$\frac{1}{2}_- \rightarrow \frac{1}{2}_-$	+ 2.90	+ 2.90 $\pm$ 0.04
6	$\frac{1}{2}_- \rightarrow 3/2_-$	+ 5.13	+ 5.14 $\pm$ 0.04

FIG. 15



to be 0.36 ± 0.04 mm/sec and 0.44 ± 0.04 mm/sec respectively at 25°C. The isomer shifts obtained with our source can be converted to those obtained with a source on stainless steel or on iron by adding 0.34 ± 0.04 mm/sec and 0.17 ± 0.04 mm/sec respectively.

The performance of the Mössbauer spectrometer was further checked by running a hyperfine split spectrum of a soft iron foil of thickness 19 mg/cm^2 and enriched to 92% with respect to Fe^{57} .

The positions of the six peaks (Figure 15) are given in Table (10) and found to be in agreement. With the results calculated from the data of Hanna *et al.*⁶ assuming the isomer shift of soft iron foil to be -0.17 ± 0.04 mm/sec with respect to Co^{57}/Cu . It would be observed that the line widths obtained by us are larger than those reported in the literature due to the effect of saturation. A thinner absorber (which was not available) would have shown smaller line width as found by other workers.

Cryostat and the Furnace

The Mössbauer experiments were performed at lower temperature by keeping the sample absorber in the cryostat shown in Fig. 16 which is self-explanatory. The sample was placed inside a brass ring which was fixed to the metal part of the glass to metal tube. The space between the double walled flask, made of pyrex glass, was evacuated to 10^{-5} mm of Hg and then kept in vacuum by closing the stop-cock S. A copper-constantan thermocouple soft soldered to the sample holder, measures the temperature of the sample. The sample

CRYOSTAT

THERMO COUPLE

LIQUID NITROGEN

PERSPEX CLAMP

BRASS STAND

B-40 GLASS JOINT

GLASS METAL JOINT

TO VACUUM PUMP

S

BRASS

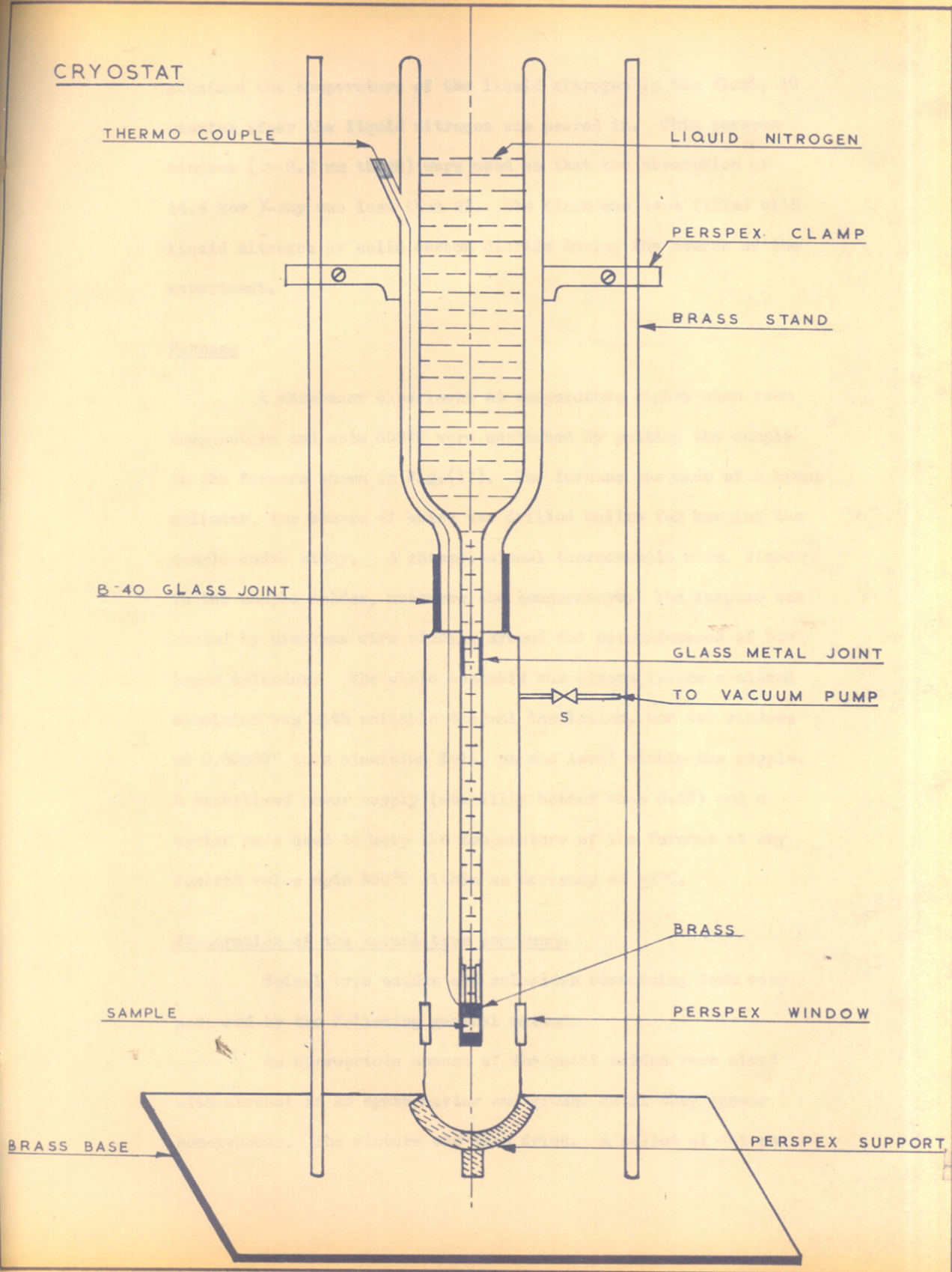
SAMPLE

PERSPEX WINDOW

BRASS BASE

PERSPEX SUPPORT

FIG. 16



attained the temperature of the liquid nitrogen in the flask, 10 minutes after the liquid nitrogen was poured in. Thin perspex windows (≈ 0.2 mm thick) were used so that the absorption of 14.4 keV γ -ray was less than 2%. The flask was kept filled with liquid nitrogen or solid carbon dioxide during the course of the experiment.

Furnace

A Mössbauer experiment at temperature higher than room temperature and upto 600°C were conducted by putting the sample in the furnace shown in Fig.(17). The furnace was made of a brass cylinder, the centre of which was drilled hallow for keeping the sample under study. A chromel-alumel thermocouple wire, fixed to the sample holder, measures the temperature. The furnace was heated by nichrome wire winding around the circumference of the brass cylinder. The whole assembly was placed inside a closed aluminium box with suitable thermal insulation, and two windows of 0.00036" thin aluminium foil, on the level within the sample. A stabilized power supply (stability better than 0.1%) and a variac were used to keep the temperature of the furnace at any desired value upto 600°C within an accuracy of $\pm 2^\circ\text{C}$.

Preparation of the spinel type compounds

Spinel type oxides and sulphides containing iron were prepared by the following general method.

An appropriate amount of the metal oxides were mixed with alcohol in an agate mortar and ground until they appear homogeneous. The mixture was then dried. A pellet of ≈ 1 cm

FURNACE

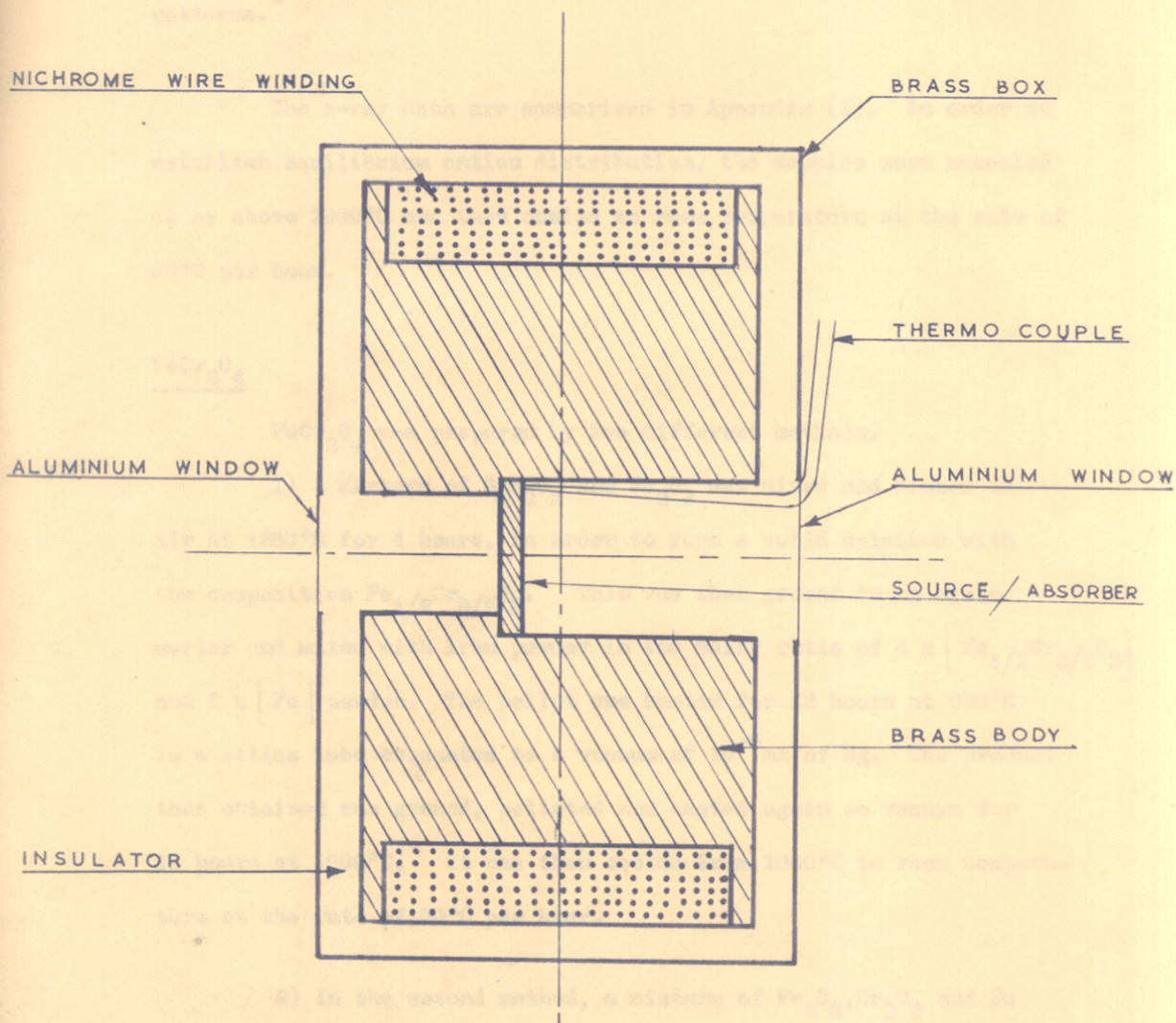


FIG. 17

diameter was prepared from it under a pressure of 3000 to 5000 p.s.i. The pellet was then heated at desired temperature for an appropriate time so that the solid-solid reaction may take place. The formation of the compounds was checked in every case from the x-ray powder patterns.

The x-ray data are summarised in Appendix (1). In order to establish equilibrium cation distribution, the samples were annealed at or above 1000°C and then cooled to room temperature at the rate of 30°C per hour.

FeCr₂O₄

FeCr₂O₄ was prepared by two different methods.

1) A mixture of 3Cr₂O₃ and Fe₂O₃ was mixed and heated in air at 1250°C for 4 hours, in order to form a solid solution with the composition Fe_{1/2}Cr_{3/2}O₃. This was then ground in an agate mortar and mixed with iron powder in the molar ratio of 4 x [Fe_{1/2}Cr_{3/2}O₃] and 1 x [Fe] powder. The pellet was heated for 12 hours at 950°C in a silica tube evacuated to a vacuum of 10⁻⁶ mm of Hg. The product thus obtained was ground, pelleted and heated again in vacuum for 12 hours at 1000°C. It was then cooled from 1000°C to room temperature at the rate of 30°C per hour.

2) In the second method, a mixture of Fe₂O₃, Cr₂O₃ and Fe powder in the ratio of 1:3:1, was ground with alcohol, dried, pelleted and heated at 1000°C in a silica tube evacuated to a pressure of 10⁻⁶ mm of Hg for 18 hours. The sample was reground, repelleted and heated again in vacuum for a further period of 12 hours when a single

phase consisting of FeCr_2O_4 was obtained. The X-ray powder pattern taken on a Mo-K α radiation shows a single phase cubic spinel structure with lattice parameter 'a' = $8.366 \text{ \AA}$ (Table 11) is in good agreement with the reported value of $8.37 \text{ \AA}$ ⁷.

GeFe_2O_4

This ferrite was prepared by heating powdered Fe_2O_3 , GeO_2 and Fe in the ratio of 2:3:2. The mixture was thoroughly ground in the presence of alcohol by an agate mortar and pestle. The mixture was dried, pelleted under a pressure of 3000 p.s.i. The pellet was heated in an evacuated silica tube at 1000°C for 18 hours. The product was recrushed, repelleted and heated once more for 12 hours at same temperature. The material was cooled to room temperature at the rate of 30°C per hour. The X-ray powder pattern taken on a Mo-K α radiation shows a single phase with lattice parameter $a = 8.4106 \text{ \AA}$ (Table 12) in good agreement with the reported value⁸ of $8.411 \text{ \AA}$.

FeCr_2S_4

The sulphochromite FeCr_2S_4 was prepared by heating a mixture of powdered iron, chromium and sulphur in a silica tube evacuated to a pressure of 10^{-6} mm of Hg. The temperature was slowly increased up to 400°C and heated at that temperature for 6 hours. The product which was a solid mass, was ground, repelleted and heated at 850°C for another 12 hours. It was finally ground, pelleted and heated again at 1000°C for 48 hours. The product when examined by X-ray powder pattern showed a single phase cubic spinel structure with

the lattice parameter 'a' equal to $9.983 \text{ \AA}^{\circ}$ (Table 13). This value agrees with that of $9.98 \text{ \AA}^{\circ}$ reported in literature.

FeIn_2S_4

FeIn_2S_4 was prepared by heating iron powder with sulphur powder and small pieces of indium metal in the atomic ratio of 1:4:2 in an evacuated silica tube at 400°C for 48 hours. The product was broken into pieces, ground to fine powder, pelleted and heated at 950°C for 48 hours again to complete the reaction. The value of the 'a' parameter for this cubic spinel was found to be $10.582 \text{ \AA}^{\circ}$ (Table 14) in agreement with reported value of $10.59 \text{ \AA}^{\circ}$.

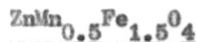
CdFe_2O_4

CdFe_2O_4 was prepared by heating a mixture of Fe_2O_3 and CdO in equimolar ratio. The powder was thoroughly ground in the presence of alcohol by an agate mortar and pestle. The mixture was dried and pelleted under a pressure of 3000 p.s.i. and heated in air at 1200°C for 12 hours. The product was recrushed, repelleted and heated for another 12 hours at the same temperature. The crystallographic 'a' parameter for this cubic spinel was found to be $8.699 \text{ \AA}^{\circ}$ (Table 15) which is in agreement with the literature value of $8.704 \text{ \AA}^{\circ}$.

ZnFe_2O_4

ZnFe_2O_4 was prepared by heating a equimolar mixture of the powdered Fe_2O_3 and ZnO . The mixture was ground in presence of alcohol, dried, pelleted and heated in air at 1200°C for 12 hours. The resulting product was recrushed, repelleted and heated once more at 1200°C for the same period. The X-ray powder pattern

indicated the presence of a single phase cubic spinel, the 'a' parameter of which was found to be $8.411\overset{\circ}{\text{\AA}}$ (Table 16) in agreement with the reported value of $8.416\overset{\circ}{\text{\AA}}$ in literature¹¹.



The ferrite with the above composition was prepared by heating a pellet made of an intimate mixture of ZnO, MnCO₃ and Fe₂O₃ in the ratio of 4:2:3, at 1200°C for 6 hours in air. The product thus obtained was recrushed, repelleted and heated at the same temperature for another 4 hours. It was then cooled to room temperature at the rate of 30°C per hour. The 'a' parameter of the cubic spinel was found to be $8.507\overset{\circ}{\text{\AA}}$ (Table 17) which is in agreement with the literature value¹².



It was prepared by heating in air at 1200°C a mixture of the powdered ZnO, MnCO₃ and Fe₂O₃ in the ratio of 2:2:1 for 12 hours. The spinel has tetragonal structure. The value of c/a was found to be equal to 1.057 (Table 18).



Specimen of CoMnFeO₄ was synthesized by firing a mixture of reagent grade CoCO₃, MnCO₃ and Fe₂O₃ in the ratio of 2:2:1 in air at 1200°C for 6 hours. A further heating for 4 hours gave the single phase cubic spinel with 'a' parameter equal to $8.409\overset{\circ}{\text{\AA}}$ (Table 19) in agreement with the literature value¹².

FeCrNiO₄ and FeMnCuO₄

FeCrNiO₄ was prepared by heating a powdered mixture of NiO, Cr₂O₃ and Fe₂O₃ enriched to 92% Fe⁵⁷, in the ratio of 2:1:1, at 1300°C for 24 hours.

FeMnCuO₄ was made by heating a powdered mixture of CuO, Mn₂O₃ and Fe₂O₃ in the ratio of 2:1:1 at 950°C for 55 hours.

The values of the 'a' parameters for FeCrNiO₄ and FeMnCuO₄ were found to be 8.299 Å and 8.336 Å respectively (Tables 20 and 21) and are comparable to earlier reported values^{13,14}.

FeAl₂O₄

FeAl₂O₄ was prepared in two ways.

1) A solid solution with composition Fe_{1/2}Al_{3/2}O₃ was prepared by heating 3 parts of Al₂O₃ with 1 part of Fe₂O₃. This solid solution was mixed with one part of Fe powder and heated.

2) An intimate mixture of Fe₂O₃, Al₂O₃ and Fe powder was heated.

Pellets were prepared for both the above samples and then heated in an atmosphere of a mixture of equimolar H₂ and CO₂ gases at 1300°C for 4 hours. The samples were ground, pelleted and then reheated for the same period at 1300°C. The samples were then sealed in separate evacuated silica tubes, annealed at 1000°C for 4 hours and cooled to room temperature at the rate of 30°C/hour to establish equilibrium cation distribution. The value of crystallographic 'a' parameter for both the samples was found to be 8.096 Å (Table 22). This may be compared with the earlier

reported values 8.10 ± 0.002^{15} , 8.125 ± 0.002^{16} and 8.14 ± 0.001^{17} .

X-Ray Analysis

X-ray powder patterns were taken on a Debye-Scherrer cameras having diameters 57.30 mm and 140.0 mm and Mo-K α ($\lambda = 0.709 \text{ \AA}$) radiation filtered through zirconium foil. The θ values were computed from the measured distances between the various diffraction lines. The interplanar spacings 'd' were obtained from the tables¹⁸ for the conversion of X-ray diffraction angles to interplanar spacings. For cubic spinels, the lattice parameter 'a' was calculated for different hkl indices from the equation

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \dots \dots \dots (1)$$

For tetragonal spinels, the 'a' and 'c' parameters were calculated from the following formula

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad \dots \dots \dots (2)$$

by the method of successive refinement. For convenience of comparison with a true cubic spinel, the tetragonal cells have been converted into bigger unit cells with $c' = c$ and $a' = a\sqrt{2}$.

X-Ray intensity calculations from powder pattern of FeAl_2O_4

X-Ray intensity calculations were carried out by means of the formula

$$I_{hkl} = |F_{hkl}|^2 \cdot n \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \dots \dots \dots (3)$$

where F_{hkl} is the structure factor, n, the number of families of

planes with the same spacing d_{hkl} (multiplicity factor) and the term within the brackets is the combined Lorentz and polarization factor for each reflections.

