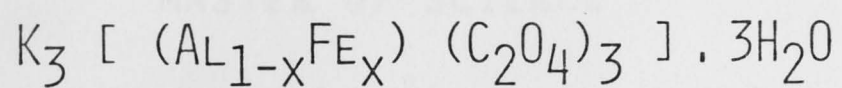


MÖSSBAUER EFFECT STUDY OF THE
PARAMAGNETIC HYPERFINE STRUCTURE
OF



Department of Chemistry

School of General Studies

The Australian National University

April 1970

MÖSSBAUER EFFECT STUDY OF THE PARAMAGNETIC HYPERFINE

STRUCTURE OF $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$

A Thesis submitted for
the Degree
of
MASTER OF SCIENCE

by

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I would like to thank Professor R.N. Harrison for the opportunity to continue my studies in this department and the Australian Government for the award of a Colombo Plan Scholarship which has enabled me to study here.

This thesis contains no material which I have presented for any other degree or diploma at any university, and to the best of my knowledge and belief, no material previously published or written by another person, except where due reference is made in the text of the thesis.

Chindarat Chirarat

Chindarat Chiraratvatana

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ABSTRACT

The objective of this study was the application of Mössbauer effect to resolve the hyperfine structure of Fe(III) ion in $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ which is greatly broadened by spin-spin relaxation and consequently to obtain information about its spin Hamiltonian.

^{57}Fe Mössbauer absorption spectra were recorded for powdered and single-crystal solid solution samples of $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ with x in the range 0.002 to 0.25 at 4.2 K. Applied magnetic fields of up to 1 kOe were also used to facilitate the resolution of the hyperfine spectra, in particular the $s_z = \pm 1/2$ Kramers' doublet. Our findings show that the resolved hyperfine spectra arise from a system of Kramers' doublets with the $\pm 1/2$ states lying lowest and small separation between Kramers' doublets because the zero-field splitting parameter D is positive and very small ($D = +0.20 \pm 0.05 \text{ cm}^{-1}$). The site symmetry of the Fe(III) ion is not axial ($\lambda \approx 0.05 \pm 0.01$). The magnetic field at the nucleus associated with the $\pm 5/2$ Kramers' doublet was found to be $540 \pm 5 \text{ kOe}$. The quadrupole interaction energy ($1/4e^2qQ$) is equal to 0.05 mm sec^{-1} and the asymmetry parameter (η) is equal to 0.15.

Additional experiments were performed which confirmed the above results. First we measured the hyperfine spectra of frozen solutions. The zero-field spectra were found to be slightly different from those of the solid solutions, but the spectra in small magnetic fields (60-500 Oe) were essentially

identical. This indicates that the states of the Fe(III) ions in these two diverse samples differ only slightly and therefore are determined predominantly by the ligands of the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ complex ion.

The spectra of solid solutions and frozen solutions were also recorded at 1.3 K and revealed an interesting phenomenon. At 1.3 K the magnetic hyperfine spectra exhibit a selective reduction in intensities and broadening of lines. A qualitative argument is presented which explains this unusual change in paramagnetic hyperfine structure as a consequence of the temperature-dependent electronic spin-spin relaxation time. The intralevel electronic spin-spin relaxation of the $\pm 1/2$ ground Kramers' doublet becomes faster as a result of depopulation of the excited Kramers' doublets at lower temperature.

CONTENTS

	Page
<u>Chapter 1</u> Introduction	1
<u>Chapter 2</u> Some aspects of Mössbauer spectroscopy of ^{57}Fe	6
2.1 Hyperfine spectra from paramagnetic ^{57}Fe	6
2.1.1 Crystal field interaction	6
2.1.2 Magnetic hyperfine interaction	8
2.1.3 Nuclear quadrupole interaction	14
2.1.3.1 Energy levels and transition probability in the presence of nuclear magnetic and quadrupole interactions	17
2.2 Relaxation effects	19
2.3 Spin relaxation mechanism	21
2.3.1 Spin-spin relaxation	21
2.3.2 Spin-lattice relaxation	23
2.4 Calculation of spectrum	24
2.5 The application of magnetic field to observe spectra from each spin states	25
<u>Chapter 3</u> Experimental	29
3.1 Mössbauer spectrometer system	29
3.1.1 Source	29
3.1.2 The spectrometer	29
3.1.3 Detector	30
3.1.4 Cryostat	30
3.1.5 Magnetic field	30
3.1.6 Variable temperature controller	30
3.1.7 Evaluation of Mössbauer spectral parameters	31
3.2 Preparation of potassium trisoxalatoferate(III) trihydrate $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	33
3.3 Preparation of potassium trisoxalatoaluminate(III) trihydrate $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	34
3.4 Preparation of solid-solution absorbers	35
3.4.1 Powdered samples	35
3.4.2 Single crystal samples	36
3.5 Preparation of frozen solution samples	37
3.6 Analysis and quality control of samples	37
3.6.1 Chemical analysis	37
3.6.2 Physical analysis	38
<u>Chapter 4</u> Results and Discussions	39
4.1 Spectra of solid solutions at various concentrations	39
4.2 Spectra of powdered samples in applied magnetic fields	42
4.3 The interpretation of experimental spectra	42
4.4 Further investigations	44

	Page
4.4.1 Application of magnetic field to single crystal sample	44
4.4.2 Measurement of resolved spectra at 1.3 K	45
4.4.3 Experiments with frozen solutions	50
4.5 Conclusion and prospect [Figs. 4.1-4.11 included]	52 55-66
APPENDIX A X-ray single crystal structure of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$	67
APPENDIX B X-ray powder diffraction pattern for $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$	69
APPENDIX C Mössbauer spectrum of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ at room temperature	70
REFERENCES	71

CHAPTER 1

INTRODUCTION

The Mössbauer effect involves the resonance of nuclear gamma radiation and can be observed during recoilless (zero-phonon transitions) emission and absorption of radiation in a solid matrix. It can be exploited as a spectroscopic method by observing chemically dependent hyperfine interactions. It was first observed by R. Mössbauer¹ in 1957. Mössbauer spectroscopy has since found applications in many diverse fields such as solid state physics, chemistry, biology, geology, etc. Its great value arises from the fact that the width of the emission (or absorption) lines resulting from transitions of metastable nuclear levels are often smaller than the interactions between the nucleus and electrons, the so-called hyperfine interactions. This extremely high degree of resolution (ca. 10^{-2}) has allowed the observation of phenomena which before the Mössbauer time were considered to be impossible, for example, a laboratory measurement gravitational red shift and observation of the Zeeman splitting of the nuclear levels.

It has been well established²⁻⁵ that Mössbauer effect is a very powerful technique for investigation of magnetic hyperfine structure in paramagnetic compounds. Paramagnetic hyperfine structure can be observed in the absence of macroscopic magnetisation if the electronic relaxation time can be made sufficiently long compared to nuclear Larmor precession time. This structure is, of course, quite sensitive to

electronic relaxation times and consequently contains a great deal of information about electronic relaxation as well as spin Hamiltonian parameters.

Potassium trisoxalatoferrate(III) trihydrate is a high-spin coordination complex. It belongs to the monoclinic crystal system with space group $P2_1/C$. There are four molecules in one unit cell and the structure is shown Figure (1.1) with atomic distance in table (A.1) and (A.2).^{*} The unit cell dimensions are $a=7.66$, $b=19.87$, $c=10.27$, $\beta=105^\circ 6'$ and the density is 2.142 gcm^{-3} . The Fe(III) ion is octahedrally coordinated by three planar bidentate oxalate ligands. The inner oxygen atoms form a slightly distorted octahedron round the central iron atom.

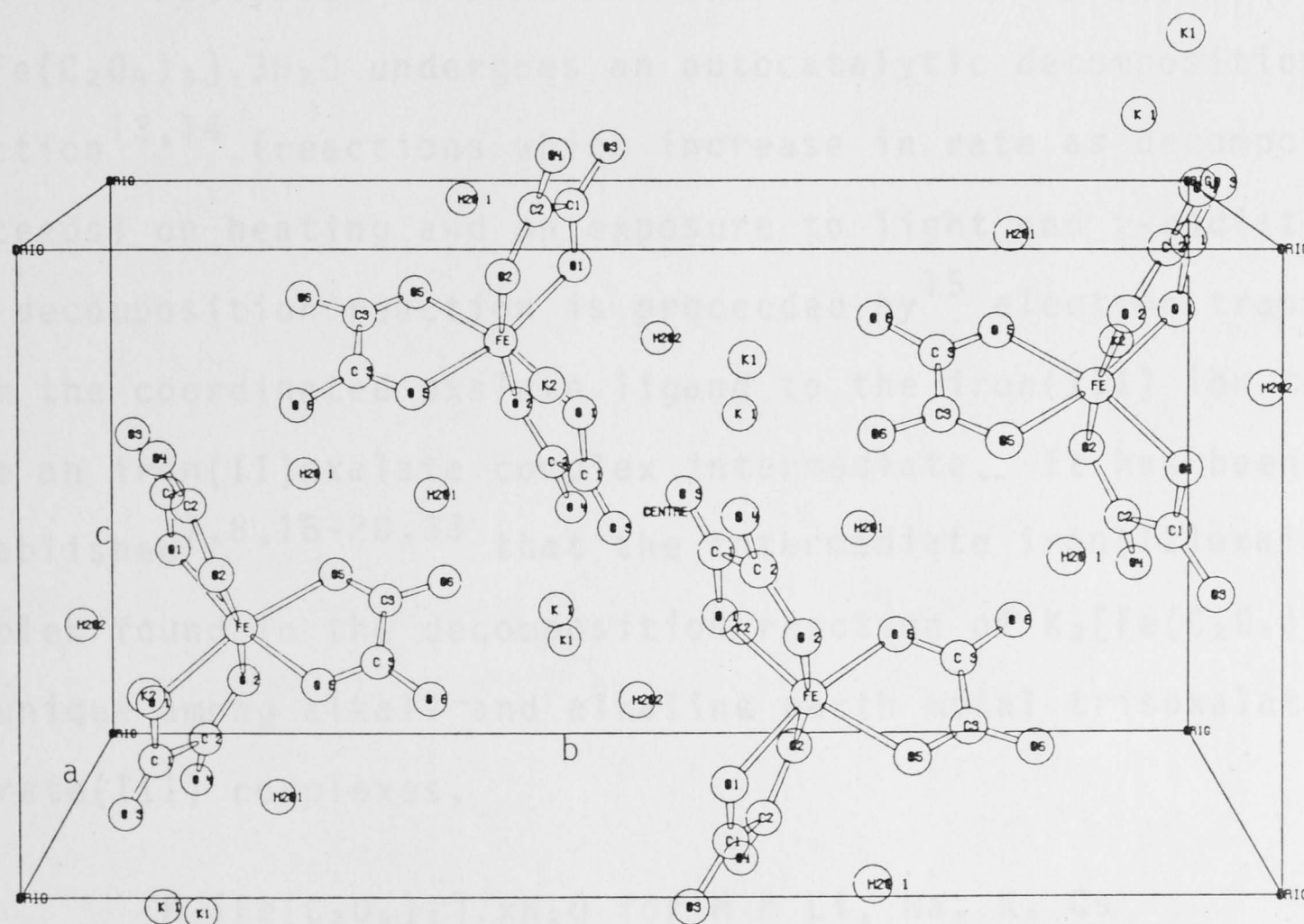
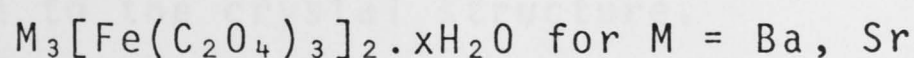
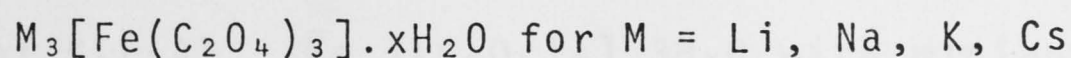


Figure (1.1) Unit cell contents of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ generated from crystal structure data from reference 6

* See Appendix A

The Mössbauer spectrum of potassium trisoxalato-ferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ is a broad singlet with a half-width around 2 mm sec^{-1} ^{7,8*} which is about ten times the natural line-width expected from the 14.4 keV state of ^{57}Fe . It has been established that the broadening is due to spin-spin relaxation involving adjacent Fe(III) ions such as is common in high-spin iron(III) complexes⁹. Barb et al.¹⁰ have simulated the broad singlet using the expression of Afanas'ev¹¹ and Blume¹² for the lineshape in the presence of electronic relaxation, but only in terms of empirical parameters that cannot be immediately related to the electronic structure of the Fe(III) ion and its environment.

Potassium trisoxalato-ferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ undergoes an autocatalytic decomposition reaction^{13,14} (reactions which increase in rate as decomposition proceeds) on heating and on exposure to light and γ -radiation. The decomposition reaction is proceeded by¹⁵ electron transfer from the coordinated oxalate ligand to the iron(III) ion to form an iron(II)oxalate complex intermediate. It has been established^{7,8,16-20,33} that the intermediate iron(II)oxalate complex found in the decomposition reaction of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ is unique among alkali and alkaline earth metal trisoxalato-ferrate(III) complexes,



According to our previous experiments²⁰, thermal decomposition in air always produces an iron(III)oxalate complex prior to

* See Appendix C

formation of the iron(II)oxalate complex intermediate. We believe that the elucidation of the identity of this compound will lead to better understanding of the unique decomposition pathway of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$. The Mössbauer spectrum of this iron(III)oxalate complex intermediate is a doublet with quadrupole splitting 0.7 mm sec^{-1} . It has been suggested¹⁶ that this doublet is produced by the anhydrous $K_3[Fe(C_2O_4)_3]$. The relaxation processes apparent in the hydrated compound were presumed to have been modified by the thermal treatment.