The effects of the absorption factor and the temperature on the X-ray intensity are small. These factors act in opposite directions¹⁹ for large value of θ , and hence have not been considered here. The reliability factor R, was defined by means of the equation

$$R = \frac{\sum |I_{cal} - I_{obs}|}{\sum |I_{obs}|} \dots \dots (4)$$

These factors were calculated for different degree of inversion (χ) of the spinel, viz. $\chi = 0.15, 0.20, 0.25$ and 0.30 (Table 23).

The intensities of the reflections were recorded by the "Lirepho 2" photoelectric recording photometer. The areas under the recorded peaks were determined and their values are given in Table (23) relative to the area under the peak for 311 reflection, which is taken as 100.

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CHAPTER III

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The identification of cation oxidation state and the site distribution in mixed oxide and sulphide systems is difficult if the cations exhibit variable valency and can occupy more than one non-equivalent site. When the metal ions can occur in different state of valencies the chemical analysis can only give the average state of valency. In several cases, e.g. in spinels containing a number of metal ions of the first transition series, the ionic distribution cannot be determined by x-rays unambiguously in view of the small differences in their scattering power. In such cases, the Mössbauer effect studies may be used to identify the cation oxidation state and the site distribution^{1,2}. Several investigators have studied the Mössbauer spectra of different spinel type compounds and have obtained a great deal of information (cf. section on "Literature Review" in Chapter I) which otherwise would not be possible to obtain by other methods. In order to correctly interpret the Mössbauer spectra of spinel type compounds containing cations of variable valency and capable of being present at both the available sites, it is desirable to first study the Mössbauer spectra of these spinel type compounds which contain cations in a known and fixed oxidation state and at only one of the two possible sites at a time. For Mössbauer studies, we have therefore, prepared a number of model compounds (Table 24) with the spinel structure containing iron such that each one of them

TABLE 24

CATION DISTRIBUTION IN MODEL CUBIC SPINEL TYPE COMPOUNDS

Spinel	Cation	Cation distribution	Site symmetry iron	Reference
FeCr_2O_4	Fe^{2+}	$\text{Fe}^{2+} \left[\text{Cr}^{3+}_2 \right] \text{O}_4$	Tetrahedral	3
FeCr_2S_4	Fe^{2+}	$\text{Fe}^{2+} \left[\text{Cr}^{3+}_2 \right] \text{S}_4$	Tetrahedral	6,15
GeFe_2O_4	Fe^{2+}	$\text{Ge}^{4+} \left[\text{Fe}^{2+}_2 \right] \text{O}_4$	Octahedral	18
FeIn_2S_4	Fe^{2+}	$\text{In}^{3+} \left[\text{Fe}^{2+} \text{In}^{3+} \right] \text{S}_4$	Octahedral	23
CdFe_2O_4	Fe^{3+}	$\text{Cd}^{2+} \left[\text{Fe}^{3+}_2 \right] \text{O}_4$	Octahedral	24
ZnFe_2O_4	Fe^{3+}	$\text{Zn}^{2+} \left[\text{Fe}^{3+}_2 \right] \text{O}_4$	Octahedral	25,26
FeCrNiO_4	Fe^{3+}	$\text{Fe}^{3+} \left[\text{Cr}^{3+} \text{Ni}^{2+} \right] \text{O}_4$	Tetrahedral	35,36
FeMnCuO_4	Fe^{3+}	$\text{Fe}^{3+} \left[\text{Mn}^{3+} \text{Cu}^{2+} \right] \text{O}_4$	Tetrahedral	37

either contains a Fe^{2+} or Fe^{3+} ion and at only one of the two sites, viz. tetrahedral (A) or octahedral (B) site.

In part (1) we discuss the Mössbauer spectra of the spinels containing Fe^{2+} ions, while in part (2) we shall discuss the Mössbauer spectra of spinels containing only Fe^{3+} ions. On the basis of the results obtained on these model compounds we have attempted to identify the site distribution in FeAl_2O_4 in which iron is present at both the tetrahedral and octahedral sites. The cation distribution have also been determined from the intensity calculation of the various reflections in the x-ray powder pattern of this spinel. The results obtained by two different methods have been found to be in agreement. These are discussed in part (3). Part (4) deals with a study of the charge distribution in the mixed spinels $\text{ZnMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$, ZnMnFeO_4 and CoMnFeO_4 where the metal ions Fe, Co and Mn can exist in a number of oxidation states.

Part (1)

(a) Fe^{2+} ions at the tetrahedral (A) sites: $\text{Fe}[\text{Cr}_2]_0\text{O}_4$ & $\text{Fe}[\text{Cr}_2]_S\text{O}_4$

(A) The Mössbauer spectra of ferrous chromite $\text{Fe}[\text{Cr}_2]_0\text{O}_4$:-

$\text{Fe}[\text{Cr}_2]_0\text{O}_4$ is a normal cubic spinel at room temperature³ and therefore all the Fe^{2+} ions are present at the tetrahedral (A) sites and all the Cr^{3+} ions are present at the octahedral (B) sites. The u parameter is reported to be 0.388^{4,5}. It is paramagnetic at room temperature and its Curie temperature has been found to be $90 \pm 5^\circ\text{K}$ ⁶. X-ray diffraction studies have

shown that $\text{Fe}[\text{Cr}_2]_4\text{O}_4$ undergoes tetragonal distortion at temperature below -80°C ³ and the degree of distortion ($c/a < 1$) increases with the decrease of temperature (Fig.18). This distortion has been attributed to cooperative Jahn-Teller Effect³.

The Mössbauer spectra of this sample were obtained at different temperatures from -194°C to 150°C , and results are summarised in Table (25). The spectrum of $\text{Fe}[\text{Cr}_2]_4\text{O}_4$ at room temperature (Fig.19) consists of a single resonance peak with an isomer shift of 0.96 ± 0.04 mm/sec characteristic of high spin Fe^{2+} compounds. This value of isomer shift also agrees with the value of 0.91 ± 0.06 mm/sec at 295°K , reported by Rossiter⁷ and is nearly equal to the isomer shifts obtained for other cubic spinels $\text{Fe}[\text{V}_2]_4\text{O}_4$ ⁷ and FeAl_2O_4 ⁸ containing Fe^{2+} ions at (A) sites only. Since the tetrahedral site in the spinel structure has a cubic point symmetry, one would expect the Mössbauer spectrum of $\text{Fe}[\text{Cr}_2]_4\text{O}_4$ at room temperature to a single line spectrum. However, at room temperature, the line-width observed by us^{9,10} and also by Rossiter⁷ is ≈ 1 mm/sec. This value is an order of magnitude larger than that expected. Rossiter attributed this large line width to the presence of $\approx 20\%$ unreacted oxide in his compound. However, the X-ray diffraction pattern of our sample showed no lines other than those of the spinel and hence the large line width at room temperature is due to some other reason. The line width decreased to 0.80 ± 0.04 mm/sec when the absorber was heated to 100°C and thereafter it remains constant up to 150°C .

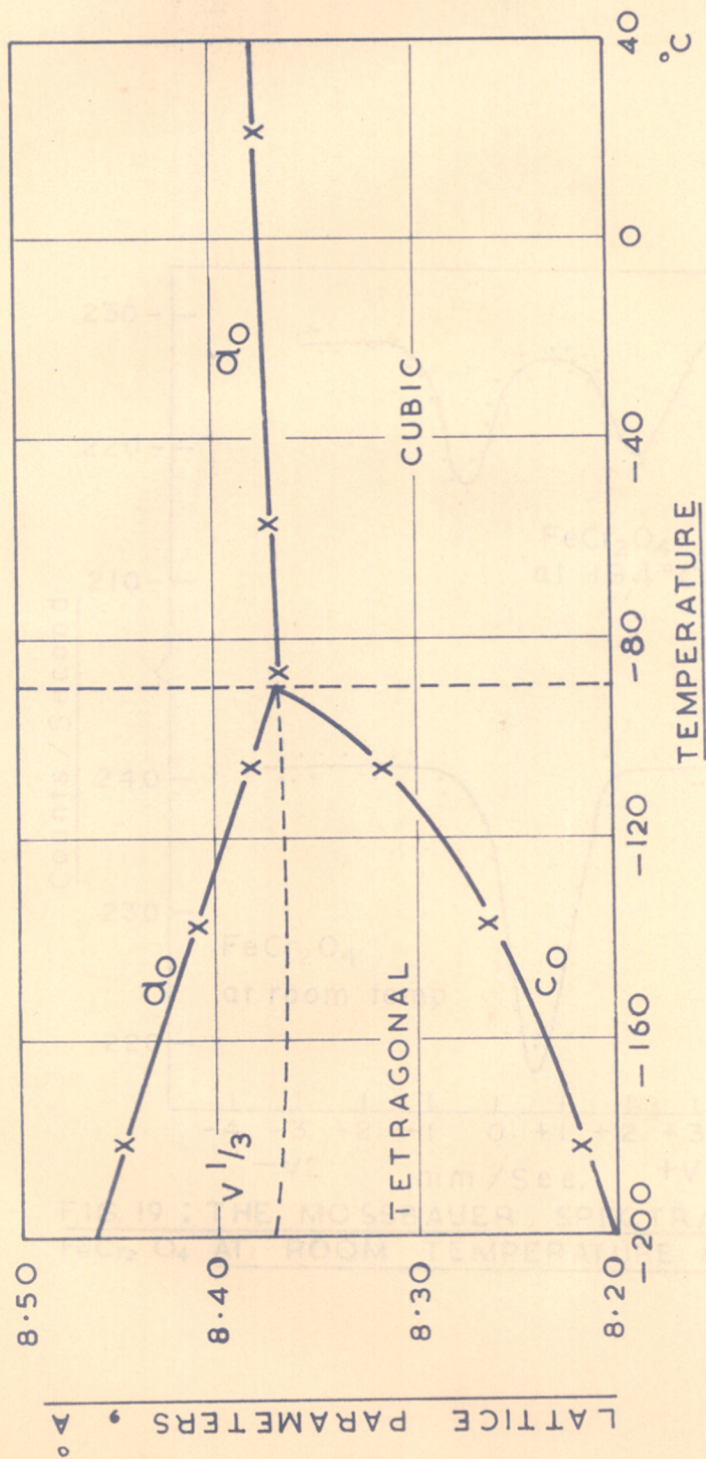


FIG. 18 : LATTICE PARAMETERS OF FeCr_2O_4

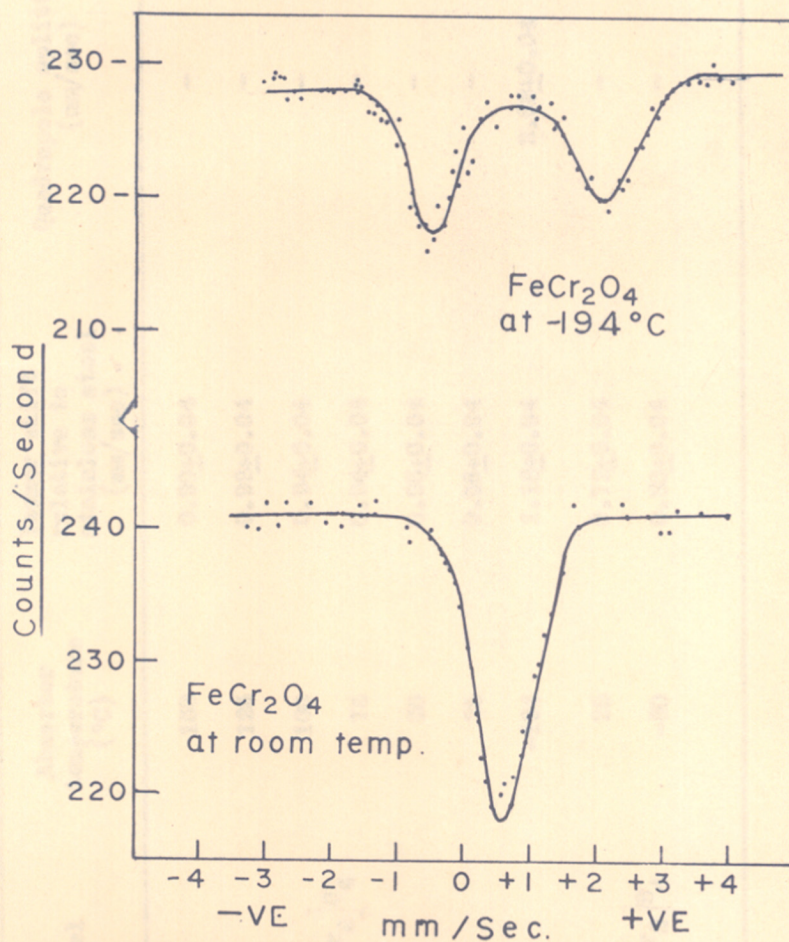


FIG. 19 : THE MOSSBAUER SPECTRA OF FeCr_2O_4 AT ROOM TEMPERATURE & AT -194°C

TABLE 25

THE MOSSBAUER PARAMETERS FOR FeCr_2O_4 AND FeCr_2S_4 (Co⁵⁷/Cu source at 25°C)

Spinel	Absorber temperature (°C)	Isomer shift relative to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)	Line width (mm/sec)
$\text{Fe}[\text{Cr}_2]_0\text{O}_4$	150	0.90 ± 0.04	-	0.80 ± 0.04
	125	0.92 ± 0.04	-	0.80 ± 0.04
	100	0.94 ± 0.04	-	0.82 ± 0.04
	75	0.94 ± 0.04	-	0.88 ± 0.04
	50	0.95 ± 0.04	-	0.94 ± 0.04
	25	0.96 ± 0.04	-	1.04 ± 0.04
	-194	1.18 ± 0.04	2.68 ± 0.04	-
$\text{Fe}[\text{Cr}_2]_S\text{S}_4$	25	0.72 ± 0.04	-	0.48 ± 0.04
	-80	0.80 ± 0.04	-	0.44 ± 0.04

It therefore indicates that the observed large line width at room temperature is due to the presence of quadrupole splitting.

It therefore shows that the degeneracy of $d_{x^2-y^2}^2$ and d_z^2 states is lifted due to a local distortion around the A sites. The population of these two levels (Fig.20) would be determined by the Boltzmann factor, $\exp(-W/kT)$, where W is the energy separation between the $d_{x^2-y^2}^2$ and d_z^2 states. The increase of temperature either removes the distortion or brings about an equal population of the two e states if the energy separation W is small. The charge distribution would then have cubic symmetry and hence the electric field gradient (EFG) at the Fe^{2+} nucleus would be zero. Such a local distortion at room temperature around the A sites was not detected by x-ray diffraction studies since it can observe only the effects of long range order or disorder. Subsequent to our work, Tanaka et al¹¹ have also confirmed by Mössbauer studies the distortion of tetrahedral symmetry around A site in $Fe[Cr_2]O_4$ above the transition temperature at which the tetragonal distortion has been reported by Francombe³ on the basis of x-ray diffraction studies. Tanaka et al. have explained this result on the basis of a model in which Fe^{2+} ion is present in a tetragonal symmetry even above the distortion temperature. However, the direction of its tetragonal axis reorients dynamically with a frequency through the three equivalent axes x, y and z maintaining the mean cubic structure of the whole crystal as determined by X-ray diffraction. The principal axis of the EFG at the nucleus changes its direction with a frequency ν_R , given by the equation

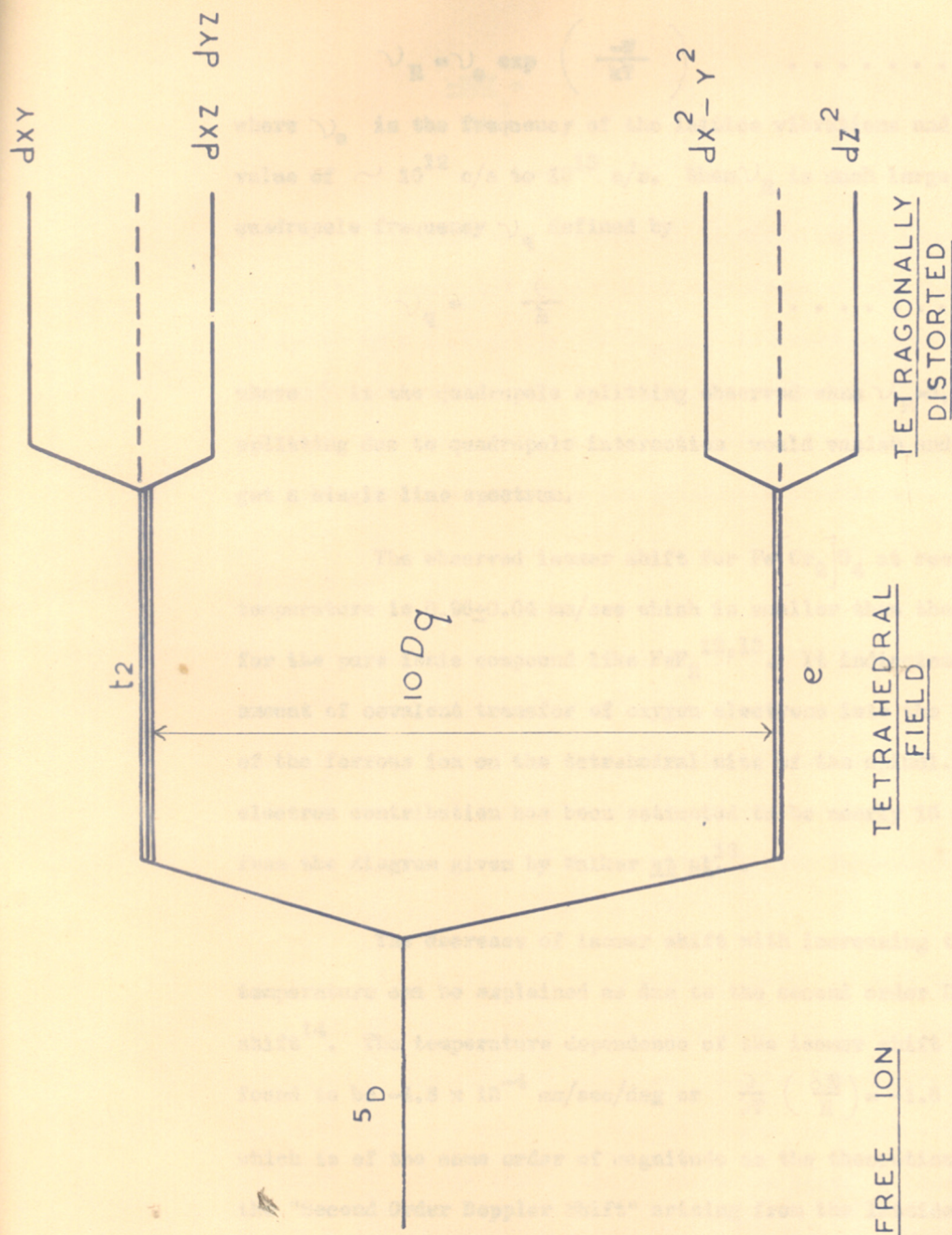


FIG. 20 - SPLITTING OF d ORBITAL ENERGY LEVELS IN A
REGULAR TETRAHEDRAL FIELD AND IN TETRAHEDRALLY
DISTORTED FIELD WITH $C/q < 1$

$$\nu_R = \nu_0 \exp \left(\frac{-W}{kT} \right) \dots \dots \dots (1)$$

where ν_0 is the frequency of the lattice vibrations and has the value of $\sim 10^{12}$ c/s to 10^{13} c/s. When ν_R is much larger than the quadrupole frequency ν_q defined by

$$\nu_q = \frac{\epsilon}{h} \dots \dots \dots (2)$$

where ϵ is the quadrupole splitting observed when $\nu_R=0$, the splitting due to quadrupole interaction would vanish and one would get a single line spectrum.

The observed isomer shift for $\text{Fe}[\text{Cr}_2]_{0.4}$ at room temperature is 0.96 ± 0.04 mm/sec which is smaller than that found for the pure ionic compound like $\text{FeF}_2^{12,13}$. It indicates a small amount of covalent transfer of oxygen electrons into the 4s orbitals of the ferrous ion on the tetrahedral site of the spinel. The 4s electron contribution has been estimated to be nearly 15 per cent from the diagram given by Walker et al.¹³.