One of the objectives of the present work was to resolve the paramagnetic hyperfine structure of the Mössbauer spectrum of this complex experimentally in order to see if the quadrupole splitting is compatible with the above suggestion. Another objective was to obtain a more detailed understanding of the relaxation broadened Mössbauer spectrum of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ in terms of the electronic structure of the Fe(III) ion and the symmetry of its environment. We accomplished these objectives by the experiments described below.

Because spin-spin relaxation is concentration-dependent, it is possible to slow it down sufficiently to resolve paramagnetic hyperfine structure by dilution in a diamagnetic host lattice. Since $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ is isomorphous with $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ we can prepare a solid solution of $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ with minimum of distortion to the crystal structure.

From the hyperfine structure and its dependence on temperature and applied magnetic fields, it is possible to estimate the sign and magnitude of the zero-field splitting parameter D and the quadrupole splitting (ΔE_Q) and consequently to deduce the details of the electronic structure of the Fe(III) ion and its interactions with neighbouring ions in the crystal.

Definitions will be given only of the essential aspects which are relevant to the work of this laboratory, in particular the hyperfine interactions from a general point of view in complexes.

2.1. Hyperfine structure from spectroscopic data

The complete spin Hamiltonian for the Fe(III) ion is expressed as a sum of operators

$$H = H_{CF} + H_{H} + H_{Q} + H_{HF} + H_{Z} \quad (2.1)$$

where H_{CF} , H_{H} and H_{Q} are the crystal field, the magnetic hyperfine and nuclear electric quadrupole interaction respectively. The last two terms represent the electron and nuclear Zeeman interactions respectively in an external magnetic field H .

2.1.1. The crystal field interaction

The crystal field Hamiltonian is conventionally written as a sum of an axial, an orthorhombic and a cubic term

$$H_{CF} = H_{ax} + H_{or} + H_{cu} \quad (2.2)$$

CHAPTER 2

SOME ASPECTS OF MÖSSBAUER SPECTROSCOPY OF ^{57}Fe

The general description of theory and instrumentation has been well documented by many authors^{21,22} and therefore it will not be given here. In this chapter outlines and definitions will be given only of the essential theoretical aspects which are relevant to the work of this thesis. In particular the hyperfine interactions from high-spin iron(III) complexes.

2.1 Hyperfine spectra from paramagnetic ^{57}Fe

The complete spin Hamiltonian for the paramagnetic Fe(III) ion is expressed as a sum of operators²³

$$\mathcal{H} = \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{M}} + \mathcal{H}_{\text{Q}} + g_e \beta_e \vec{H} \cdot \vec{S} - g_N \beta_N \vec{H} \cdot \vec{I} \quad , \quad (2.1)$$

where $\mathcal{H}_{\text{CF}}$, $\mathcal{H}_{\text{M}}$ and $\mathcal{H}_{\text{Q}}$ are the crystal field, the magnetic hyperfine and nuclear electric quadrupole interaction respectively. The last two terms represent the electronic and nuclear Zeeman interactions respectively in an external magnetic field H .

2.1.1 The crystal field interaction

The crystal field Hamiltonian is conventionally written as a sum of an axial, an orthorhombic and a cubic term

$$\mathcal{H}_{\text{CF}} = \mathcal{H}_{\text{ax}} + \mathcal{H}_{\text{rh}} + \mathcal{H}_{\text{cub}} \quad , \quad (2.2.1)$$

$$\text{where } \mathcal{H}_{ax} = D[S_z^2 - \frac{1}{3}S(S+1)] \quad (2.2.2)$$

$$\mathcal{H}_{rh} = E[S_x^2 - S_y^2]$$

$\mathcal{H}_{cub}$ contains terms of fourth order in S , but it is often negligible compared to $\mathcal{H}_{ax}$ and $\mathcal{H}_{rh}$ when the crystal field splitting is large compared to the electronic Zeeman term²⁸. The crystal field interaction for the 6S ground state of the Fe(III) ion which reflects the local symmetry around the Fe(III) ion, has been given in general form by Bleaney and Stevens as²⁴

$$\begin{aligned} \mathcal{H}_{CF} = & \frac{a}{6}[S_\epsilon^4 + S_\eta^4 + S_\rho^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] + D[S_z^2 - \frac{1}{3}S(S+1)] \\ & + \frac{F}{180}[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2] \\ & + E(S_x^2 - S_y^2), \end{aligned} \quad (2.2.3)$$

where (ϵ, η, ρ) are the axes of cubic (or octahedral) symmetry which in general may not coincide with the axes (x, y, z) of lower symmetry. The term 'a' represents the basic cubic symmetry, whereas D , F and E represent the second order axial (trigonal or tetragonal distortion), fourth order axial (usually very small) and the orthorhombic terms respectively. For axial symmetry $\lambda = E/D = 0$ and for orthorhombic symmetry $0 < \lambda \leq 1/3$.

According to Kramers' theorem Fe(III) ion has time-reversed spin states that are always degenerate provided there

is no magnetic field present. The crystal field splits the 6S state into three Kramers' doublets; their eigenstates are, in general, the appropriate linear combinations of the three doublets with $S_z = |\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$. As the zero-field splitting parameter D is the most important term in the crystal field, the ordering of spin levels and their Boltzmann populations are determined mainly by the sign and magnitude of D itself. The zero-field splitting between the $\pm 1/2$ and $\pm 3/2$ states being $2D[1 + 3(E/D)^2]^{1/2} \approx 2D$ if $D \gg E$, and between the $\pm 3/2$ and $\pm 5/2$ states $\approx 4D$. If D is negative, the $\pm 5/2$ state is lowest, whereas if it is positive, the $\pm 1/2$ state is lowest. The above concepts are perhaps best summarised by means of an energy level diagram in Figure (2.1).

2.1.2 Magnetic hyperfine interaction

The magnetic hyperfine interaction Hamiltonian $\mathcal{H}_M$, which represents the coupling between the electrons and the nucleus is given by^{25,26}

$$\mathcal{H}_M = -g_N \beta_N g_e \beta_e \left[\frac{8\pi}{3} \delta(r) \vec{S} + \frac{\vec{L}}{r^3} + \left(\frac{3(\vec{S} \cdot \vec{r})\vec{r}}{r^5} - \frac{\vec{S}}{r^3} \right) \right] \cdot \vec{I} \quad , \quad (2.3)$$

where g_N and β_N are the nuclear g-value and nuclear magneton, and g_e and β_e are the electronic g-value and Bohr magneton respectively. $\vec{L}$ and $\vec{S}$ represent the electronic orbital and spin angular momentum of the atom, and $\vec{I}$ is the nuclear spin. $\delta(r)$ represents the s-electron density at the nucleus (where $r = 0$).