The decrease of isomer shift with increasing the temperature can be explained as due to the second order Doppler shift¹⁴. The temperature dependence of the isomer shift was found to be -4.8×10^{-4} mm/sec/deg or $\frac{\partial}{\partial T} \left(\frac{\delta E}{E} \right) = -1.6 \times 10^{-15}/\text{deg}$ which is of the same order of magnitude as the theoretical value of the "Second Order Doppler Shift" arising from the lattice vibrations. If we take specific heat at constant volume $C_v = 3R$ then the temperature coefficient must approach the theoretical limit:

$$\frac{-3kT}{2Mc^2} = -\frac{3}{2} \frac{C_L}{Mc^2}$$

$$= -2.44 \times 10^{-15} / \text{deg K}$$

The Mössbauer spectrum at liquid nitrogen temperature shows a well separated doublet with a quadrupole splitting of 2.68 ± 0.04 mm/sec (Fig.19). $\text{Fe}[\text{Cr}_2]_0\text{S}_4$ is known to undergo tetragonal distortion³ due to cooperative Jahn-Teller Effect below -80°C . This would produce a net EFG at Fe^{2+} ion nucleus and hence would give rise to the quadrupole interaction.

$\text{Fe}[\text{Cr}_2]\text{S}_4$:-

$\text{Fe}[\text{Cr}_2]\text{S}_4$ is a "normal" cubic spinel at room temperature^{6,15}, therefore all the Fe^{2+} ions are present at the (A) sites and all the Cr^{3+} ions are present at the (B) sites. The neutron diffraction data¹⁶ also show that the degree of inversion for $\text{Fe}[\text{Cr}_2]\text{S}_4$ is zero. It is paramagnetic at room temperature and becomes ferrimagnetic below 195°K ^{6,17}.

In a perfectly tetrahedrally symmetric environment of Fe^{2+} ion, the two e_g states are degenerate, and hence equally populated by the sixth d electron. Such an equal mixture of the two states has cubic symmetry and hence the Mössbauer spectrum of $\text{Fe}[\text{Cr}_2]\text{S}_4$ should show a single resonance line. It does show a single line Mössbauer spectrum Fig. (21) with an isomer shift of 0.72 ± 0.04 mm/sec with respect to stainless steel at 25°C .

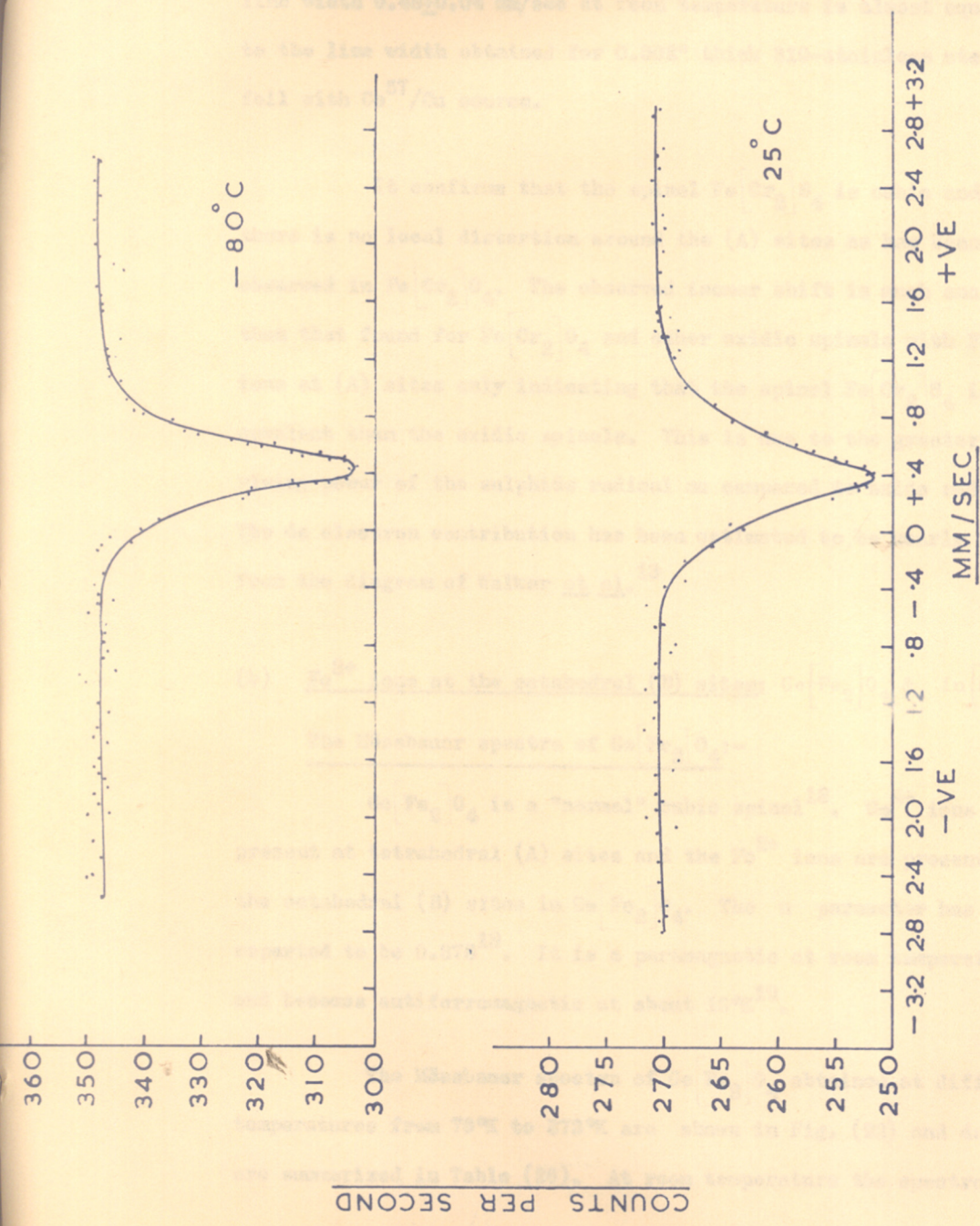


FIG. 21: MÖSSBAUER SPECTRA OF FeCr_2S_4 AT 25°C & -80°C

The Mössbauer spectrum at -80°C is shown in Fig. (21) and the Mössbauer parameters are summarized in Table (25). The observed line width 0.48 ± 0.04 mm/sec at room temperature is almost equal to the line width obtained for 0.002" thick 310-stainless steel foil with Co^{57}/Cu source.

It confirms that the spinel $\text{Fe}[\text{Cr}_2]\text{S}_4$ is cubic and there is no local distortion around the (A) sites as has been observed in $\text{Fe}[\text{Cr}_2]\text{O}_4$. The observed isomer shift is much smaller than that found for $\text{Fe}[\text{Cr}_2]\text{O}_4$ and other oxidic spinels with Fe^{2+} ions at (A) sites only indicating that the spinel $\text{Fe}[\text{Cr}_2]\text{S}_4$ is more covalent than the oxidic spinels. This is due to the greater polarising power of the sulphide radical as compared to oxide radical. The 4s electron contribution has been estimated to be nearly 25% from the diagram of Walker *et al.*¹³

(b) Fe^{2+} ions at the octahedral (B) sites: $\text{Ge}[\text{Fe}_2]\text{O}_4$ & $\text{In}[\text{FeIn}]\text{S}_4$

The Mössbauer spectra of $\text{Ge}[\text{Fe}_2]\text{O}_4$:-

$\text{Ge}[\text{Fe}_2]\text{O}_4$ is a "normal" cubic spinel¹⁸. Ge^{4+} ions are present at tetrahedral (A) sites and the Fe^{2+} ions are present at the octahedral (B) sites in $\text{Ge}[\text{Fe}_2]\text{O}_4$. The u parameter has been reported to be 0.375 ¹⁸. It is a paramagnetic at room temperature and becomes antiferromagnetic at about 10°K ¹⁹.

The Mössbauer spectra of $\text{Ge}[\text{Fe}_2]\text{O}_4$ obtained at different temperatures from 79°K to 373°K are shown in Fig. (22) and data are summarized in Table (26). At room temperature the spectrum

COUNTS PER SECOND

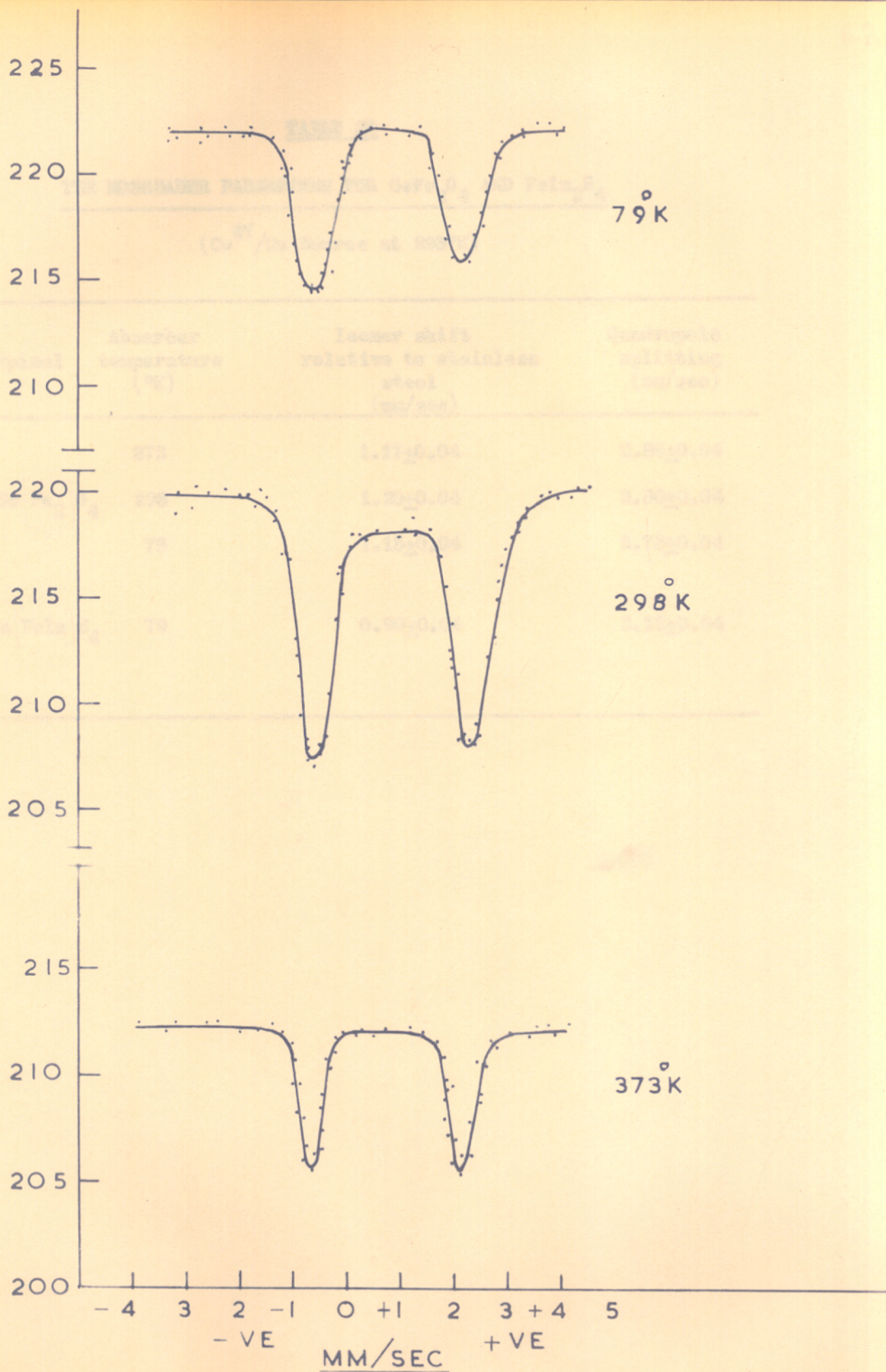


FIG. 22: THE MOSSBAUER SPECTRA OF GeFe_2O_4 AT DIFFERENT TEMPERATURES

TABLE 26

THE MOSSBAUER PARAMETERS FOR GeFe_2O_4 AND FeIn_2S_4 (Co⁵⁷/Cu Source at 298°K)

Spinel	Absorber temperature (°K)	Isomer shift relative to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)
$\text{Ge}[\text{Fe}_2]\text{O}_4$	373	1.17 ± 0.04	2.86 ± 0.04
	298	1.20 ± 0.04	2.80 ± 0.04
	79	1.15 ± 0.04	2.78 ± 0.04
$\text{In}[\text{FeIn}]\text{S}_4$	79	0.90 ± 0.04	3.12 ± 0.04

consists of a well defined doublet with an isomer shift of 1.20 ± 0.04 mm/sec with respect to stainless steel and a quadrupole splitting of 2.80 ± 0.04 mm/sec or $\frac{e^2 q Q}{2h} = 32.48 \pm 0.46$ Mc/sec. It therefore indicates that there is an electric field gradient at the Fe^{2+} nucleus on the (B) site. This was later confirmed by the work of Rossiter and Shtikman²¹ who also studied the Mössbauer spectra of $\text{Ge}[\text{Fe}_2]_4\text{O}_4$. The value of quadrupole splitting was found to be independent of temperature from 373°K to 79°K.

In an octahedrally symmetric environment the three t_{eg} states are degenerate and hence equally populated by the sixth electron of the d^6 ions. Such a mixture of three states would have cubic symmetry and therefore there would be no electric field gradient (EFG) at the iron nucleus on the (B) site. However our results do show an EFG at the B site. The value of a parameter for $\text{Ge}[\text{Fe}_2]_4\text{O}_4$ is 0.375, the value for an ideal spinel.

Though the six nearest oxygen ions around the B site are in perfect octahedral environment the cubic symmetry of the B site, as pointed out by Smit *et al.*²² is destroyed by the next nearest neighbours which produce a trigonal field at the B site resulting in quadrupole interactions. The trigonal field has its axis in one of the three $\langle 111 \rangle$ directions. It lifts the degeneracy of the triply degenerate t_{2g} states which are split into a lower singlet and upper doublet (Fig. 23). It may be noted that the temperature independent value of the

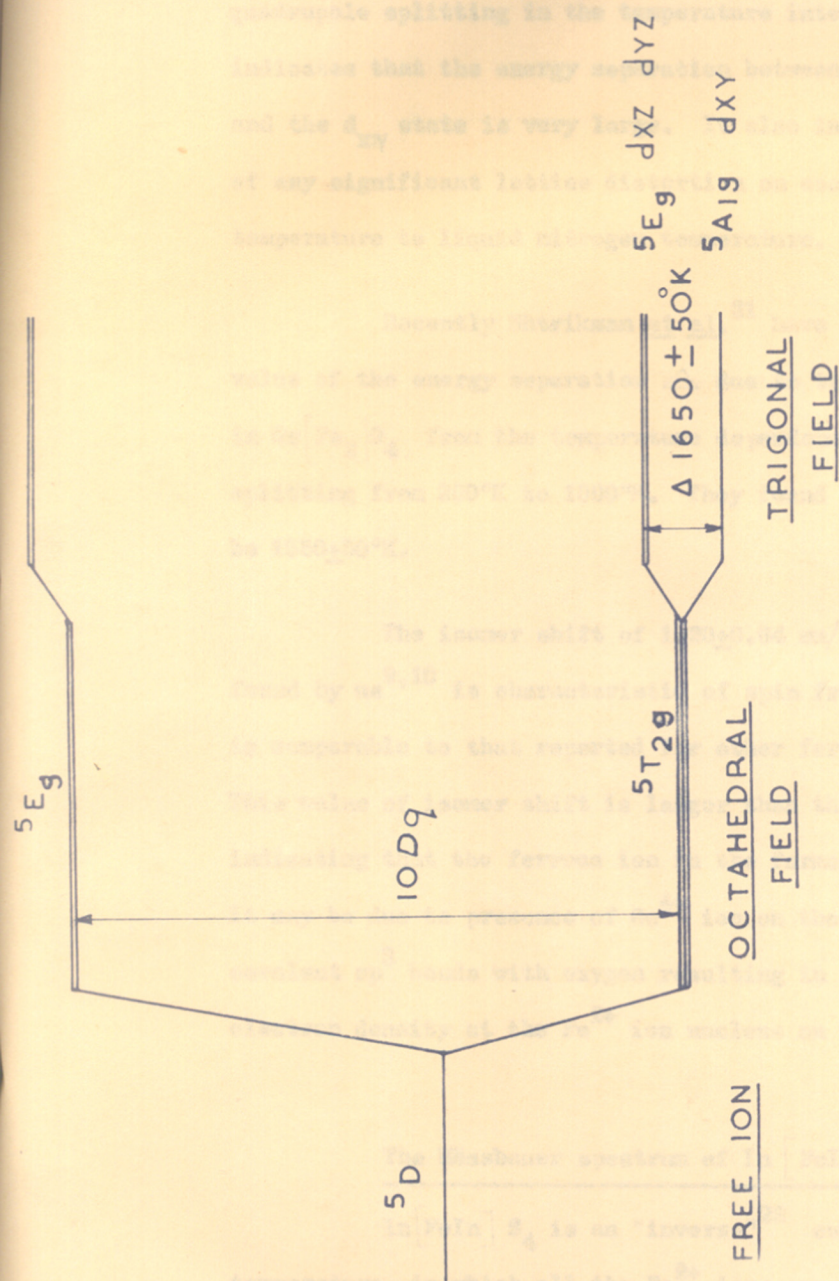


FIG. 23 THE ORBITAL SPLITTING DIAGRAM OF Fe^{2+} IN GeFe_2O_4

quadrupole splitting in the temperature interval 79°K-373°K, indicates that the energy separation between d_{xz} , d_{yz} states and the d_{xy} state is very large. It also indicates the absence of any significant lattice distortion on cooling from room temperature to liquid nitrogen temperature.

Recently Shtrikman et al.²¹ have calculated the value of the energy separation Δ due to the trigonal field in $\text{Ge}[\text{Fe}_2]\text{O}_4$ from the temperature dependence of the quadrupole splitting from 300°K to 1000°K. They found the value of Δ to be $1650 \pm 50^\circ\text{K}$.

The isomer shift of 1.20 ± 0.04 mm/sec for $\text{Ge}[\text{Fe}_2]\text{O}_4$ found by us^{9,10} is characteristic of spin free Fe^{2+} ions and is comparable to that reported for other ferrous compounds^{1,13}. This value of isomer shift is larger than that found for $\text{Fe}[\text{Cr}_2]\text{O}_4$ indicating that the ferrous ion in the former is less covalent. It may be due to presence of Ge^{4+} ion on the A site which forms covalent sp^3 bonds with oxygen resulting in a decrease of the electron density at the Fe^{2+} ion nucleus on the B site.

The Mössbauer spectrum of $\text{In}[\text{FeIn}]\text{S}_4$:-

$\text{In}[\text{FeIn}]\text{S}_4$ is an "inverse"²³ cubic spinel at room temperature, in which all the Fe^{2+} ions are present at the B sites and the In^{3+} ions are equally distributed among the A and B sites. The u parameter has been reported to be 0.387^{23} .

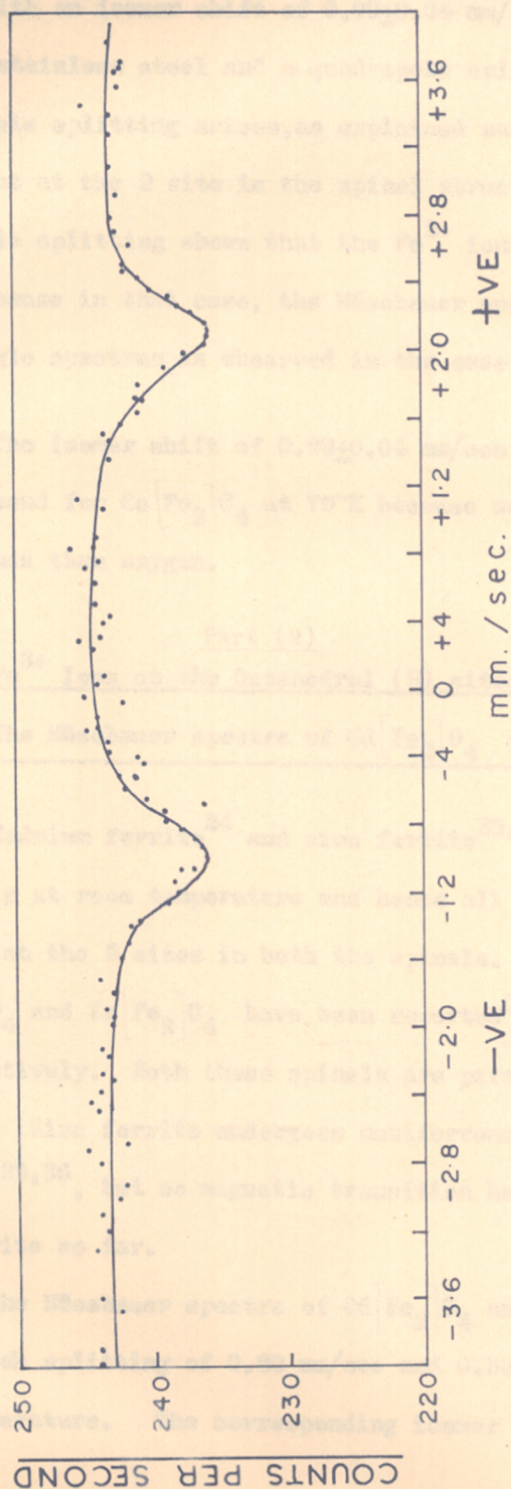


FIG. 24 : THE MÖSSBAUER SPECTRUM OF FeIn_2S_4 AT 79°K

At room temperature, $\text{In}[\text{FeIn}]_4\text{S}_4$ showed little resonance absorption but at 79°K, we obtained a good Mössbauer spectrum (Fig. 24) with an isomer shift of 0.90 ± 0.04 mm/sec (Table 26) with respect to stainless steel and a quadrupole splitting of 3.12 ± 0.04 mm/sec. The quadrupole splitting arises, as explained earlier, due to trigonal field present at the B site in the spinel structure. The presence of quadrupole splitting shows that the Fe^{2+} ions are not present at A sites, because in that case, the Mössbauer spectrum would have given a single spectrum as observed in the case of $\text{Fe}[\text{Cr}_2]_4\text{O}_4$.

The isomer shift of 0.90 ± 0.04 mm/sec at 79°K is smaller than that found for $\text{Ge}[\text{Fe}_2]_4\text{O}_4$ at 79°K because sulphur forms more covalent bonds than oxygen.

Part (2)

(a) Fe^{3+} Ions at the Octahedral (B) sites:

The Mössbauer spectra of $\text{Cd}[\text{Fe}_2]_4\text{O}_4$ and $\text{Zn}[\text{Fe}_2]_4\text{O}_4$:

Cadmium ferrite²⁴ and zinc ferrite^{25,26} are "normal" cubic spinels at room temperature and hence all the Fe^{3+} ions are present at the B sites in both the spinels. The u parameters for $\text{Cd}[\text{Fe}_2]_4\text{O}_4$ and $\text{Zn}[\text{Fe}_2]_4\text{O}_4$ have been reported²⁷ to be 0.386 and 0.380 respectively. Both these spinels are paramagnetic at room temperature. Zinc ferrite undergoes antiferromagnetic transition below 9°K^{28,29,30}, but no magnetic transition has been reported for cadmium ferrite so far.

The Mössbauer spectra of $\text{Cd}[\text{Fe}_2]_4\text{O}_4$ and $\text{Zn}[\text{Fe}_2]_4\text{O}_4$ (Fig. 25) show quadrupole splitting of 0.80 mm/sec and 0.38 mm/sec respectively at room temperature. The corresponding isomer shifts are

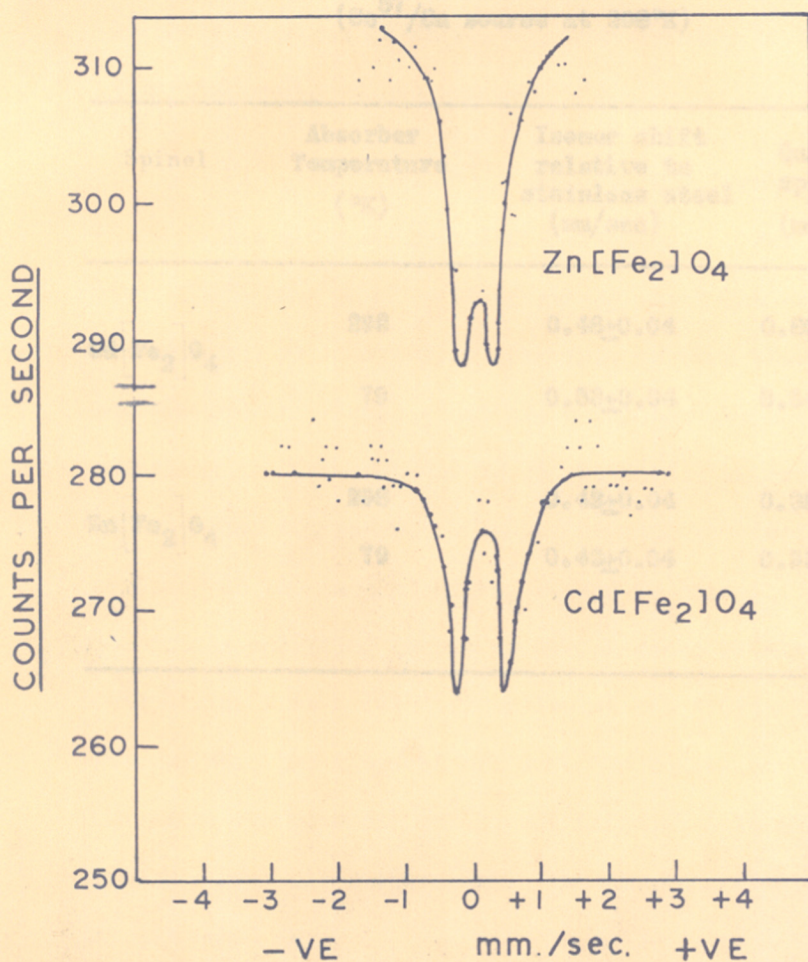


FIG. 25: THE MÖSSBAUER SPECTRA OF CdFe_2O_4 AND ZnFe_2O_4 AT 298°K

TABLE 27
MOSSBAUER DATA FOR CdFe_2O_4 AND ZnFe_2O_4
 (Co^{57}/Cu source at 298°K)

Spinel	Absorber Temperature (°K)	Isomer shift relative to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)
$\text{Cd}[\text{Fe}_2]\text{O}_4$	298	0.48 ± 0.04	0.80 ± 0.04
	79	0.53 ± 0.04	0.64 ± 0.04
$\text{Zn}[\text{Fe}_2]\text{O}_4$	298	0.42 ± 0.04	0.38 ± 0.04
	79	0.42 ± 0.04	0.32 ± 0.04

0.48 and 0.42 mm/sec (Table 27) with respect to stainless steel. The Mössbauer parameters are summarized in Table (27). Goldanskii et al.³¹ and Mizoguchi et al.⁸ have also found evidence for the presence of EFG in $\text{Zn}[\text{Fe}_2]\text{O}_4$. Goldanskii was not able to get a doublet but he obtained rather large line width in the Mössbauer spectrum of $\text{Zn}[\text{Fe}_2]\text{O}_4$, due probably to the intrinsic large line width of his source.

Zn^{2+} , Cd^{2+} and Fe^{3+} ions have electronic configurations which do not cause Jahn-Teller distortion. Iron in its trivalent state ($3d^5$) has ${}^6S_{5/2}$ ground state, which has no angular momentum and is spherically symmetric so that there would not be any EFG due to valence electrons and hence the observed quadrupole splitting in $\text{Cd}[\text{Fe}_2]\text{O}_4$ and $\text{Zn}[\text{Fe}_2]\text{O}_4$ should be due to the EFG arising from the asymmetry in the crystal lattice. As explained earlier, in the case of $\text{Ge}[\text{Fe}_2]\text{O}_4$ and $\text{In}[\text{FeIn}]\text{S}_4$, the observed quadrupole splitting is due to the presence of the trigonal field with its axis in $\langle 111 \rangle$ direction at the B site in the spinel structures. The value of EFG q at the B site can be estimated by the point charge model taking the trigonal axis as the principal axis in the $\langle 111 \rangle$ direction. The electric field gradient may be expressed as

$$q = \frac{1}{e} \frac{\partial^2 V}{\partial z^2} = \sum_i \left(\frac{z_i}{r_i^3} \right) (3 \cos^2 \theta_i - 1)$$

where z_i and (r_i, θ_i) are the charge and radial coordinates of the i^{th} ion in the lattice, and the sum is over all ions in the

lattice.

For $\text{Cd}[\text{Fe}_2]_4$, 'a' the lattice parameter is $8.699 \text{ \AA}$ and the oxygen parameter $u = 0.386^{23}$. The value of q would then be

For

$$1^{\text{st}} \text{ nearest } 6 \text{ O}^{2-} \text{ ions : } q = -2.197 \times 10^{23} \text{ cm}^{-3}$$

$$2^{\text{nd}} \text{ nearest } 6 \text{ Fe}^{3+} \text{ ions : } q = +6.16 \times 10^{23} \text{ cm}^{-3}$$

$$3^{\text{rd}} \text{ nearest } 6 \text{ Cd}^{2+} \text{ ions : } q = -2.32 \times 10^{23} \text{ cm}^{-3}$$

$$4^{\text{th}} \text{ nearest } 8 \text{ O}^{2-} \text{ ions : } q = -0.183 \times 10^{23} \text{ cm}^{-3}$$

The point charge model gives $q = 1.46 \times 10^{23} \text{ cm}^{-3}$ if we take into consideration the contribution up to the fourth nearest neighbours of the Fe^{3+} ion. If we take $Q = +0.41 \times 10^{-24} \text{ cm}^2$ ³² for the $3/2$ state in Fe^{57} and a Sternheimer antishielding factor $(1 - \gamma_\infty) = 10.14$ ³³ for the Fe^{3+} ion, the value of quadrupole splitting ζ would be

$$\begin{aligned} \zeta &= \frac{1}{2} e^2 q_{\text{lattice}} (1 - \gamma_\infty) Q \\ &= 0.9144 \text{ mm/sec} \end{aligned}$$

The calculated value is in very good agreement with the experimental value of the quadrupole splitting. A similar calculation for $\text{Zn}[\text{Fe}_2]_4$ gives the value of $\zeta = 1.773 \text{ mm/sec}$ if u is taken to be $0.380^{24,27}$. The calculated value of $\zeta = 1.098 \text{ mm/sec}$, if u is taken to be $0.385^{34,35}$. The calculated value of the quadrupole splitting is an order of magnitude larger than the experimental value. This discrepancy may be due to the uncertainty in the value of u parameter for $\text{Zn}[\text{Fe}_2]_4$.

The observed quadrupole splitting for $\text{Cd}[\text{Fe}_2]\text{O}_4$ is larger than that for $\text{Zn}[\text{Fe}_2]\text{O}_4$ due to the presence at the A sites of Cd^{2+} ions which are 25 per cent larger than Zn^{2+} ions. In order to accommodate larger Cd^{2+} ions at the A sites, the tetrahedra composed of the nearest four oxygen ions expand by moving the anions in $[111]$ direction away from the nearest A site from their ideal position but preserving the cubic symmetry (Fig. 11). This would be reflected in the larger value of u parameter for $\text{Cd}[\text{Fe}_2]\text{O}_4$ as compared to that for $\text{Zn}[\text{Fe}_2]\text{O}_4$. At the same time, the six nearest oxygen ions which are in the octahedral position around the B site would deviate from the cubic symmetry. This would therefore account for the larger quadrupole splitting observed in $\text{Cd}[\text{Fe}_2]\text{O}_4$ as compared to that in $\text{Zn}[\text{Fe}_2]\text{O}_4$. The larger the size of the cation on the A site as compared to the cation on the B site the greater would be the departure from the ideal spinel structure. The Goldschmidt radii of Ge^{4+} , Zn^{2+} and Cd^{2+} are 0.44, 0.82 and 1.03 Å respectively. The u parameter of $\text{Ge}[\text{Fe}_2]\text{O}_4$ has a value of 0.375^{18,27} the value for an ideal spinel structure, because the Ge^{4+} is smaller than the Fe^{2+} (0.72 Å). The u parameter for $\text{Zn}[\text{Fe}_2]\text{O}_4$ is 0.380²⁷ and for $\text{Cd}[\text{Fe}_2]\text{O}_4$ it is 0.386²⁷.

It would be observed that the quadrupole splitting in both the $\text{Zn}[\text{Fe}_2]\text{O}_4$ and $\text{Cd}[\text{Fe}_2]\text{O}_4$ decreases with the decrease of temperature. This would indicate that the contraction of the cations at the A sites is larger than those at the B sites, when the $\text{Cd}[\text{Fe}_2]\text{O}_4$ and $\text{Zn}[\text{Fe}_2]\text{O}_4$ are cooled to liquid nitrogen

temperature. These two spinels on cooling to liquid nitrogen temperature therefore approach closer to the ideal spinel structure. The percentage change in quadrupole splitting on cooling is larger in $\text{Cd}[\text{Fe}_2]\text{O}_4$ than in $\text{Zn}[\text{Fe}_2]\text{O}_4$. The EFG at the B site of the spinel structure arises due to (i) departure of six nearest oxygen neighbours from their octahedral symmetry, (ii) trigonal field due to the next nearest neighbours. Whereas in $\text{Ge}[\text{Fe}_2]\text{O}_4$ for which a parameter has the value 0.375, the contribution due to the first factor is absent, in $\text{Cd}[\text{Fe}_2]\text{O}_4$ and $\text{Zn}[\text{Fe}_2]\text{O}_4$, the EFG is contributed by both the factors. The comparatively large quadrupole splitting observed in the case of $\text{Ge}[\text{Fe}_2]\text{O}_4$ than in the case of $\text{Cd}[\text{Fe}_2]\text{O}_4$ and $\text{Zn}[\text{Fe}_2]\text{O}_4$ is due to the presence of ferrous ion in $\text{Ge}[\text{Fe}_2]\text{O}_4$ since Fe^{2+} ion is a more sensitive probe for the electric field gradient than the ferric ion.

(b) Fe^{3+} ions at the tetrahedral (A) sites:-

The Mössbauer spectra of $\text{Fe}[\text{CrNi}]\text{O}_4$ and $\text{Fe}[\text{MnCu}]\text{O}_4$:-

The "inverse" cubic spinel $\text{Fe}[\text{CrNi}]\text{O}_4$ ^{35,36} contains Fe^{3+} ions at the A sites only. It is paramagnetic above 325°C with a Curie point of 325°C³⁷, below which it is ferrimagnetic. The "inverse" cubic spinel $\text{Fe}[\text{MnCu}]\text{O}_4$ is also ferrimagnetic at room temperature with Curie point of 270°C³⁷ and on the basis of the relative site preference energies (Table 8) it is expected that the Fe^{3+} ions would be present at the A sites only.

The Mössbauer spectra of $\text{Fe}[\text{CrNi}]\text{O}_4$ were taken at eight different temperatures from 79°K to 738°K and the results are

summarized in Table (28). In the ferrimagnetic state a hyperfine split spectrum with no quadrupole splitting was obtained. Though the spectrum in Fig. (26) shows a small asymmetry in line width and intensity, between the right and left half of the spectrum, further tests on a number of hyperfine split spectra at different temperatures indicate that the effect is largely instrumental. The isomer shift of 0.42 ± 0.04 mm/sec at 298°K with respect to stainless steel is characteristic of high spin ferric compounds. The change in isomer shift with temperature (Table 28) may be attributed to the second order Doppler Effect¹⁴. The observed temperature coefficient of $\frac{\partial}{\partial T} \left(\frac{\delta E}{E} \right) = -1.8 \times 10^{-15}$ per °K was comparable to the theoretical value of the second order Doppler shift arising from the lattice vibrations (page 64).

The Mössbauer spectrum in the paramagnetic state showed a pair of lines of equal intensity and may be interpreted as the quadrupole splitting. The nature of the spectrum in the paramagnetic state does not change with the increase of temperature. At 738°K the value of quadrupole splitting was found to be 0.44 ± 0.04 mm/sec with an isomer shift of 0.18 ± 0.04 mm/sec. Mizoguchi and Tanaka⁸ have also taken the Mössbauer spectrum of this spinel in the paramagnetic state. Their values of the isomer shift and the quadrupole splitting are in good agreement with our values.

The observed quadrupole splitting in the paramagnetic state of this spinel indicates the presence of an EFG at the A sites. As explained earlier the A sites in the spinel have a cubic point symmetry. With an increase in size of cation on the A site, the tetrahedron composed of the first nearest four oxygen

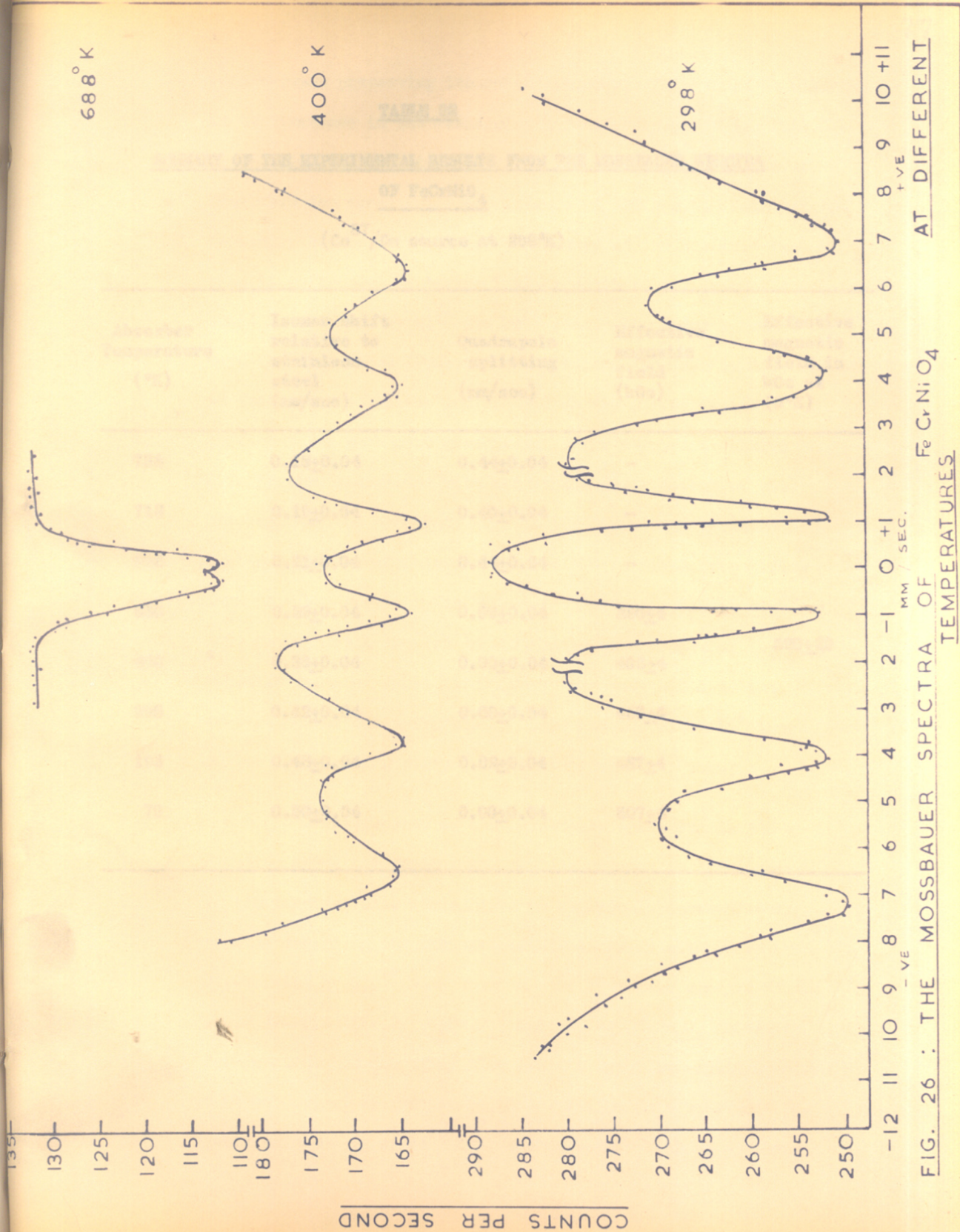


FIG. 26 : THE MOSSBAUER SPECTRA OF FeC_2NiO_4 AT DIFFERENT TEMPERATURES

TABLE 28

SUMMARY OF THE EXPERIMENTAL RESULTS FROM THE MOSSBAUER SPECTRA

OF FeCrNiO_4 (Co⁵⁷/Cu source at 298°K)

Absorber Temperature (°K)	Isomer shift relative to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)	Effective magnetic field (kOe)	Effective magnetic field in kOe at (0°K)
738	0.18±0.04	0.44±0.04	-	
718	0.19±0.04	0.40±0.04	-	
688	0.21±0.04	0.44±0.04	-	
530	0.29±0.04	0.00±0.04	390±4	520±20
400	0.36±0.04	0.00±0.04	405±4	
298	0.42±0.04	0.00±0.04	455±4	
193	0.48±0.04	0.02±0.04	487±4	
79	0.50±0.04	0.00±0.04	507±4	

ions expands preserving its cubic symmetry. This would be observed in the increase in the value of u parameter (page 74). The d^5 electronic configuration of ferric ion cannot give rise to any EFG. Therefore the cause for the existence of EFG may be sought in the asymmetry of the next nearest neighbours of the A site. Each A site is surrounded by twelve B sites which in the present case would be occupied by Ni^{2+} and Cr^{3+} ions. There are a number of ways in which these divalent and trivalent ions can be distributed on these twelve B sites and the EFG on the A site would be different for each such arrangement. The asymmetric charge distribution associated with the random distribution of the divalent and the trivalent ions on the B sites surrounding each A site would therefore produce a net EFG at the A site giving rise to a quadrupole split Mössbauer spectrum. Cox et al.³⁸ also found a well ^{defined} doublet in the Mössbauer spectrum of the paramagnetic state of cubic $LiFeO_2$ which was attributed to the coexistence of the trivalent Fe^{3+} ions and univalent Li^+ ions on the neighbouring equivalent sites around Fe^{3+} ions.