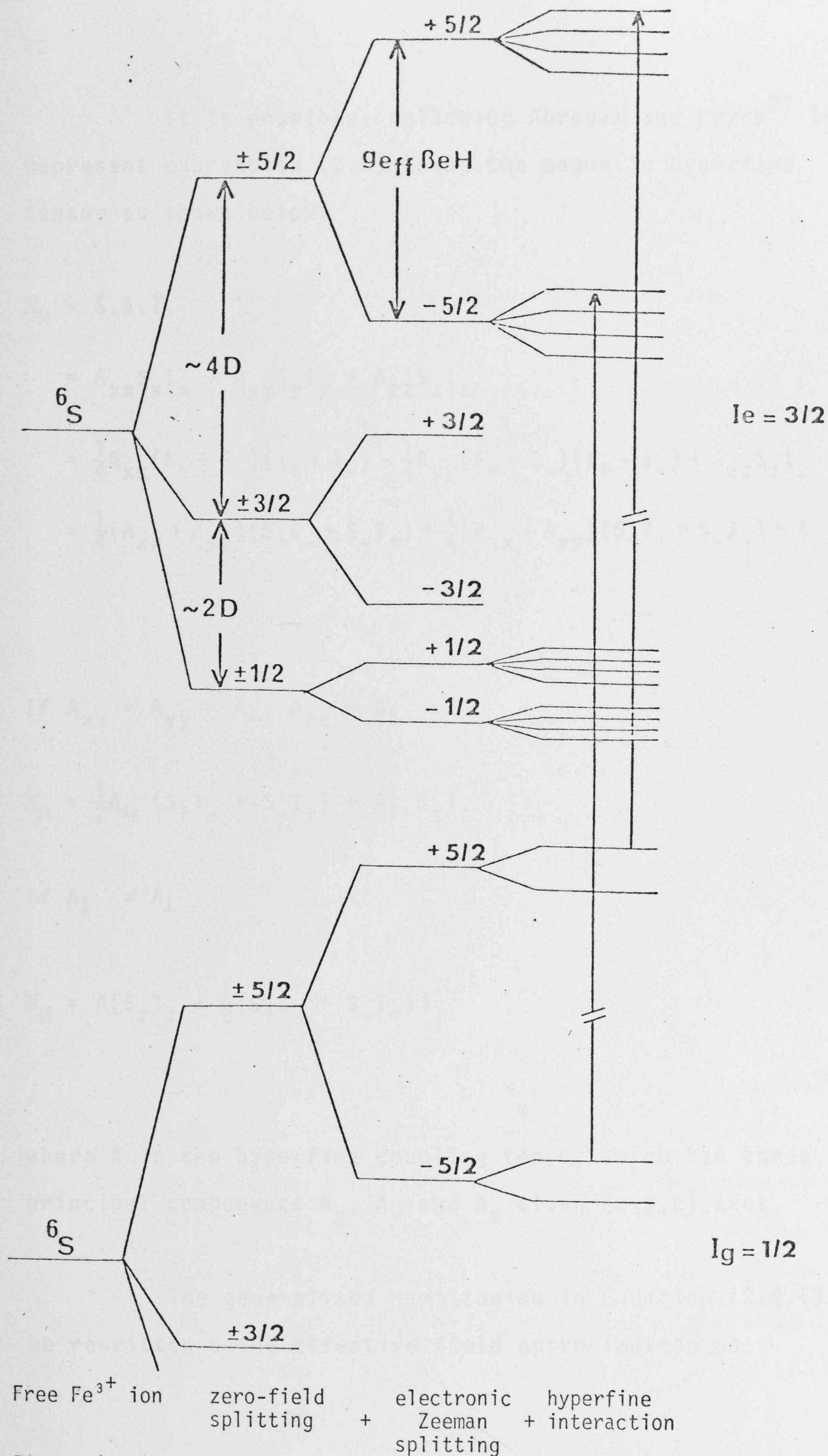


Figure (2.1) Energy level diagram for the ground state 6S of a high-spin Fe^{3+} ion. Two typical Mössbauer transition are indicated.

It is possible, following Abragam and Pryce²⁷ to represent expression (2.3) using the magnetic hyperfine tensor as shown below.

$$\mathcal{H}_M = \vec{S} \cdot \mathbf{A} \cdot \vec{I}. \quad (2.4.1)$$

$$\begin{aligned} &= A_{xx} S_x I_x + A_{yy} S_y I_y + A_{zz} S_z I_z \\ &= \frac{1}{4} A_{xx} (S_+ + S_-)(I_+ + I_-) - \frac{1}{4} A_{yy} (S_+ - S_-)(I_+ - I_-) + A_{zz} S_z I_z \\ &= \frac{1}{4} (A_{xx} + A_{yy}) (S_+ I_- + S_- I_+) + \frac{1}{4} (A_{xx} - A_{yy}) (S_+ I_+ + S_- I_-) + A_{zz} S_z I_z \end{aligned} \quad (2.4.2)$$

$$\text{If } A_{xx} = A_{yy} = A_{\perp}, \quad A_{zz} = A_{\parallel}$$

$$\mathcal{H}_M = \frac{1}{2} A_{\perp} (S_+ I_- + S_- I_+) + A_{\parallel} S_z I_z \quad (2.4.3)$$

$$\text{If } A_{\parallel} = A_{\perp}$$

$$\mathcal{H}_M = A [S_z I_z + \frac{1}{2} (S_+ I_- + S_- I_+)] \quad (2.4.4)$$

where A is the hyperfine coupling tensor which has three principal components A_x , A_y and A_z along (x, y, z) axes.

The generalised Hamiltonian in Equation (2.4.1) may be rewritten using effective field approximation as

$$\mathcal{H}_M = \langle \vec{S} \cdot \vec{A} \rangle \cdot \vec{I}$$

and $\vec{H}_{\text{eff}} \propto \langle \vec{S} \cdot \vec{A} \rangle$ (2.5.1)

where $\vec{H}_{\text{eff}}$ is the effective magnetic hyperfine field.

The coupling between the nuclear magnetic moment μ and the electrons may be rewritten:

$$\begin{aligned} \mathcal{H}_M &= - \mu \cdot \vec{H}_{\text{eff}} \\ &= - g_N \beta_N \vec{H}_{\text{eff}} \cdot \vec{I} \end{aligned} \quad (2.5.2)$$

In the simplest case of an effective magnetic field along the z axis, this interaction becomes²⁸

$$\mathcal{H}_M = - g_N \beta_N \vec{H}_{\text{eff}} \cdot \vec{I}_z \quad (2.5.3)$$

The effective field approach is a simplified description of the interaction that is valid under certain circumstances. One considers that the electron interact with the nucleus via a magnetic field at the nucleus produced by the electrons. As a consequence of treating the interaction this way the back effect of the nuclear magnetic moment on the electronic system is ignored. Therefore the electronic system is assumed to be

unaffected by the interaction and any admixture of electronic states is negligible. Generally if the electronic level separation is large compared to the magnetic hyperfine interaction energy ($\sim 10^{-2} \text{ cm}^{-1}$) this approximation is perfectly valid. However, if they are the same order of magnitude there may be mixing of the electronic states by the hyperfine operators and the effective field approximation will not be applicable.

The hyperfine tensor, A , may be considered to be the sum of two anisotropic contributions, arising from orbital and spin-dipolar fields and an isotropic term, i.e. when

$$\mathcal{H}_M = \mathcal{H}_L + \mathcal{H}_D + \mathcal{H}_C \quad (2.6)$$

$$\vec{H}_{\text{eff}} = \vec{H}_L + \vec{H}_D + \vec{H}_C \quad (2.7)$$

The contributing terms are

(1) $\vec{H}_C$ represents the Fermi contact magnetic field at the nucleus. The Fermi contact interaction arises from the direct coupling between the nuclear magnetic moment and the s-electron density at the nucleus, is given by^{29,30}

$$\vec{H}_C = - \frac{8\pi}{3} g_e \beta_e \vec{S} \langle \sum_s [\psi_{s\uparrow}^2(0) - \psi_{s\downarrow}^2(0)] \rangle, \quad (2.8)$$

$$= - g_e \beta_e \langle r^{-3} \rangle K \langle \vec{S} \rangle \quad (g_e = 2)$$

where $\psi_{s\uparrow}^2(0)$ and $\psi_{s\downarrow}^2(0)$ are the s-electron densities at the nucleus ($r=0$) with spin-up and spin-down respectively, K is a constant describing the spin density and r is the 3d electron radial coordinate.

(2) $\vec{H}_L$ is the orbital magnetic field at the nucleus produced by the orbital magnetic moment of the electron given by^{30,24}

$$\vec{H}_L = g_e \beta_e \langle r^{-3} \rangle \langle \vec{L} \rangle, \quad (2.9)$$

$$= g_e \beta_e \langle r^{-3} \rangle (g - 2) \langle \vec{S} \rangle$$

where $\langle \vec{L} \rangle$ is the expected value of the orbital angular momentum and r is the radius of the electronic orbit.

(3) $\vec{H}_D$ the dipolar magnetic field at the nucleus produced by the net spin of the ion is given by^{24,26,30}

$$\vec{H}_D = g_e \beta_e \langle r^{-3} \rangle \left[\frac{3(\vec{S} \cdot \vec{r})}{r^2} - S \right]. \quad (2.10)$$

In an axially symmetric crystal field,

$$\vec{H}_D = g_e \beta_e \langle r^{-3} \rangle \langle 3\cos^2\theta - 1 \rangle \langle \vec{S} \rangle \quad (2.11)$$

Using Stevens'²⁴ method of operator equivalents, Equation (2.10) becomes

$$\vec{H}_D = -2\beta_e \langle r^{-3} \rangle \alpha \left[\frac{3}{2} \vec{L}(\vec{L} \cdot \vec{S}) + \frac{3}{2} (\vec{L} \cdot \vec{S}) \vec{L} - L(L+1) \vec{S} \right], \quad (2.12)$$

where α is a constant which depends on the electronic configuration of the ion.

This contribution is non-zero only when the orbitals are such that there is an aspherical spin density.

As expected, $\vec{H}_{\text{eff}} = h \langle \vec{S} \rangle$; in fact $\vec{H}_{\text{eff}} = h' \langle r^{-3} \rangle \langle \vec{S} \rangle$, where h and h' are constants. It is of importance to know, if only approximately, the value of the constant h for the various ionic states encountered.

When high-spin Fe(III) is in a pure 6S state, H_L is zero (no orbital moment), H_D is zero (the ion has spherical symmetry) and so the hyperfine field is equal to H_C . The calculated unrestricted Hartree-Fock value for free ion, $S = 5/2$ Fe(III) is -630 kOe ³⁰. Experimentally, hyperfine

field of -622 kOe in FeF_3 ³¹ and -572 kOe in ferric ammonium alum diluted in aluminium ammonium alum³² have been observed, but more usually, the hyperfine field is found to be approximately -550 kOe^{2,34}, so the empirical relation for the hyperfine field per spin expectation value in "ionic" high spin Fe(III) compounds is

$$H_{\text{eff}} = -220 \langle S_z \rangle \text{ kOe} \quad (2.13)$$

The magnitude of the hyperfine field is decreased by covalency, since in symmetry lower than cubic, a small dipolar field is produced by covalent mixing of electrons from the ligands and the dipolar contribution is usually positive, opposing the negative core polarisation term. In addition when the electrons of the iron ion are delocalised on to the ligands to covalent bonding, the spin density at the nucleus may be reduced, leading to a direct reduction in the hyperfine field. In fact for high-spin Fe(III) compounds, the hyperfine field appears to be much more sensitive than the isomer shift to small changes in chemical bonding^{35,36}.

2.1.3 Nuclear quadrupole interaction

The spin Hamiltonian which describes the nuclear quadrupole interaction can be written as³⁷

$$H_Q = \frac{eQ}{2I(2I-1)} (V_{zz} I_z^2 + V_{yy} I_y^2 + V_{xx} I_x^2) \quad (2.14)$$

where $-e$ is the charge of the electron, Q is the nuclear quadrupole moment, I is the nuclear spin, I_j is the projection of I on the j axis, V is the electric potential, and $-V_{ii} = \frac{\partial^2 V}{\partial i^2}$ is the i th component of the electric field gradient (EFG) tensor in the principal axis system (x,y,z) . Since the electric field is a vector, the gradient operator produces a symmetric 3×3 second-rank tensor which can be diagonalised in the principal axis system and completely specified by V_{xx} , V_{yy} and V_{zz} . In the region of the nucleus only s electrons have a finite charge density. These electrons have a spherically symmetric distribution and do not contribute to the EFG. Only non- s -electrons and charges external to the atom contribute to the EFG. Therefore, in the nuclear vicinity there are no free charges which contribute to EFG, and Laplace's equation requires the EFG to be a traceless tensor, i.e.:

$$V_{xx} + V_{yy} + V_{zz} = 0 \quad (2.15)$$

so that only two independent parameters are needed to specify an arbitrary EFG. Since the trace determines the mean of the eigenvalues, it is obvious that although the quadrupole interaction may partially remove the degeneracy of a level, it does not shift the centroid of this level. It is convenient to specify the EFG in terms of a quantity q defined by $V_{zz} = eq$ and an asymmetry parameter η defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (2.16)$$

with $|V_{zz}| > |V_{yy}| > |V_{xx}|$ for which $0 < \eta < 1$. The Hamiltonian, given by expression (2.14), can then be rewritten in terms of the two independent quantities q and η as

$$\mathcal{H}_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)] \quad (2.17)$$

The nuclear ground state of ^{57}Fe , with $I = \frac{1}{2}$, is spherically symmetric and hence has zero quadrupole moment. The first excited state, 14.4 keV level of this nucleus has $I = 3/2$; the eigen values of which are

$$E_Q = \pm \frac{e^2 q Q}{4} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \quad (2.18)$$

Thus the presence of an EFG leads to a splitting of this state into two levels separated in energy by

$$\Delta E_Q = \frac{e^2 q Q}{2} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \quad (2.19)$$

which is the peak separation observed in a quadrupole-split spectrum of ^{57}Fe .