The presence of the quadrupole splitting in the spectrum above the Curie point and its absence in the spectrum in the ferrimagnetic state, give us apparently contradictory results regarding the presence of EFG at the A site in $Fe[CrNi]O_4$. Hryniewicz et al.³⁹ have reported the Mössbauer spectra of the cubic spinels $NiFe_2O_4$, $CoFe_2O_4$, $MnFe_2O_4$ and $MgFe_2O_4$ in their ferrimagnetic state. They also found a hyperfine split spectrum with no quadrupole splitting, and explained this behaviour due to the cubic surrounding of Fe^{3+} ion, a conclusion which we now know

to be incorrect. The observed doublet in the Mössbauer spectrum of the $\text{Fe}[\text{CrNi}]_4\text{O}_4$ in the paramagnetic state indicates the presence of an EFG at the A site. The quadrupole splitting ϵ , in the presence of an axially symmetric electric field gradient tensor with the symmetry axis at an angle θ with respect to the magnetic axis is given by the equation²² (22, see page 21).

For $I = 3/2$ and $\gamma = 0$, this equation may be written as:

$$\epsilon = \frac{e^2 q Q}{8} (3 \cos^2 \theta - 1) \dots \dots \dots (3)$$

If the magnetic field H is inclined at an angle $\theta = \cos^{-1} \sqrt{\frac{1}{3}}$ to the symmetry axis of the EFG, the quantity within the bracket would become zero, and hence the value of ϵ would also be zero. The hyperfine spectrum in the ferrimagnetic state therefore would not show any quadrupole splitting even in the presence of the EFG. If the Mössbauer spectra of the spinels studied by Hryniewicz et al³⁹ are taken in their paramagnetic state, one would observe quadrupole splitting even though the spectra in the ferrimagnetic state show the absence of quadrupole interaction. Confirmatory evidence is provided by the observed quadrupole splitting in the Mössbauer spectra of MnFe_2O_4 ⁴⁰ and CoFe_2O_4 ⁴¹ in the paramagnetic state.

The effective fields acting on the Fe^{3+} nuclei at A sites in $\text{Fe}[\text{CrNi}]_4\text{O}_4$ in the ferrimagnetic state were calculated from the separation of the lines in the hyperfine split spectrum are given in Table (28). On extrapolation to 0°K, (Fig. 27) a value of 520 ± 20 kOe was obtained. This value may be compared with the average value of the effective magnetic field³⁹ of

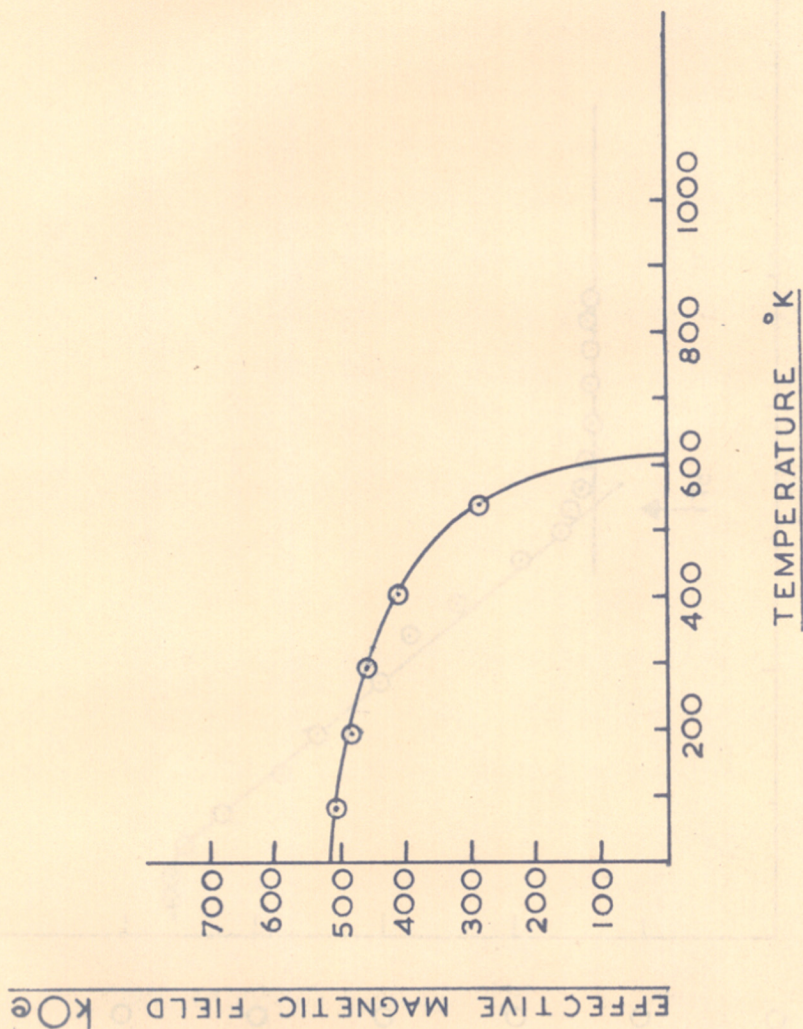


FIG. 27 : A PLOT OF THE EFFECTIVE MAGNETIC
FIELD (H_{eff}) VS. TEMPERATURE IN °K
FOR FeCrNiO_4

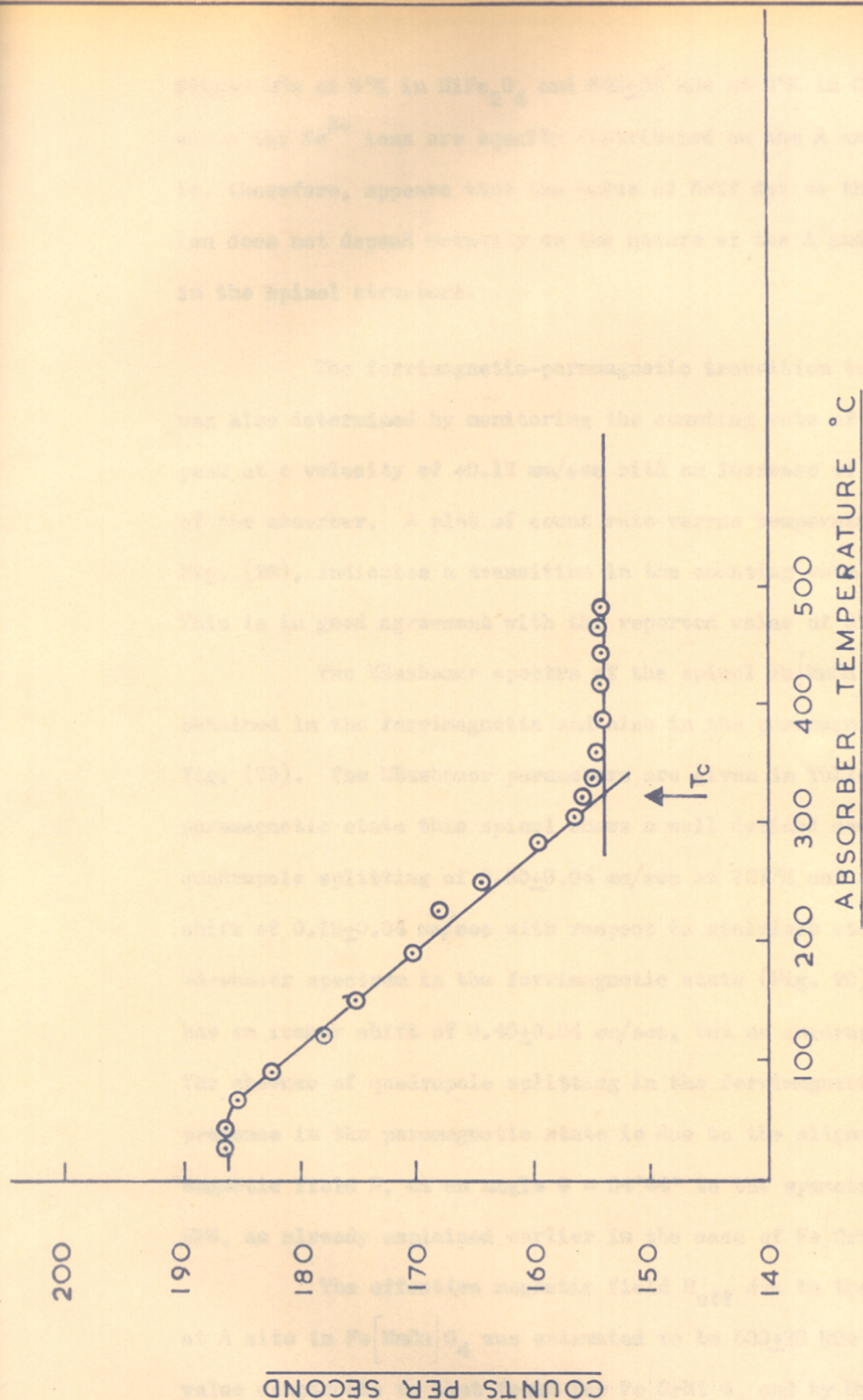


FIG. 28 : MAGNETIC TRANSITION IN FeCrNiO_4 POWERED SAMPLE :
COUNTS PER SECOND VS. SAMPLE TEMPERATURE

520 ± 20 kOe at 0°K in NiFe_2O_4 and 546 ± 20 kOe at 0°K in CoFe_2O_4 , where the Fe^{3+} ions are equally distributed on the A and B sites. It, therefore, appears that the value of H_{eff} due to the Fe^{3+} ion does not depend markedly on the nature of the A and B sites in the spinel structure.

The ferrimagnetic-paramagnetic transition temperature was also determined by monitoring the counting rate of the 14.4 keV peak at a velocity of $+0.12$ mm/sec with an increase of temperature of the absorber. A plot of count rate versus temperature shown in Fig. (28), indicates a transition in the counting rate at $330^\circ\text{C} \pm 2^\circ\text{C}$. This is in good agreement with the reported value of 325°C .

The Mössbauer spectra of the spinel $\text{Fe}[\text{MnCu}]_4\text{O}_4$ were obtained in the ferrimagnetic and also in the paramagnetic states Fig. (29). The Mössbauer parameters are given in Table (29). In the paramagnetic state this spinel shows a well defined doublet with a quadrupole splitting of 0.50 ± 0.04 mm/sec at 727°K and an isomer shift of 0.19 ± 0.04 mm/sec with respect to stainless steel. The Mössbauer spectrum in the ferrimagnetic state (Fig. 29) at 298°K has an isomer shift of 0.46 ± 0.04 mm/sec, but no quadrupole splitting. The absence of quadrupole splitting in the ferrimagnetic state and its presence in the paramagnetic state is due to the alignment of the magnetic field H , at an angle $\theta = 54^\circ 44'$ to the symmetry axis of the EFG, as already explained earlier in the case of $\text{Fe}[\text{CrNi}]_4\text{O}_4$.

The effective magnetic field H_{eff} due to the Fe^{3+} nuclei at A site in $\text{Fe}[\text{MnCu}]_4\text{O}_4$ was estimated to be 530 ± 20 kOe at 0°K , a value comparable to that found for $\text{Fe}[\text{CrNi}]_4\text{O}_4$ and by Hryniewicz *et al.*³⁹ for a number of spinels containing Fe^{3+} ions.

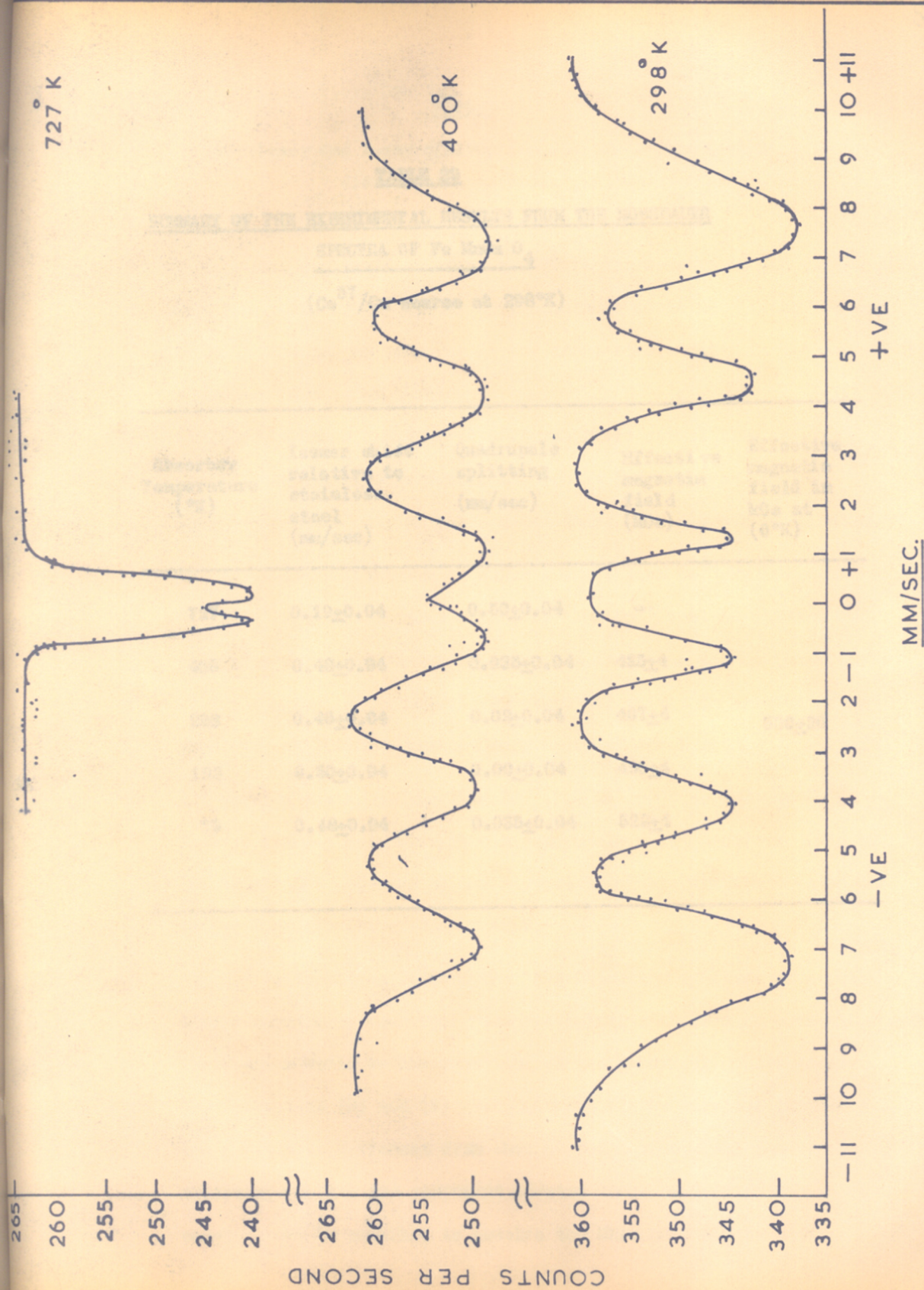


FIG 29 : THE MÖSSBAUER SPECTRA OF Fe Mn Cu O_4 AT DIFFERENT TEMPERATURES

TABLE 29

SUMMARY OF THE EXPERIMENTAL RESULTS FROM THE MOSSBAUER

SPECTRA OF $\text{Fe MnCu}_4\text{O}_4$ (Co 57 /Cu source at 298°K)

Absorber Temperature (°K)	Isomer shift relative to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)	Effective magnetic field (kOe)	Effective magnetic field in kOe at (0°K)
727	0.19±0.04	0.50±0.04	-	
406	0.42±0.04	0.035±0.04	425±4	
298	0.46±0.04	0.02±0.04	467±4	530±20
193	0.50±0.04	0.00±0.04	490±4	
79	0.48±0.04	0.035±0.04	522±4	

Part 3

Mössbauer and X-ray diffraction studies on the cation distribution in FeAl_2O_4 :-

Our earlier studies on the Mössbauer spectra in the paramagnetic state of the spinel type compounds containing either Fe^{2+} or Fe^{3+} ions and at only one of the two possible sites in the spinel structure have shown that:

- (1) The Mössbauer spectrum of a normal cubic spinel like $\text{Fe}^{2+}[\text{Cr}_2^{3+}]_4\text{S}_4$ should show a single resonance absorption line because the Fe^{2+} ions are present only at the A sites which have a cubic point symmetry.
- (2) The Mössbauer spectra of cubic spinels like $\text{Ge}^{4+}[\text{Fe}_2^{2+}]_4\text{O}_4$ and $\text{Cd}^{2+}[\text{Fe}_2^{3+}]_4\text{O}_4$ which contain either Fe^{2+} or Fe^{3+} ions at the B sites only show a quadrupole splitting. This is due to the trigonal field at the B sites in the spinel structure and arises on account of the asymmetry of the next nearest neighbours of the B site.
- (3) Inverse cubic spinels like $\text{Fe}^{3+}[\text{Cr}^{3+}\text{Ni}^{2+}]_4\text{O}_4$ containing Fe^{3+} ions at A sites only also show a quadrupole split spectrum. This is due to the EFG produced by the asymmetric charge distribution on the twelve B neighbours of each A site.

It therefore follows that the Mössbauer spectrum of a partially inverse or completely inverse spinel with iron at both the A and the B sites would be the resultant of two quadrupole split spectra, due to reasons (2) and (3) given above. If the value of the EFG at the A sites is different from that at the B sites, the quadrupole splittings of the two component spectra would be different. In such cases it may be possible to resolve the Mössbauer spectrum of an

inverse spinel into two separate quadrupole split Mössbauer spectra.

$\text{Fe}^{2+}\text{Al}_2^{3+}\text{O}_4$ is expected to be a partially inverse spinel and hence its ionic distribution may be represented as $\text{Fe}_{1-x}^{2+}\text{Al}_x^{3+} \left[\text{Fe}_x^{2+}\text{Al}_{2-x}^{3+} \right] \text{O}_4$ where x is called the degree of inversion and has a value between 0 and 1. The cation distribution in this spinel can be determined with a reasonable accuracy by X-ray diffraction since the X-ray scattering power of Fe^{2+} ions and Al^{3+} ions are very different. It would then be possible to compare the cation distribution in FeAl_2O_4 determined by two different techniques.