The electric quadrupole interaction is angular dependent; however, for a randomly-oriented polycrystalline sample, the relative line intensities are in the ratio 1:1 (assuming that the recoil-free fraction in the polycrystalline material is isotropic).

For free ion electronic configuration of Fe(III) is $^6S, (3d)^5$. A weak octahedral crystal field gives rise to a high spin $(t_{2g})^3(e_g)^2, ^6A_1$ ground state. As the five 3d

electrons in high-spin Fe(III) are in half filled shell, the situation is similar to that for low-spin Fe(II) when any quadrupole splitting must arise from the field gradient due to neighbouring charges and/or inequivalence of the radial parts of the d-orbitals.

2.1.3.1 Energy levels and transition probabilities in the presence of nuclear magnetic and quadrupole interaction

Both the magnetic and quadrupole hyperfine interaction express a directional interaction of the nucleus with its environment. However, when the two are present together, their respective principal axes are not necessarily colinear, and consequently the nuclear states will, in general, not be pure state (i.e. there will be mixing of nuclear substates). The formal Hamiltonian which is the sum of the electric quadrupole and magnetic dipole Hamiltonian has no general solution, but the spectrum may always be obtained by numerical computation. A method of computing the spectrum appropriate to any given symmetry has been given by Gabriel et al.^{38,39,41}

One of the few useful restricted solutions for an $I = \frac{1}{2} \rightarrow \frac{3}{2}$ transition is the case where the quadrupole interaction is very much weaker than the magnetic term. Here the quadrupole interaction can be treated as a first-order perturbation (in other words only for the case where $|m\rangle$ is a good quantum number) to the magnetic interaction.

In the presence of the magnetic interaction only (assuming a small quadrupole splitting) the nuclear excited state ($I_e = 3/2$) splits into four ($m_I = \pm\frac{3}{2}, \pm\frac{1}{2}$) and the ground state ($I_g = \frac{1}{2}$) into two ($m_I = \pm\frac{1}{2}$) energy levels. The 14.4 keV nuclear transition is a pure magnetic dipole one, and the relative intensities of the transitions are given by^{40,41}

$$I(\theta) = [\langle I_0 m_0 | T_L^m | I_1 m_1 \rangle]^2 F(\theta) , \quad (2.20)$$

where T_L^m ($L = 1, m = 0, \pm 1$) is the magnetic dipole operator and $F(\theta)$ represents the angular distribution of dipole radiation. The term within brackets of the above expression is simply given by the Clebsch-Gordan coefficient^{40,41}.

For the simple case of an axially symmetric EFG with H_{eff} along the EFG symmetry axis⁴⁰

$$F(\theta) = 2\sin^2\theta, \text{ for } m_e - m_g = \Delta m_I = 0$$

$$F(\theta) = (1 + \cos^2\theta), \text{ for } m_e - m_g = \Delta m_I = \pm 1 \quad (2.21)$$

where θ is the angle between the γ -ray direction and the magnetic field. Using the values of the Clebsch-Gordan coefficients the relative intensities of the various transitions become⁴¹

$$\begin{aligned} I(\theta) &= (1 + \cos^2\theta), & \pm\frac{3}{2} &\rightarrow \pm\frac{1}{2} \\ &= \frac{4}{3} \sin^2\theta, & \pm\frac{1}{2} &\rightarrow \pm\frac{1}{2} \\ &= \frac{1}{3} (1 + \cos^2\theta), & \pm\frac{1}{2} &\rightarrow \mp\frac{1}{2} \end{aligned} \quad (2.22)$$

For polycrystalline spectra the intensities have to be averaged over all possible orientations of θ and give $\langle \cos^2 \theta \rangle = \frac{1}{3}$, $\langle \sin^2 \theta \rangle = \frac{2}{3}$. This makes the intensities of the above transitions in ratio 3:2:1 respectively for polycrystalline spectra which consist of 6 absorption lines⁴¹.

In general, if the magnetic field H is along $(\bar{\theta}, \bar{\phi})$ with respect to the z -directions of the EFG axis (x, y, z) the magnetic interaction can be written as⁴²

$$\mathcal{H}_M = -g_N \beta_N H_{\text{eff}} \left[\cos \bar{\theta} I_z + \frac{\sin \bar{\theta}}{2} \left(e^{-i\bar{\phi}} I_+ + e^{i\bar{\phi}} I_- \right) \right] \quad (2.23)$$

The mixing between the nuclear substates in this case gives rise to eight-line spectra⁴². The relative intensities of the lines then depends upon the angle $(\bar{\theta}, \bar{\phi})$.

2.2 Relaxation effects

In the presence of a paramagnetic hyperfine interaction the two following characteristic times have to be considered⁴³⁻⁴⁵:

- (a) the relaxation time of the electron spin, τ_s
- (b) the nuclear Larmor precession time, ω_L^{-1}

If the relaxation time is long compared to the nuclear Larmor precession time, i.e. $\tau_s \gg \omega_L^{-1}$ and the excited state life time is longer than nuclear Larmor precession time

then a static magnetic hyperfine interaction due to individual spin states is present at the nucleus and a hyperfine spectrum with sharp lines is expected.

If the relaxation time is short compared to the nuclear Larmor precession time, i.e. $\tau_s \ll \omega_L^{-1}$ then the hyperfine interaction produces an average value as a result of a rapidly fluctuating spin $\langle S_z \rangle_{av} = 0$ and the magnetic hyperfine splitting collapses to a singlet or a doublet. Determination by Mössbauer spectroscopy of the effective magnetic field at the nucleus in paramagnetic compounds which have fast electronic spin relaxation ($\tau_s \ll \omega_L^{-1}$) is only possible when an external magnetic field of sufficient magnitude to produce an appreciable magnetisation is applied. In practice, field ≥ 30 kOe at 4 K are required⁸².

Under the condition $\tau_s \approx \omega_L^{-1}$ the spectrum becomes "dynamic" and dependent upon electron spin relaxation time, thus resulting in a broadening of the lines due to an inward collapse (motional narrowing) of the hyperfine spectrum⁴¹. For detailed calculation of lineshape of Mössbauer spectra in the presence of time varying fields, the readers are referred to the treatment of Blume and Tjon^{12,47}. For Fe(III) high-spin state ($^6S_{5/2}$), 5×10^{-8} sec $> \tau_s > 5 \times 10^{-9}$ sec, the relaxation time dependent spectra will be observed.

This is the subject of interest in the present work, by varying magnetic concentration and temperature the relaxation rate can be modulated to achieve the case where $\tau_s \gg \omega_L^{-1}$.

2.3 Spin relaxation mechanism

The spin relaxation arises from two different types of interactions categorised as spin-spin and spin-lattice relaxations.

2.3.1 Spin-spin relaxation

Spin-spin relaxation causes the ion to make transitions between the different electronic sublevels, thereby giving rise to a randomly varying-time dependent magnetic field at the nucleus.

The 'dipolar' (G) and 'exchange' (J) interaction between i^{th} and j^{th} spins are given by^{46,26,49}

$$\mathcal{H}_{ss} = A + B + C + C^* + D + D^* \quad (2.24)$$

where $G = g_i g_j \beta_e^2 / r_{ij}^3$

$$A = [J_{ij} + G(1-3\cos^2\theta_{ij})]S_{iz}S_{jz}$$

$$B = \left[\frac{J_{ij}}{2} - \frac{G}{4} (1-3\cos^2\theta_{ij}) \right] (S_{i+}S_{j-} + S_{i-}S_{j+})$$

$$C = -\frac{3}{2}G\sin\theta_{ij}\cos\theta_{ij}e^{-i\phi_{ij}}(S_{i+}S_{jz} + S_{iz}S_{j+})$$

$$D = -\frac{3}{4}G\sin^2\theta_{ij}e^{-2i\phi_{ij}}S_{i+}S_{j+},$$

and θ_{ij} , ϕ_{ij} are the polar angles of the radius vector $\vec{r}_{ij}$ connecting the i^{th} and j^{th} ions with respect to the z axis.

It may be noted that S_i and S_j are the effective spins and the corresponding g-factors may differ from 2.

The diagonal component A usually does not induce any transition (except Fe^{2+} ion in CaCO_3 and CdCO_3 ⁴⁸) and simply represents a type of local magnetic field at the ion. Spin-spin relaxations take place due to transitions induced mainly by the B term, which involves simultaneous spin-flips by two ions so that $\Delta S_{iz} = -\Delta S_{jz} = 1$. The transition probability for this process is given by^{45,49}

$$W_{ij} = \frac{G^2}{16} (1 - 3\cos^2\theta_{ij})^2 |\langle S_{z+1} | S_+ | S_z \rangle|^2 |\langle S_z | S_- | S_{z+1} \rangle|^2, \quad (2.25)$$

neglecting the exchange term, when only one type of paramagnetic ion is involved. The total energy of the spin system, as well as its angular momentum, is conserved in this process.

CROSS RELAXATION

When more than one type of paramagnetic species is present the situation becomes different. The crystal field energy and Zeeman splittings of different types of paramagnetic ions will usually be different. In such a situation the dipolar interactions between spins may induce a series of transitions in which the sum of the crystal field and Zeeman energy is nearly conserved, and any balance of energy is taken up or given out by the dipolar interactions. A good discussion of cross relaxation has been given by Stevens⁵⁰ and by Bloembergen, et al.⁴⁹ Examples of cross relaxation have been described by Wertheim et al.², by Date⁷⁵ and by Bates et al.⁷⁶

The spin-spin relaxation can be effectively eliminated by keeping the paramagnetic ions sufficiently far apart in a diamagnetic host lattice, so that dipole or exchange coupling becomes negligible.

2.3.2 Spin-lattice relaxation

The fluctuations of spin states due to spin-phonon coupling is known as spin-lattice relaxation. The dynamic crystalline field at the central paramagnetic ion due to vibrations of surrounding ligands induces transitions between the orbital state of the ion. The spin of the ion is coupled to lattice vibrations (phonons) via spin-orbit coupling L.S.^{51,52}, the lattice vibrations having a direct influence only on the orbital angular momentum.

There is no spin-orbit coupling within a pure 6S ground state of Fe(III) ion ($L = 0$), however the spin-orbit coupling mixes a small amount of the excited 4P state into the ground state 6S , and consequently the Fe(III) ion is only weakly coupled to the lattice vibrations. This makes the spin-lattice relaxation rate of Fe(III) ion usually very slow compared to Fe(II) ion. Because the process involves lattice phonons, this type of relaxation is strongly temperature dependent, becoming longer with decreasing temperature.

2.4 Calculation of Spectrum²³

The electron-nuclear basis states for the Hamiltonians (2.1) are taken as $|S, S_z\rangle |I, m_I\rangle$ so that the electronic and nuclear operators operate as $|S, S_z\rangle$ and $|I, m_I\rangle$ parts respectively. The numbers of such basis states $(2S + 1)(2I + 1)$ are 12 for the nuclear ground state and 24 for the nuclear excited state. The diagonalisation of the corresponding matrices gives 12 ground and 24 excited eigenstates. In the Mössbauer effect, transitions are induced between states of the Hamiltonian for the ground state hyperfine levels and levels of the excited state given by Hamiltonian. The allowed transitions between the ground and excited levels are only those for which $\Delta m_I = 0$ or ± 1 and $\Delta S_z = 0$ hold simultaneously. The selection rule $\Delta S_z = 0$ comes from the fact that the magnetic dipole operator for nuclear transitions cannot connect different electronic substates. Transition energies and probabilities were then calculated.

The intensity of a typical transition is given by

$$I(\theta) = |\langle \psi_g | T_L^m | \psi_e \rangle|^2 F(\theta) \quad , \quad (2.26)$$

where ψ_g and ψ_e are the ground and excited eigenstates.

Other terms have already been explained in Equation (2.20).

At low temperatures when all the levels are not equally populated, the thermal weighted intensity is obtained by multiplying the intensity expression $I(\theta)$ by a population factor

$$p = \frac{e^{-E_g/KT}}{\sum e^{-E_g/KT}}, \quad (2.27)$$

where E_g is the energy of the appropriate level.

Finally, the Lorenzians centred at the energy of transitions and with appropriate depths are generated for the chosen linewidth and the superposition of all such Lorenzians gives the calculated spectra. The energy levels of paramagnetic Fe(III) ion and the transition scheme are given in Figure (2.1).

2.5 The application of magnetic field to observe spectra from each spin states

The possibility of successfully using Mössbauer effect for investigation of the hyperfine structure of nuclear levels in paramagnetic substances in the limit of long spin relaxation times was first established by A.M. Afanas'ev and Yu.M. Kagan^{54,69}. The Fe(III) ion in $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ exists in a ${}^6S_{5/2}$ state which is split in an axially symmetric crystal field into three Kramers' doublets; $|\pm 5/2\rangle$, $|\pm 3/2\rangle$, $|\pm 1/2\rangle$. When the separation in energy between any two of these doublets is much greater than hyperfine interaction, in the limit of long spin relaxation times, the Mössbauer spectrum consists of a superposition of three spectra, one arising from each Kramers' doublet, with each contribution weighted by the appropriate Boltzmann factor determined by the temperature of the system and the splittings of the doublets.