FeAl_2O_4 was first reported to be a normal cubic spinel by Barth and Posnjak⁴² and Romeijn³⁵. Dunitz and Orgel⁴³ as well as McClure⁴⁴ calculated the stabilization energies for the tetrahedral and octahedral coordination in terms of the crystal field stabilization parameter $10 D_q$. McClure has given the value of the octahedral site preference energies for the various transition metal ions and these have been reproduced in Table (7) (page 28). Miller⁴⁵ extended the concept of the octahedral site preference energy in a spinel structure to include the Madelung and short-ranged terms in addition to the crystal field terms. The values of the octahedral site preference energies for different ions, as given by Miller, are reproduced in Table (8) (page 30). A perusal of Table (8) would show that a spinel like FeCr_2S_4 would have normal cationic distribution because the Cr^{3+} ions have a strong preference for the octahedral B sites as compared to the Fe^{2+} ions. The octahedral site preference energy for the In^{3+} ion is more negative (-40.2 k cal/g) than that for the Fe^{2+} ion (-9.9 k cal/g) and hence it will replace all the Fe^{2+} ions from

the tetrahedral A sites as found in the inverse spinel $\text{In}[\text{FeIn}]\text{S}_4$. Though the octahedral site preference energy for the Fe^{2+} ion is more negative than that for Al^{3+} , yet these values do not differ very much, and hence there is a possibility that some of the Fe^{2+} ions would be found at B sites in FeAl_2O_4 giving it a partially inverse cation distribution as observed in CoAl_2O_4 .⁴⁶

The Mössbauer spectrum of FeAl_2O_4 has been studied by a number of workers who have obtained conflicting results. Mizoguchi and Tanaka⁸ observed a single resonance line spectrum with an isomer shift of 0.98 mm/sec relative to stainless steel. This indicates that the spinel had a normal cation distribution as found in FeCr_2S_4 . The Mössbauer spectrum of FeAl_2O_4 obtained by Rossiter⁷ showed a quadrupole splitting of 1.60 ± 0.06 mm/sec with an isomer shift of 1.08 ± 0.06 mm/sec. His value of isomer shift is in agreement with that of Mizoguchi and Tanaka⁸. A distinct asymmetry in the intensity of the two lines of the doublet obtained by Rossiter was indicated from his spectrum which has been reproduced in Fig.(30). One *et al.*^{47,48} measured the Mössbauer spectra of FeAl_2O_4 at 600°K, 200°K and 20°K. They observed two well resolved lines of equal intensity. At 20°K they found an additional peak which they attributed to the presence of Fe^{3+} impurity. The value of isomer shift was not given by these authors but the value of quadrupole splitting has been estimated to be ~ 1.5 mm/sec at 298°K. The earlier results on the Mössbauer spectrum of FeAl_2O_4 are summarized in Table (30).

TOTAL COUNT, THOUSANDS

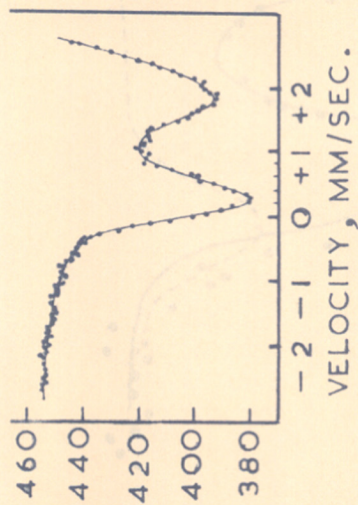


FIG. 30 : MÖSSBAUER SPECTRUM OF FeAl_2O_4 AT ROOM TEMPERATURE.
REPRODUCED FROM ROSSITER M.J. (7)

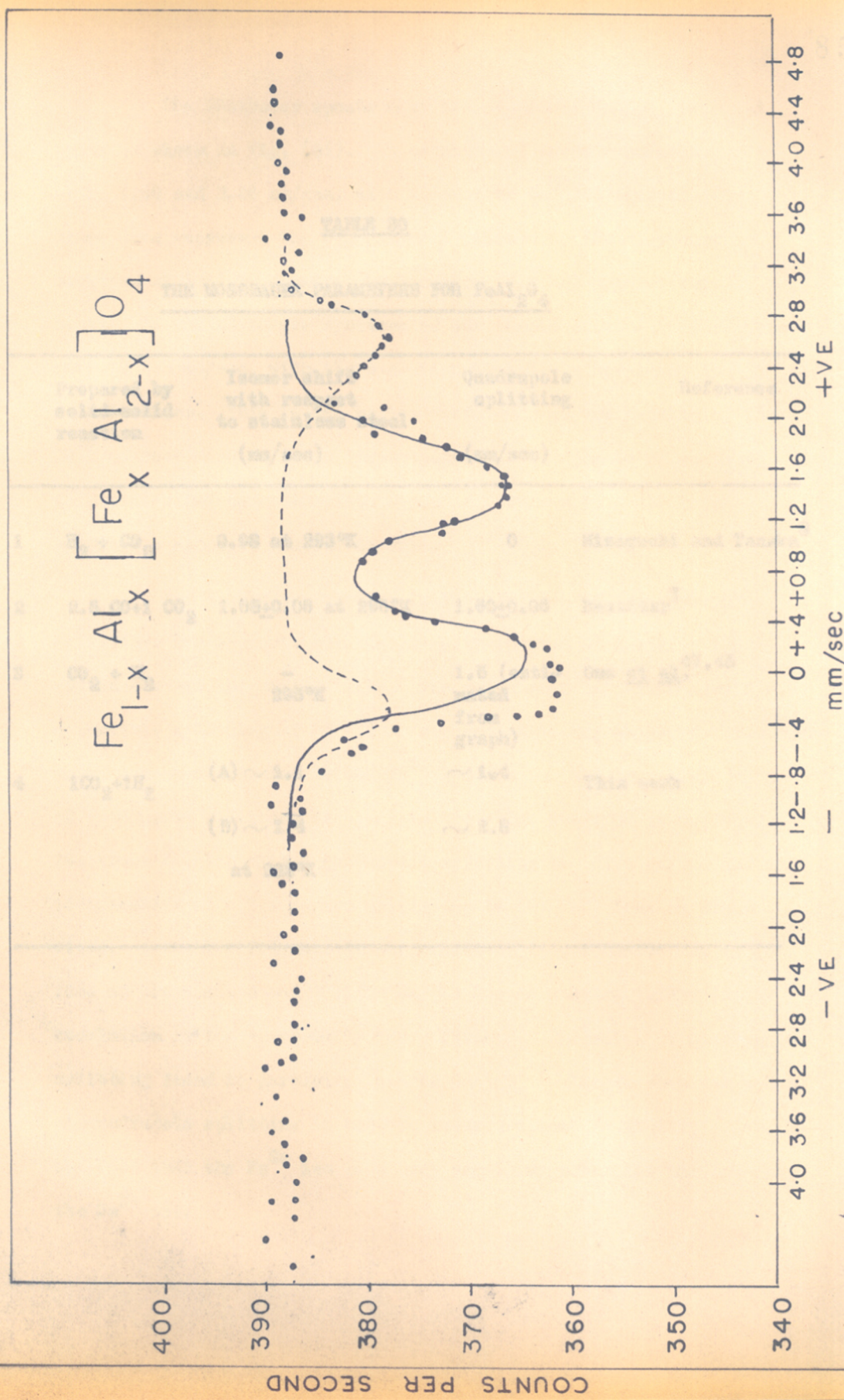


FIG. (31): THE MÖSSBAUER SPECTRUM OF $\text{Fe}_{1-x}\text{Al}_x [\text{Fe}_x\text{Al}_{2-x}]_4\text{O}_4$ AT 25°C

TABLE 30

THE MOSSBAUER PARAMETERS FOR FeAl_2O_4

	Prepared by solid-solid reaction	Isomer shift with respect to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)	Reference
1	$\text{H}_2 + \text{CO}_2$	0.98 at 293°K	0	Mizoguchi and Tanaka ⁸
2	$2.5 \text{ CO} + 1 \text{ CO}_2$	1.08 ± 0.06 at 295°K	1.60 ± 0.06	Rossiter ⁷
3	$\text{CO}_2 + \text{H}_2$	- 295°K	1.5 (esti- mated from graph)	Ono <u>et al.</u> ^{47,48}
4	$1 \text{ CO}_2 + 1 \text{ H}_2$	(A) ~ 1.1 (B) ~ 1.4 at 298°K	~ 1.4 ~ 2.8	This work

The Mössbauer spectrum of the sample of FeAl_2O_4 prepared by us is shown in Fig. (31). It consists of three resonance peaks at 0, 1.46 and 2.56 mm/sec, with respect to Co^{57}/Cu source. The black dots represent the experimental points. The Mössbauer spectrum of FeAl_2O_4 obtained by Rossiter (Fig.30) appears very similar to the Mössbauer spectrum of our sample up to a Doppler velocity of 2.4 mm/sec, with the exception that it is displaced by $\sim +0.3$ mm/sec. This is due to the difference in the backing of the Co^{57} sources used in these investigations. It appears to us that if Rossiter had taken the data beyond 2.7 mm/sec he would have obtained a spectrum similar to ours.

The Mössbauer spectrum in Fig.(31) was resolved graphically into two separate quadrupole split spectra as shown by the continuous and the dotted lines. The outer pairs of lines give a quadrupole splitting of ~ 2.8 mm/sec and an isomer shift of ~ 1.4 mm/sec which can be attributed to the Fe^{2+} ions at the B sites. This value of quadrupole splitting is equal to the value observed in $\text{Ge}[\text{Fe}_2]\text{O}_4$. The inner doublet with a quadrupole splitting of ~ 1.4 mm/sec and an isomer-shift of ~ 1.1 mm/sec arises due to the Fe^{2+} ions at the A sites. A small difference in the values of isomer shifts due to Fe^{2+} ions at the A sites and B sites may be due to an uncertainty in the resolution of the spectrum by curve fitting. The value of quadrupole splitting found in partially inverse FeAl_2O_4 is larger than the value of quadrupole splitting in another inverse spinel $\text{Fe}[\text{CrNi}]\text{O}_4$ ¹⁰ due to the fact that the Fe^{2+} ion is a more sensitive probe for the EFG than the Fe^{3+} ion.

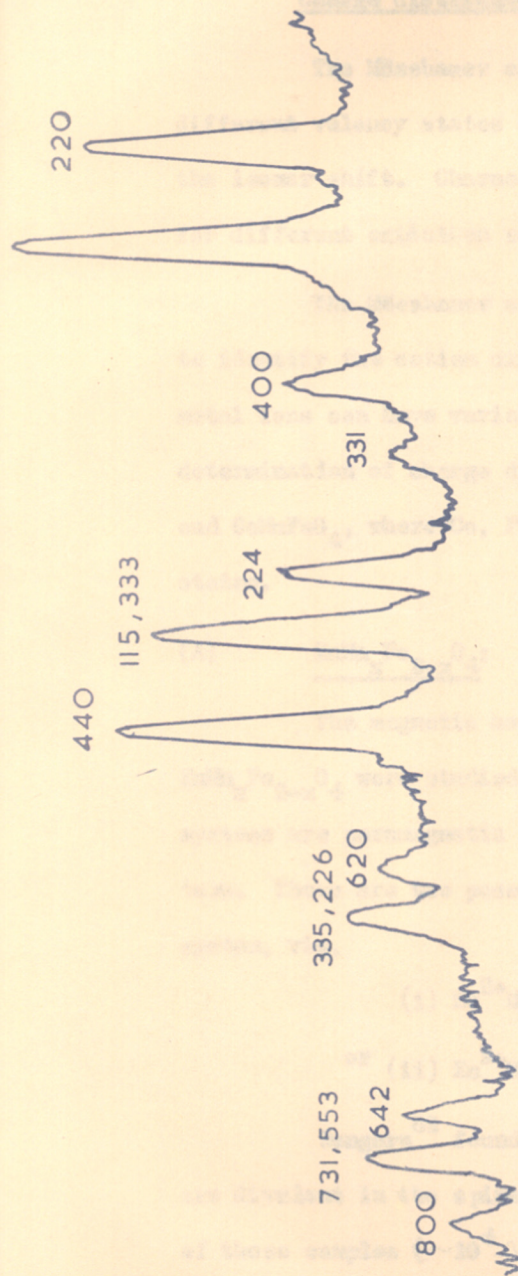
If we assume that the Lamb-Mössbauer factors for the Fe^{2+} ions at the A and the B sites of FeAl_2O_4 are equal, then it is possible to determine the degree of inversion x in $\text{Fe}_{1-x}\text{Al}_x[\text{Fe}_x\text{Al}_{2-x}]_0_4$ by comparing the area under the two resolved Mössbauer spectra. The value of x has been found to be 23%.

The cation distribution was also determined by X-ray diffraction method. The X-ray powder diffraction pattern of FeAl_2O_4 is shown in Fig.(32) along with its photometer reading. By comparing the observed intensities of the reflection for different planes in the X-ray diffraction pattern of FeAl_2O_4 , with those calculated for different degrees of inversion. The calculated intensities for $x=0.15, 0.20, 0.25$ and 0.30 are given in Table (23) along with the values of the observed intensities. The u parameter was taken as 0.3885^{49} . The value of reliability factor

$$R = \frac{\sum |I_{\text{cal}} - I_{\text{obs}}|}{\sum |I_{\text{obs}}|}$$

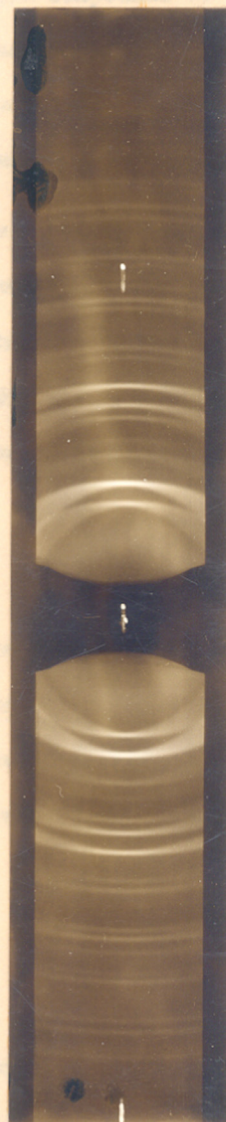
was found to be minimum (0.086) for $x = 0.25$. The degree of inversion found by X-ray diffraction method is in good agreement with that found from the Mössbauer spectroscopy. Roth⁴⁹ has reported the degree of inversion in FeAl_2O_4 to be 15% from his neutron diffraction experiments. Different methods of preparation of FeAl_2O_4 and may produce small differences in the degree of inversion. This may explain the difference in the value of x reported by Roth from neutron diffraction and that found by us by X-ray diffraction and Mössbauer spectroscopy.

INTENSITY (ARBITRARY UNITS)



← 2θ

FIG. 32 : (A) MICROPHOTOMETRIC RECORD OF X-RAY POWDER PATTERN OF FeAl_2O_4



(B) X-RAY POWDER PATTERN OF FeAl_2O_4

Part 4

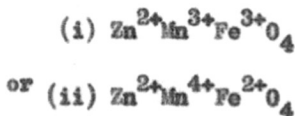
Charge distribution in the mixed oxide spinels: $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$ & $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$

The Mössbauer experiments on high spin compounds of iron in different valency states show a systematic behaviour with respect to the isomer shift. Characteristic values of isomer shift are obtained for different oxidation states of iron as given in Table (4) (page 15).

The Mössbauer study can therefore be used to give information to identify the cation oxidation state in mixed oxide systems where the metal ions can have variable valency. This chapter deals with the determination of charge distribution in the mixed oxides ZnMnFeO_4 and CoMnFeO_4 , where Co, Fe and Mn can exist in different oxidation states.

(A) $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$:

The magnetic and crystallographic properties of the system $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$ were studied by Blasse^{50,51} in great detail. These systems are paramagnetic at room temperature and have a spinel structure. There are two possibilities of the charge distribution in this system, viz,



Bongers⁵² found that the Mn is tetravalent and Co and Ni are divalent in the spinels $\text{Zn}[\text{MnCo}]\text{O}_4$ and $\text{Zn}[\text{NiMn}]\text{O}_4$. The resistivity of these samples ($\sim 10^4 \Omega \text{ cm}$ for $0 < x < 2$ and $10^6 \Omega \text{ cm}$ for $x=2$) and the occurrence of tetragonal distortion⁵³ for $x \geq 0.6$ indicate that the combination $\text{Fe}^{3+} - \text{Mn}^{3+}$ is more stable than the alternative

TABLE 31

THE MOSSBAUER RESULTS FOR $\text{ZnMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$ AND ZnMnFeO_4 (Co 57 /Cu source at 298°K)

Spinel	Absorber temperature (°K)	Isomer shift relative to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)
$\text{ZnMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$	298	0.47 ± 0.04	0.34 ± 0.04
	193	0.60 ± 0.04	0.36 ± 0.04
ZnMnFeO_4	298	0.47 ± 0.04	0.50 ± 0.04
	193	0.57 ± 0.04	0.58 ± 0.04

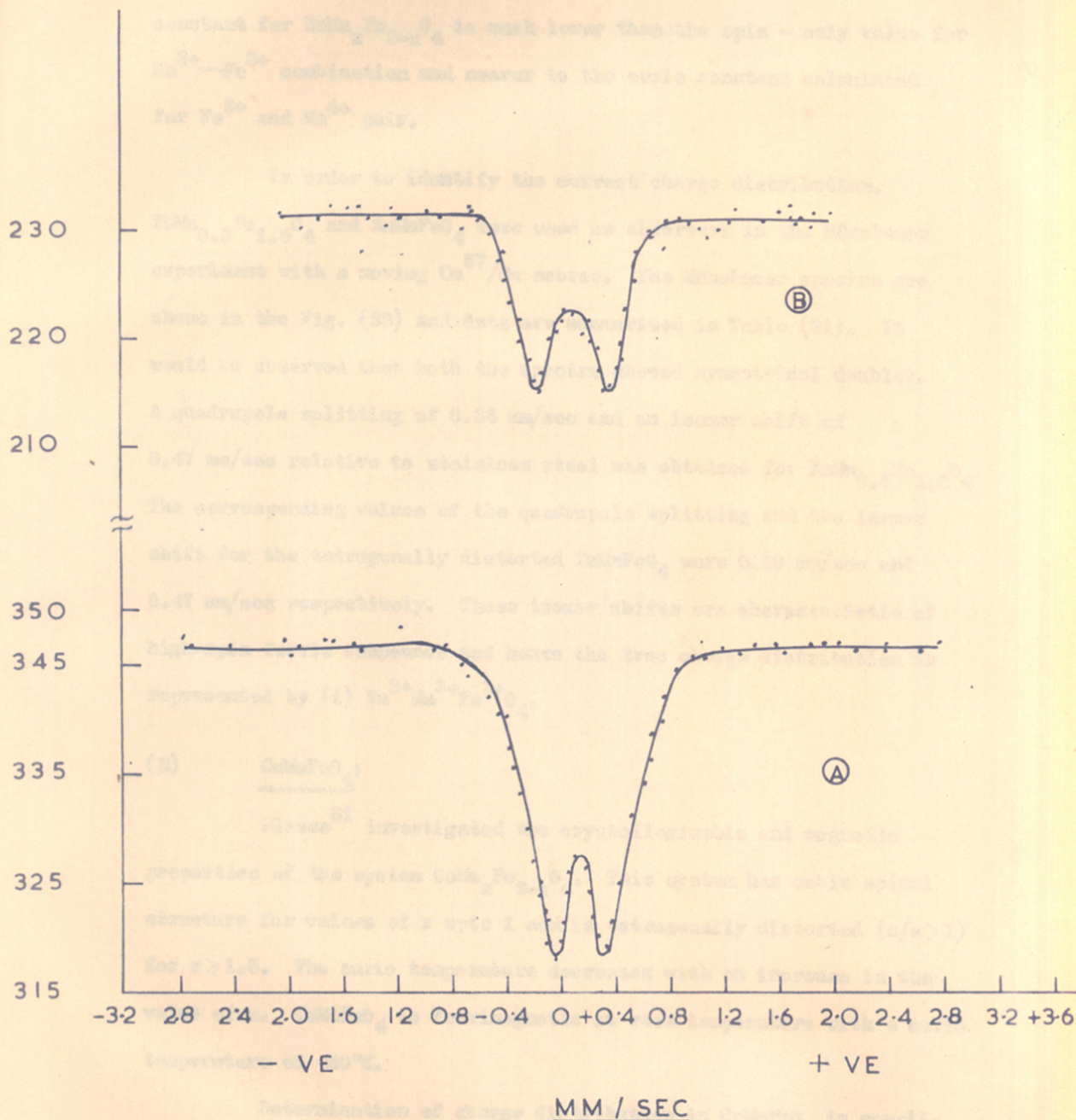


FIG (33) : MÖSSBAUER SPECTRA OF (A) $\text{ZnMn}_{1.5}\text{Fe}_{1.5}\text{O}_4$ AND
(B) ZnMnFeO_4 AT 298°K

combination of $\text{Fe}^{2+} - \text{Mn}^{4+}$ in this system. The tetragonal distortion shows the presence of the Jahn-Teller ion Mn^{3+} . However the curie constant for $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$ is much lower than the spin - only value for $\text{Mn}^{3+} - \text{Fe}^{3+}$ combination and nearer to the curie constant calculated for Fe^{2+} and Mn^{4+} pair.

In order to identify the correct charge distribution, $\text{ZnMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$ and ZnMnFeO_4 were used as absorbers in the Mössbauer experiment with a moving Co^{57}/Cu source. The Mössbauer spectra are shown in the Fig. (33) and data are summarized in Table (31). It would be observed that both the spectra showed symmetrical doublet. A quadrupole splitting of 0.34 mm/sec and an isomer shift of 0.47 mm/sec relative to stainless steel was obtained for $\text{ZnMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$. The corresponding values of the quadrupole splitting and the isomer shift for the tetragonally distorted ZnMnFeO_4 were 0.50 mm/sec and 0.47 mm/sec respectively. These isomer shifts are characteristic of high-spin ferric compounds and hence the true charge distribution is represented by (i) $\text{Zn}^{2+}\text{Mn}^{3+}\text{Fe}^{3+}\text{O}_4$.

(B) CoMnFeO_4 :

Blasse⁵¹ investigated the crystallographic and magnetic properties of the system $\text{CoMn}_x\text{Fe}_{2-x}\text{O}_4$. This system has cubic spinel structure for values of x upto 1 and is tetragonally distorted ($c/a > 1$) for $x \geq 1.5$. The curie temperature decreases with an increase in the value of x. CoMnFeO_4 is ferrimagnetic at room temperature with a curie temperature of 450°K.

Determination of charge distribution in CoMnFeO_4 is complicated and has not been attempted so far because all the cations present

TABLE 32

THE MOSSBAUER RESULTS FOR CoMnFeO_4

Source and its temperature (°K)	Absorber	Isomer shift relative to stainless steel (mm/sec)	Quadrupole splitting (mm/sec)
Co^{57}/Cu at 298	CoMnFeO_4 at 548°K	0.27 ± 0.04	0.38 ± 0.04
	773°K	-0.04 ± 0.04	0.25 ± 0.04
$\text{CoMnFeO}_4 : \text{Co}^{57}$	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ at 298°K		
550	-do-	0.12 ± 0.04	0.32 ± 0.04
663	-do-	0.05 ± 0.04	0.26 ± 0.04
773	-do-	-0.04 ± 0.04	0.24 ± 0.04

Note: The isomer shift has been converted with respect to stainless steel by subtracting 0.08 mm/sec from the values obtained with respect to potassium ferrocyanide absorber.

can have different valencies (Co: 2 and 3, Mn: 2, 3 & 4 and Fe: 2 and 3). The large resistivity of CoMnFeO_4 ($10^4 \sim \text{cm}$) indicates that it does not contain ions of the same element with different oxidation states. There are thus four possible ways of charge distribution in this spinel, viz,

- (i) $\text{Co}^{2+}\text{Mn}^{3+}\text{Fe}^{3+}\text{O}_4$
- (ii) $\text{Co}^{2+}\text{Mn}^{4+}\text{Fe}^{2+}\text{O}_4$
- (iii) $\text{Co}^{3+}\text{Mn}^{3+}\text{Fe}^{2+}\text{O}_4$
- (iv) $\text{Co}^{3+}\text{Mn}^{2+}\text{Fe}^{3+}\text{O}_4$

The Mössbauer spectrum of CoMnFeO_4 was taken in its paramagnetic state in order to avoid the effects of nuclear Zeeman splitting. The spectrum taken at 548°K is shown in Fig. (34). It gives an isomer shift of 0.27 ± 0.04 mm/sec with respect to stainless steel and a quadrupole splitting of 0.38 mm/sec. This value of isomer shift is characteristic of spin free Fe^{3+} ions and hence rules out the charge distribution indicated in (ii) and (iii). In order to choose between the charge distribution represented by (i) and (iv), Mössbauer studies were undertaken with Co^{57} doped CoMnFeO_4 as a source and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ as the moving absorber. The Mössbauer spectra were taken with the source at 550°, 663° and 773°K and the $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber at 298°K. The absorber was prepared from Fe metal enriched to 92% Fe^{57} and was 0.8 mg/cm^2 thick. The spectra are shown in Fig. (35) and the data are summarized in Table (32). A quadrupole split spectrum was obtained in every case. At 550°K the value of the isomer shift was 0.12 mm/sec with respect to stainless steel with a temperature coefficient $\frac{\partial \delta}{\partial T} = -7.22 \times 10^{-4} \text{ mm/sec/}^\circ\text{K}$ in the temperature interval 550 — 773°K. If it is assumed that the

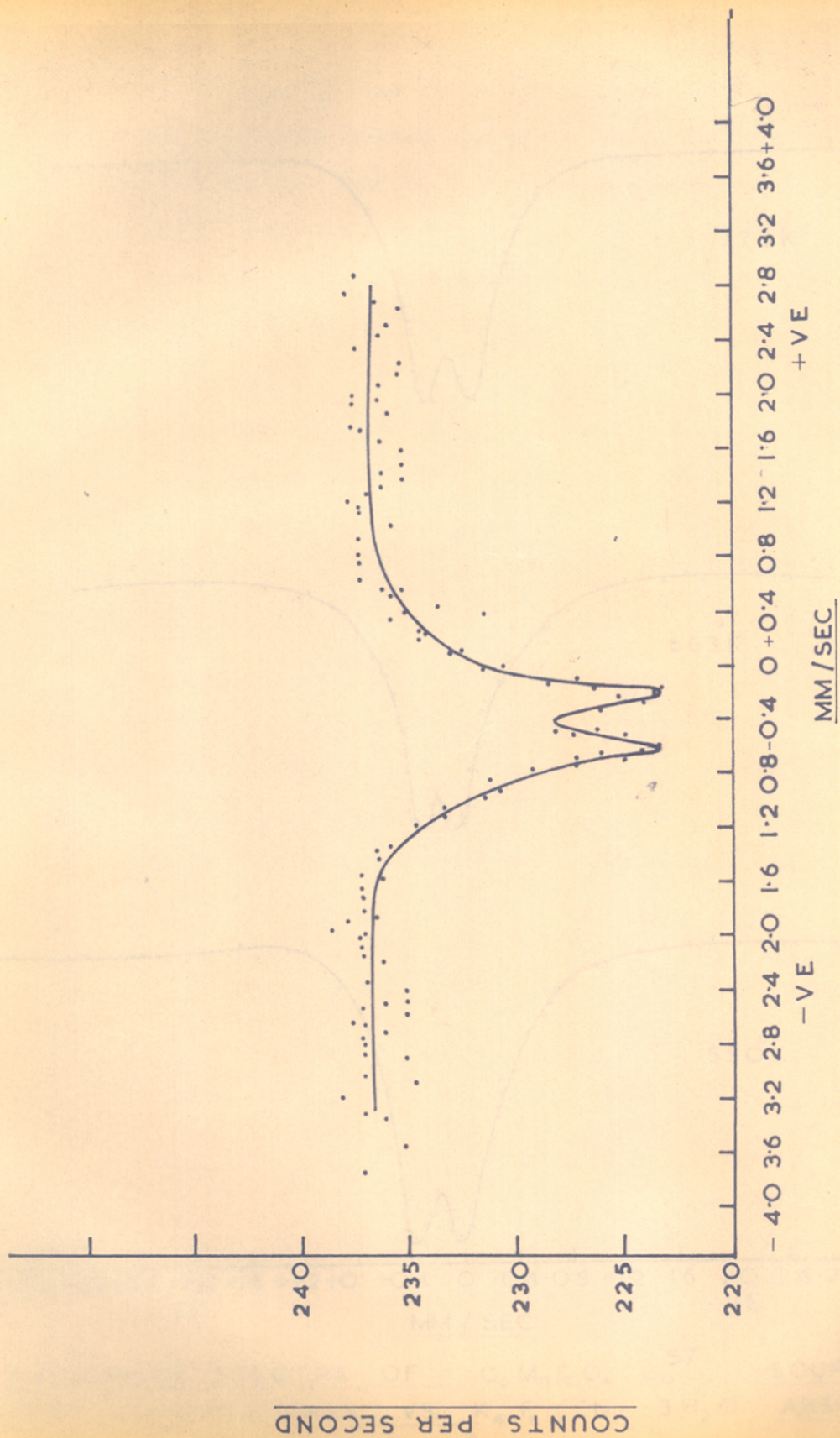


FIG.(34):MÖSSBAUER SPECTRUM OF CoMnFeO_4 AT 548°K

COUNTS PER SECOND

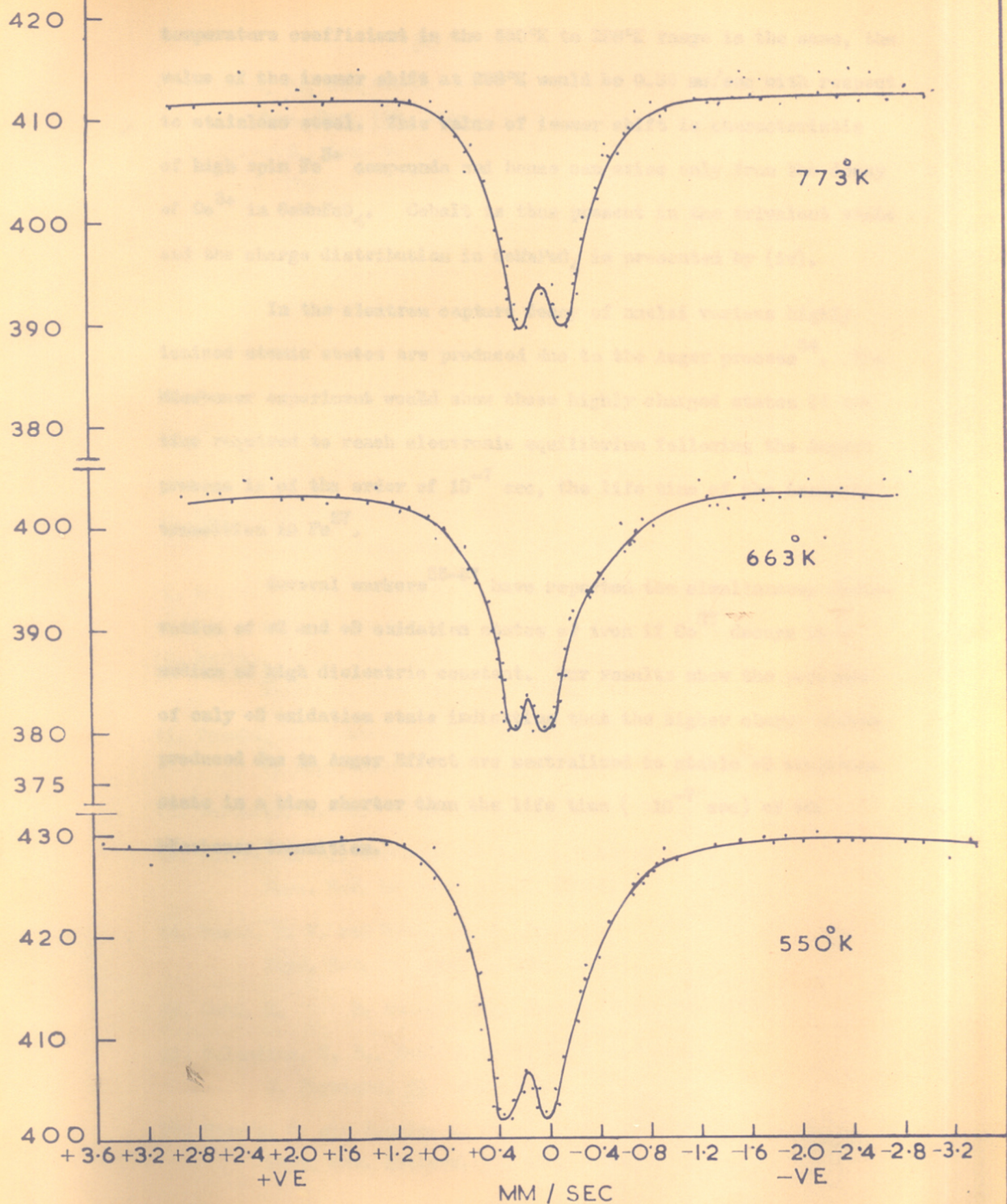


FIG. 35 THE MÖSSBAUER SPECTRA OF $\text{CoMnFeO}_4 : \text{Co}^{57}$ SOURCE AT
DIFFERENT TEMPERATURES VS. $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ ABSORBER
AT 298°K

temperature coefficient in the 550°K to 298°K range is the same, the value of the isomer shift at 298°K would be 0.30 mm/sec with respect to stainless steel. This value of isomer shift is characteristic of high spin Fe^{3+} compounds and hence can arise only from the decay of Co^{3+} in CoMnFeO_4 . Cobalt is thus present in the trivalent state and the charge distribution in CoMnFeO_4 is presented by (iv).

In the electron capture decay of nuclei various highly ionized atomic states are produced due to the Auger process⁵⁴. The Mössbauer experiment would show these highly charged states if the time required to reach electronic equilibrium following the Auger process is of the order of 10^{-7} sec, the life time of the isomeric transition in Fe^{57} .

Several workers⁵⁵⁻⁵⁷ have reported the simultaneous observation of +2 and +3 oxidation states of iron if Co^{57} decays in a medium of high dielectric constant. Our results show the presence of only +3 oxidation state indicating that the higher charge states produced due to Auger Effect are neutralized to stable +3 oxidation state in a time shorter than the life time (10^{-7} sec) of the Mössbauer transition.

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S U M M A R Y

This thesis deals with the use of the Mössbauer Effect to obtain useful information on the cation oxidation state and site distribution in mixed oxide or sulphide systems with spinel structure, especially those containing cations of variable valency which can occupy more than one possible site.

A number of model cubic spinel type compounds were prepared and their Mössbauer spectra studied. These spinels were so chosen that they contained either a Fe^{2+} ion or Fe^{3+} ion and at only one of the two possible sites viz., tetrahedral (A) or octahedral (B) sites. These are:

1) Normal spinels: $\text{Fe}[\text{Cr}_2]_4\text{O}_4$ and $\text{Fe}[\text{Cr}_2]_4\text{S}_4$ which have Fe^{2+} ions at only A sites.

2) Normal spinels $\text{Ge}[\text{Fe}_2]_4\text{O}_4$ and Inverse spinel $\text{In}[\text{FeIn}]_4\text{S}_4$ which contain Fe^{2+} ions only at (B) sites.

3) Inverse spinels $\text{Fe}[\text{CrNi}]_4\text{O}_4$ and $\text{Fe}[\text{MnCu}]_4\text{O}_4$ which contain Fe^{3+} ions at the A sites only.

4) Normal spinels $\text{Cd}[\text{Fe}_2]_4\text{O}_4$ and $\text{Zn}[\text{Fe}_2]_4\text{O}_4$ in which Fe^{3+} ions are at the B sites.

Mössbauer spectrum of $\text{Fe}[\text{Cr}_2]_4\text{S}_4$ at 25°C shows a single resonance absorption peak with an isomer shift of 0.72 ± 0.04 mm/sec and line-width of 0.48 ± 0.04 mm/sec. On the other hand, the Mössbauer spectrum at 25°C of $\text{Fe}[\text{Cr}_2]_4\text{O}_4$ which also contains Fe^{2+} ions at A sites only, shows a resonance absorption peak with an isomer shift of 0.96 ± 0.04 mm/sec but a line-width of 1.04 ± 0.04 mm/sec which is an order of magnitude larger than that of $\text{Fe}[\text{Cr}_2]_4\text{S}_4$. The

line width of the resonance line in the Mössbauer spectra of $\text{Fe}[\text{Cr}_2]_4\text{O}_4$ decreases to 0.80 ± 0.04 mm/sec when the absorber is heated to 100°C and thereafter it remains constant upto 150°C . The fact that the line width decreases with the increase of temperature, shows that the degeneracy of the $d_{x^2-y^2}$ and d_{z^2} states is lifted due to a local distortion around the A sites, which has not been determined by X-ray diffraction since the latter can only detect the effect of long range order. The Mössbauer spectrum at -194°C has a well separated doublet with a quadrupole splitting of 2.68 ± 0.04 mm/sec. This can be attributed to the tetragonal distortion of the lattice on account of Jahn-Teller Effect.

The Mössbauer spectra at 79°K of $\text{Ge}[\text{Fe}_2]_4\text{O}_4$ and $\text{In}[\text{FeIn}]_4\text{S}_4$, the two spinels which contain Fe^{2+} ions at the B sites show a quadrupole splitting of 2.78 ± 0.04 and 3.12 ± 0.04 mm/sec respectively. In an octahedrally symmetric environment, the three t_{2g} states are degenerate and hence equally populated by sixth electron of d^6 ion. Such a mixture of three d states would have cubic symmetry and should not give rise to quadrupole splitting. The observed quadrupole splitting in the spectra of these compounds has been explained due to the presence of a trigonal field at the B sites of the spinel structure.

$\text{Cd}[\text{Fe}_2]_4\text{O}_4$ and $\text{Zn}[\text{Fe}_2]_4\text{O}_4$ are "normal" cubic spinels in which Fe^{3+} ions are present at the B sites only. Their Mössbauer spectra at 79°K show quadrupole splitting of 0.64 ± 0.04 mm/sec and 0.32 ± 0.04 mm/sec respectively. Cd^{2+} and Fe^{3+} ions have electronic configuration which do not cause Jahn-Teller distortion. As pointed out earlier in the case of $\text{Ge}[\text{Fe}_2]_4\text{O}_4$, the observed quadrupole splittings in

$\text{Cd}[\text{Fe}_2]\text{O}_4$ and $\text{Zn}[\text{Fe}_2]\text{O}_4$ are due to the presence of the trigonal field at the B sites of the spinel structure. The comparatively larger quadrupole splitting observed for $\text{Ge}[\text{Fe}_2]\text{O}_4$ than for $\text{Cd}[\text{Fe}_2]\text{O}_4$ and $\text{Zn}[\text{Fe}_2]\text{O}_4$ is due to the presence of Fe^{2+} ion which is a more sensitive probe for the electric field gradient than the Fe^{3+} ions. The quadrupole splitting for $\text{Cd}[\text{Fe}_2]\text{O}_4$ found to be larger than that for $\text{Zn}[\text{Fe}_2]\text{O}_4$. This has been explained due to the presence at A sites of Cd^{2+} ions which are 25% larger in size than Zn^{2+} ions. The quadrupole splitting in both these spinels decreases with the decrease of temperature indicating that these two compounds on cooling to liquid nitrogen temperature approach closer to the ideal spinel structure.

The inverse cubic spinels $\text{Fe}[\text{CrNi}]\text{O}_4$ and $\text{Fe}[\text{MnCu}]\text{O}_4$ which contain Fe^{3+} ions at the (A) sites only are ferrimagnetic at room temperature. The Mössbauer spectra of these two spinels in their paramagnetic state have a well defined doublet with quadrupole splitting of 0.44 ± 0.04 mm/sec at 738°K and 0.50 ± 0.04 mm/sec at 727°K respectively. Their corresponding isomer shifts of 0.18 ± 0.04 and 0.19 ± 0.04 mm/sec respectively lie in the region of spin free Fe^{3+} compounds. The d^5 electronic configuration of the Fe^{3+} ion and the cubic point symmetry of the A sites cannot give rise to any EFG. The observed quadrupole splitting has been attributed to a EFG at the A sites on account of asymmetric charge distribution associated with the random distribution of trivalent and divalent ions on the neighbouring twelve (B) sites, which surround each (A) site. In the ferrimagnetic state, these spinels show a six-finger pattern with no quadrupole splitting. The quadrupole splitting (- ,

in the presence of axially symmetric EFG tensor with the symmetry axis at an angle θ , with respect to the magnetic axis is given by

$$C = \frac{e^2 q Q}{8I(2I-1)} [3m^2 - I(I+1)] (3 \cos^2 \theta - 1)$$

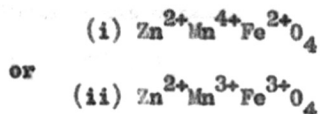
For $I = 3/2$,

$$C = \frac{e^2 q Q}{8} (3 \cos^2 \theta - 1)$$

If the magnetic field H is inclined at an angle $\theta = \cos^{-1} \frac{1}{\sqrt{3}}$ to the symmetry axis of the EFG, the hyperfine spectrum in the ferrimagnetic state would not show any quadrupole splitting. The effective magnetic fields in $\text{Fe}[\text{CrNi}]_4\text{O}_4$ and $\text{Fe}[\text{MnCu}]_4\text{O}_4$ have been found to be 507 ± 4 kOe and 522 ± 4 kOe at 79°K which on extrapolation to 0°K give a value of 520 ± 20 kOe and 530 ± 20 kOe respectively.

These results from the Mössbauer spectra of the above model cubic spinels have been used to determine the degree of inversion in FeAl_2O_4 . The cation distribution in FeAl_2O_4 is expected to be partially inverse. The Mössbauer spectrum at 298°K of FeAl_2O_4 shows three resonance peaks which can be resolved into two quadrupole split spectra with quadrupole splittings of 1.40 ± 0.04 and 2.80 ± 0.04 mm/sec, due to the Fe^{2+} ions on A sites and B sites respectively. Assuming the Lamb-Mössbauer factor to be equal for the Fe^{2+} ion at the A and B sites of FeAl_2O_4 , the percentage of Fe^{2+} ions at the B sites have been calculated to be 23%. The cation distribution was also determined by comparing the calculated and the observed intensities of the diffraction lines in the X-ray powder pattern. It was found that 25% of Fe^{2+} ions are present at the B sites, in agreement with the results obtained from the Mössbauer studies.

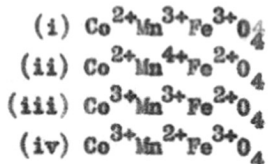
Mössbauer studies were also undertaken to determine the charge distribution in the spinels ZnMnFeO_4 and CoMnFeO_4 , in which the valencies of the cations have so far not been unambiguously established, since the elements Fe, Co and Mn can exist in a number of oxidation states. The charge distribution in ZnMnFeO_4 may be expressed in two possible ways:



The resistivity data and the value of lattice constants in the system $\text{ZnMn}_x\text{Fe}_{2-x}\text{O}_4$ indicate that the $\text{Fe}^{3+} - \text{Mn}^{3+}$ combination is more stable than the $\text{Fe}^{2+} - \text{Mn}^{4+}$ pair. On the other hand, the value of the curie constant calculated for the combination $\text{Mn}^{4+} - \text{Fe}^{2+}$ than the $\text{Mn}^{3+} - \text{Fe}^{3+}$ combination. The Mössbauer spectra of an absorber made of ZnMnFeO_4 , has an isomer shift of 0.47 ± 0.04 mm/sec and a quadrupole splitting of 0.50 ± 0.04 mm/sec, the Mössbauer parameters characteristic of spin-free Fe^{3+} ions, and hence it can be said without doubt that in the spinel ZnMnFeO_4 , Fe and Mn are in their trivalent states.

Determination of charge distribution in CoMnFeO_4 is more complicated and has not been attempted so far because all the three cations can have different valencies (Mn: 2 or 3 and 4, Fe: 2 and 3, Co: 2 and 3).

There are four possible ways of charge distribution in this spinel:



The Mössbauer spectrum of CoMnFeO_4 absorber at 548°K gives an isomer shift of 0.27 ± 0.04 mm/sec and quadrupole splitting of 0.38 ± 0.04 mm/sec. The value of isomer shift is characteristic of spin free Fe^{3+} ions, and hence the charge distribution indicated in (ii) and (iii) can be ruled out. Further information on the charge distribution was obtained by using Co^{57} doped CoMnFeO_4 as a source and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber in Mössbauer experiments. An isomer shift of 0.12 mm/sec at 550°K and a quadrupole splitting of 0.32 mm/sec can arise only if Co^{57} is in 3^+ state in CoFeMnO_4 . Hence the charge distribution should be $\text{Co}^{3+}\text{Mn}^{2+}\text{Fe}^{3+}\text{O}_4$.

The Mössbauer spectra were obtained on a constant velocity drive in which the source can be moved with respect to a stationary absorber with velocities upto 3.6 cm/sec in steps of 0.0036 cm/sec or its multiple. Co^{57} source was prepared on Cu backing. The spinels were prepared by solid-solid reaction.

CHAPTER V

APPENDIX

(a) X-ray diffraction results

TABLE 11 .
X-RAY DIFFRACTION RESULTS FOR FeCr_2O_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	M	111	4.840	8.380	
2	M	200	4.185	8.370	
3	S	220	2.950	8.350	
4	V.S.	113	2.530	8.370	
5	V.W.	222	2.408	8.350	
6	M	400	2.095	8.370	
7	V.W.	331	1.924	8.370	
8	W	420	1.869	8.360	8.366
9	M	115,333	1.613	8.370	
10	S	440	1.484	8.380	
11	V.W.	620	1.323	8.360	
12	W	335	1.278	8.385	
13	V.W.	444	1.210	8.370	
14	V.V.W.	642	1.120	8.370	
15	W	553,731	1.090	8.360	
16	V.V.W.	800	1.047	8.370	

V.S. Very strong
 S Strong
 M Medium
 W Weak
 V.W. Very weak
 V.V.W. Very very weak

TABLE 12
X-RAY DIFFRACTION RESULTS FOR GeFe_2O_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	S	220	2.985	8.410	
2	V.S.	113	2.545	8.420	
3	M	400	2.096	8.384	
4	W	422	1.716	8.410	
5	S	115,333	1.620	8.410	
6	V.S.	440	1.485	8.410	
7	V.V.W.	620	1.325	8.400	8.4106
8	W	622	1.270	8.425	
9	V.W.	642	1.124	8.410	
10	M.S.	553,731	1.0948	8.410	
11	V.W.	800	1.053	8.424	
12	V.W.	822	0.993	8.410	
13	M.S.	555,751	0.977	8.390	

TABLE 13X-RAY DIFFRACTION RESULTS FOR FeCr_2S_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	M.S.	111	5.763	9.985	
2	S	220	3.530	9.990	
3	V.S.	113	3.008	9.976	
4	S	400	2.498	9.994	
5	W	422	2.040	9.999	
6	M.S.	115,333	1.920	9.980	
7	M.S.	440	1.761	9.960	
8	V.W.	620	1.580	9.999	
9	V.W.	622	1.505	9.975	9.983
10	V.W.	444	1.439	9.960	
11	V.V.W.	711,551	1.390	9.926	
12	V.W.	553,731	1.304	10.000	
13	W	800	1.260	10.080	
14	W	733	1.22	9.990	
15	V.V.W.	822	1.169	9.920	
16	V.W.	840	1.120	10.000	

TABLE 14
X-RAY DIFFRACTION RESULTS FOR FeIn_2S_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	M.S.	220	3.739	10.580	
2	V.S.	113	3.190	10.590	
3	M.S.	400	2.633	10.532	
4	W	422	2.163	10.580	
5	M.S.	115,333	2.036	10.585	
6	M.S.	440	1.869	10.575	
7	V.V.W.	620	1.669	10.585	
8	V.W.	335	1.615	10.590	10.582
9	V.W.	444	1.530	10.595	
10	V.W.	642	1.419	10.620	
11	W	553,731	1.378	10.580	
12	W	800	1.324	10.592	
13	V.V.W.	822	1.247	10.590	
14	W	555,751	1.222	10.585	
15	W	840	1.182	10.590	

TABLE 15
X-RAY DIFFRACTION RESULTS FOR CaFe_2O_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	S	220	3.076	8.699	
2	V.S.	113	2.630	8.721	
3	W	400	2.178	8.712	
4	W	331	2.000	8.716	
5	M.S.	422	1.774	8.690	
6	S	115, 333	1.705	8.680	
7	V.S.	440	1.540	8.707	8.699
8	W	620	1.375	8.690	
9	M.S.	622	1.310	8.690	
10	V.W.	642	1.160	8.690	
11	M.S.	553, 731	1.130	8.685	
12	W	800	1.086	8.691	
13	W	822	1.026	8.700	

TABLE 16

X-RAY DIFFRACTION RESULTS FOR ZnFe_2O_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	W	111	4.855	8.415	
2	S	220	2.975	8.416	
3	V.S.	113	2.534	8.405	
4	M.S.	400	2.098	8.392	
5	M.S.	422	1.719	8.420	
6	M.S.	115,333	1.620	8.415	8.411
7	S	440	1.485	8.395	
8	V.V.W.	620	1.330	8.420	
9	W	335	1.283	8.405	
10	V.W.	642	1.125	8.425	
11	V.W.	553,731	1.096	8.420	
12	V.W.	800	1.051	8.412	
13	W	751	0.970	8.405	

TABLE 17X-RAY DIFFRACTION RESULTS FOR $\text{ZnMn}_{0.5}\text{Fe}_{1.5}\text{O}_4$

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	V.V.W.	200	4.245	8.490	
2	M.S.	220	2.999	8.490	
3	S	222	2.453	8.495	
4	V.W.	422	1.735	8.500	
5	W	115,333	1.635	8.500	
6	M.S.	531	1.450	8.550	8.507
7	V.V.W.	731,553	1.105	8.490	
8	W	800	1.070	8.560	
9	V.W.	733	1.039	8.495	
10	W	662	0.962	8.500	

TABLE 18

X-RAY DIFFRACTION RESULTS FOR ZnMnFeO_4

Intensity I	Indices hkl	$\frac{1}{d^2}$ d_{obs}^2	$\frac{1}{d^2}$ d_{cal}^2	Lattice parameters
W	101	0.0448	0.0444	
M.S.	112	0.1150	0.1161	
S.	211	0.1666	0.1672	$c' = c = 8.540 \text{ \AA}$
V.V.W.	204	0.3450	0.3420	$a = 5.713 \text{ \AA}$
W	303	0.399	0.3991	$a' = 8.079 \text{ \AA}$
W	224	0.462	0.4641	$\frac{c'}{a'} = 1.057$
V.V.W.	305	0.621	0.6184	

TABLE 19
X-RAY DIFFRACTION RESULTS FOR CoInFeO_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	W	111	4.856	8.420	8.409
2	M.S.	220	2.970	8.400	
3	S	113	2.534	8.405	
4	W	400	2.098	8.392	
5	V.W.	422	1.710	8.410	
6	W	115,333	1.620	8.410	
7	V.W.	440	1.485	8.410	
8	W	642	1.124	8.410	
9	W	553,731	1.095	8.410	
10	V.V.W.	800	1.054	8.432	
11	W	751,555	0.998	8.400	

TABLE 20
X-RAY DIFFRACTION RESULTS FOR FeCrNiO₄

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in ° Å	Average value of 'a' in ° Å
1	W	111	4.807	8.325	
2	V.V.W.	200	4.149	8.298	
3	M.S.	220	2.940	8.300	
4	S	113	2.495	8.280	
5	V.V.W.	222	2.398	8.300	
6	M.S.	400	2.080	8.320	
7	V.V.W.	420	1.855	8.295	
8	W	422	1.694	8.295	8.295
9	M.S.	115,333	1.595	8.280	
10	S	440	1.469	8.310	
11	W	620	1.310	8.300	
12	W	335	1.260	8.275	
13	V.V.W.	444	1.200	8.320	
14	V.V.W.	711,551	1.160	8.280	
15	V.V.W.	642	1.109	8.310	

TABLE 21X-RAY DIFFRACTION RESULTS FOR FeMnCuO_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	V.W.	111	4.830	8.370	
2	M.S.	220	2.960	8.370	
3	S	311	2.510	8.333	
4	V.W.	400	2.035	8.340	
5	V.W.	422	1.699	8.330	8.336
6	W	115,333	1.600	8.320	
7	M.S.	440	1.469	8.305	
8	V.V.W.	531	1.405	8.315	
9	M.S.	622	1.260	8.360	
10	W	553,731	1.084	8.340	
11	W	751,555	0.959	8.315	

TABLE 22

X-RAY DIFFRACTION RESULTS FOR FeAl_2O_4

Ring No.	Intensity I	Indices hkl	d	Lattice parameter 'a' in Å	Average value of 'a' in Å
1	S	220	2.865	8.103	
2	V.S.	113	2.448	8.117	
3	V.W.	400	2.032	8.128	
4	V.V.W.	331	1.862	8.116	
5	M	422	1.651	8.088	
6	S	115,333	1.558	8.080	
7	S	440	1.431	8.093	
8	V.W.	620	1.283	8.113	
9	W	335	1.235	8.097	8.096
10	V.W.	642	1.082	8.096	
11	W	731,553	1.055	8.103	
12	V.V.W.	800	1.015	8.120	
13	V.V.W.	822	0.9532	8.083	
14	W	751,555	0.9346	8.094	
15	W	931	0.8506	8.110	
16	W	844	0.8265	8.110	

TABLE 23

X-RAY INTENSITIES FROM FeAl_2O_4 POWDER PATTERN $(X\text{-ray}) = 0.70926 \text{ \AA}; a_o = 8.096 \text{ \AA}; u = 0.3885$

hkl	I_{obs}	I_{cal} for $\chi = 0.15$	I_{cal} for $\chi = 0.20$	I_{cal} for $\chi = 0.25$	I_{cal} for $\chi = 0.30$
220	67.70	68.25	66.70	64.50	60.40
113	100.00	100.00	100.00	100.00	100.00
400	26.80	17.30	18.60	22.00	23.80
331	3.92	5.28	3.74	3.82	2.92
224	25.50	26.30	25.40	24.90	22.20
115,333	55.90	57.90	57.50	58.25	56.60
440	82.90	74.50	76.60	77.00	76.00
620	11.00	9.85	9.90	9.35	8.60
335,226	23.80	18.05	19.55	18.90	18.60
642	13.30	14.20	14.60	13.30	12.70
731,553	14.10	25.30	26.00	26.20	26.20
800	11.80	9.30	9.55	9.80	9.50
Reliability factor	$R = \frac{\sum I_{\text{cal}} - I_{\text{obs}} }{\sum I_{\text{obs}}}$	0.116	0.098	0.086	0.090

Structure Factor of Cubic Spinels

<u>hkl</u>	<u>F_{hkl} (Structure factor)</u>
111	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} f_0 \times (\cos^3 2\pi u + \sin^3 2\pi u)$
220	$8 f_A + 32 f_0 \times \cos^2 4\pi u$
311	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 \times (\cos^2 2\pi u \cos 6\pi u - \sin^2 2\pi u \sin 6\pi u)$
222	$16 f_B + 32 f_0 \sin^3 4\pi u$
400	$8 f_A - 16 f_B + 32 f_0 \times \cos 8\pi u$
331	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} f_0 (\cos^2 6\pi u \cos 2\pi u + \sin^2 6\pi u \sin 2\pi u)$
422	$8 f_A + 32 f_0 \times \cos 8\pi u \cos^2 4\pi u$
511	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 (\cos 10\pi u \cos^2 2\pi u + \sin 10\pi u \sin^2 2\pi u)$
333	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 (\cos^3 6\pi u - \sin^3 6\pi u)$
440	$8 f_A + 16 f_B + 32 f_0 \cos^2 8\pi u$
531	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} f_0 \times (\cos 2\pi u \cos 6\pi u \cos 10\pi u - \sin 2\pi u \sin 6\pi u \sin 10\pi u)$
442	$32 f_0 \times \sin^2 8\pi u \sin 4\pi u$
620	$8 f_A + 32 f_0 \times \cos 12\pi u \cos 4\pi u$
533	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 (\cos 10\pi u \cos^2 6\pi u + \sin 10\pi u \sin^2 6\pi u)$
622	$16 f_B - 32 f_0 \times \sin 12\pi u \sin^2 4\pi u$
444	$8 f_A - 16 f_B + 32 f_0 \cos^3 8\pi u$
711	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} f_0 (\cos^2 2\pi u \cos 14\pi u - \sin^2 2\pi u \sin 14\pi u)$
551	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} f_0 (\cos^2 10\pi u \cos 2\pi u + \sin^2 10\pi u \sin 2\pi u)$
642	$8 f_A + 32 f_0 \times \cos 12\pi u \cos 8\pi u \cos 4\pi u$

hklF_{hkl}

731	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 (\cos 2\pi u \cos 6\pi u \cos 14\pi u + \sin 2\pi u \sin 6\pi u \sin 14\pi u)$
553	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 (\cos^2 10\pi u \cos 6\pi u - \sin^2 10\pi u \sin 6\pi u)$
800	$8 f_A + 16 f_B + 32 f_0 \cos 16\pi u$
733	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} f_0 (\cos 14\pi u \cos^2 6\pi u - \sin 14\pi u \sin^2 6\pi u)$
644	$32 f_0 \times \sin 12\pi u \sin^2 8\pi u$
822	$8 f_A + 32 f_0 \times \cos^2 12\pi u$
751	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 (\cos 14\pi u \cos 10\pi u \cos 2\pi u - \sin 14\pi u \sin 10\pi u \sin 2\pi u)$
555	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 (\cos^3 10\pi u + \sin^3 10\pi u)$
662	$16 f_B + 32 f_0 \times \sin^2 12\pi u \sin 4\pi u$
840	$8 f_A - 16 f_B + 32 f_0 \times \cos 16\pi u \cos 8\pi u$
911	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} (\cos 18\pi u \cos^2 2\pi u + \sin 18\pi u \sin^2 2\pi u)$
753	$4\sqrt{2} f_A - 8 f_B + 16\sqrt{2} f_0 (\cos 14\pi u \cos 10\pi u \cos 6\pi u + \sin 14\pi u \sin 10\pi u \sin 6\pi u)$
842	$32 f_0 \times \sin 16\pi u \sin 8\pi u \sin 4\pi u$
664	$8 f_A + 32 f_0 \times \cos^2 2\pi u \cos 8\pi u$
931	$4\sqrt{2} f_A + 8 f_B + 16\sqrt{2} f_0 \times (\cos 18\pi u \cos 16\pi u \cos 2\pi u - \sin 18\pi u \sin 16\pi u \sin 2\pi u)$
844	$8 f_A + 16 f_B + 32 f_0 \times \cos 16\pi u \cos^2 8\pi u$

where

 f_A = Atomic scattering factor of atom on A sites f_B = Atomic scattering factor of atom on B sites f_0 = Atomic scattering factor of oxygen

Calculation of interatomic distance in cubic spinel.

$$M_{\text{oct}} - 0 = a \sqrt{\frac{1}{16} - \frac{1}{2} + 3\delta^2}$$

$$M_{\text{tet}} - 0 = a \left(\frac{1}{8} + \delta \right) \sqrt{3}$$

$$M_{\text{oct}} - M_{\text{oct}} = \frac{1}{4} a \sqrt{2}$$

$$M_{\text{oct}} - M_{\text{tet}} = \frac{1}{8} a \sqrt{11}$$

$$M_{\text{tet}} - M_{\text{tet}} = \frac{1}{4} a \sqrt{3}$$

where a = cell edge, $\delta = u - 3/8$