The spectra of the $\pm 5/2$ and $\pm 3/2$ doublets are simple six-line spectra corresponding to different magnetic fields at the nucleus. The field in each case is approximately proportional to $\langle S_z \rangle$ (see Equation 2.13) because of the rapid precession of S about the trigonal axis (the z axis), averaging to zero all other components of S . The $\pm 1/2$ case does not correspond to an average field at the nucleus because of the contribution of off-diagonal elements of the hyperfine Hamiltonian ($I_+ S_-$ and $I_- S_+$). The zero-field spectrum of the $\pm 1/2$ doublet consists of 11 lines (for example see reference 54). When all three Kramers' doublets are significantly populated the hyperfine structure is very complex.

In previous studies^{43,46} of relaxation of the three Kramers' doublets of the Fe(III) ion, it was shown that in an axial crystal field the spin-spin relaxation time is longest for the $\pm 5/2$ doublet and shortest for the $\pm 1/2$ one. The spin-lattice relaxation time for doublet $\pm 5/2$ is also larger than for the doublet $\pm 3/2$, but no such direct comparison is possible for the doublet $\pm 1/2$ without detailed knowledge of the phonon spectrum of the system^{67,68}. Furthermore, it has been indicated⁶⁹ that at low temperatures dipolar relaxation involving the spins of neighbouring nuclei is an important process which affects the $\pm 1/2$ doublet most severely. Afanas'ev and Kagan⁶⁹ have shown that the Mössbauer spectra associated with the $\pm 3/2$ and $\pm 5/2$ doublets are insensitive to small local dipolar fields when axial symmetry is present. Therefore the application of

a small magnetic field can be used to sharpen the spectra^{23,69,73} through the disruption of the small dipolar coupling between the nuclear and electronic spins. The external field polarises the Fe(III) ion electrons by producing an electronic Zeeman interaction that dominates the dipolar coupling between the Fe(III) ion and any adjacent nuclei having a nuclear magnetic moment and stabilizes in particular the spectrum from $\pm 1/2$ doublet. The spin Hamiltonian used in calculating the theoretical spectra is mentioned in Equation (2.1).

When the site symmetry of the Fe(III) ion is not axial, a non-zero value of λ produces mixing between the $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$ spin states and the effective field approximation for the spin doublets $\pm 5/2$ and $\pm 3/2$ may not remain valid. However as the $\pm 5/2$ states are well separated from the $\pm 1/2$ states, the effective field approximation remains almost reasonable. Thus for $\lambda \neq 0$ the spectra from the spin states $\pm 3/2$ and $\pm 1/2$ are substantially modified⁶⁶. B.L. Dickson and K.K.P. Srivastana^{70,71} reported that for high value of λ the effect of local dipolar field is reduced and the zero-field spectrum is better resolved (for example see spectra of Fe(III):LiScO₂ and MgAl₂O₄^{70,71} compared to the zero-field spectrum of an Fe(III) ion in axial crystal field where $\lambda \approx 0$ as seen in spectra of Fe(III):Al₂O₃ and LiAl₅O₈^{23,72,73}).

There are two different types of relaxation which can occur among Kramers' doublets, one involving transition

between Kramers' doublets (interlevel relaxation) and the other involving transitions among the hyperfine levels of a single Kramers' doublets (intralevel relaxation). The rapid relaxation which prevents the $\pm 1/2$ spectrum from being resolved is relaxation within the doublet (intralevel). It is not surprising to find very rapid intralevel relaxation within the $\pm 1/2$ but not within the other doublets. The angular momentum change required for relaxation within either the $\pm 3/2$ or $\pm 5/2$ doublets is large and this "forbids" intralevel relaxation in this case.

It has long been known^{49,74} that the rates of spin-spin relaxation between levels can be quite sensitive to the energy differences involved if these energy differences are of the same order of magnitude as the dipolar interaction between the ion. The relaxation rate decreases with increasing energy difference. Consequently, intralevel relaxation among the hyperfine levels of the $\pm 1/2$ doublet is far more rapid than interlevel relaxation between Kramers' doublets and is at least partially responsible for failure to resolve the $\pm 1/2$ doublet.

CHAPTER 3

EXPERIMENTAL

3.1 Mössbauer spectrometer system

3.1.1 Source

A commercially-available $^{57}\text{Co}/\text{Rh}$ source was used and for all the spectra recorded the source was maintained at room temperature.

3.1.2 The spectrometer

The Mössbauer spectrometer used for this work is based on a mini-computer, similar to that described by Window et al.⁵⁵ It utilises a constant acceleration source drive waveform and a transmission geometry arrangement of the source, absorber and detector. The mini-computer, a PDP 11/10 with 8K of core store, generates a very smooth drive waveform and also may accumulate up to a maximum of eight spectra simultaneously. The velocity reference signal was a linear ramp during the period of data accumulation followed by a fly-back period, similar to that proposed by Cranshaw⁵⁶, with an overall sweep frequency of 13 Hz. In normal operation eight spectra can be accumulated, each with 256 channels. It is possible, however, to combine these groups to obtain spectra with 512 or 1024 channels, thereby achieving greater resolution.

A conventional electromechanical transducer (loudspeaker type) was used. In this type of design two loudspeaker magnets are mounted back to back. Two coils are wound on a

former which has its axis coincident with the common axis of the magnets. One of the coils, the pick-up coil, develops an emf proportional to the velocity of the transducer. The signal from this monitoring coil is compared with the reference signal generated by the computer and a correction signal derived from this comparison drives the transducer via the drive coil. A more detailed account of such transducer is given by Kalvius and Kankeleit⁵⁷.

The spectrometer was calibrated using the spectrum of a natural iron foil absorber at room temperature and the data of Violet and Pipkorn⁵⁸. Zero velocity was taken to be at the centroid of the iron foil spectrum.

3.1.3 Detector

Argon-10% methane filled proportional counters were used to count γ -photons.

3.1.4 Cryostat

The liquid helium cryostat of the type described by Cranshaw⁵⁹ was used for low temperature work.

3.1.5 Magnetic field

Magnetic fields up to 1kOe were generated by an electromagnet.

3.1.6 Variable temperature controller

The temperature of the sample was measured by a copper-constantan thermocouple kept in good thermal contact with the sample. The accuracy of the measurement was within ± 0.50 K for temperatures below 20 K and ± 0.25 K for higher

temperature; at low temperature the copper-constantan thermocouple is less sensitive.

A variable temperature insert similar to that described by Cranshaw⁵⁹ was used for accumulating spectra in the temperature range 4.2 K - 295 K. The absorber was maintained at any temperature in this range by heating against a thermal leak to a liquid helium or liquid nitrogen bath. The electronic circuit of the temperature controller was basically the same as given by Window⁶⁰. A carbon-sensor (15Ω at 300 K) was used for temperatures below 30 K and a copper-sensor (100Ω at 300 K) for temperature above 30 K. In addition a separate constantan heater (40Ω at 300 K) parallel to the bridge was used. When the balancing bridge, containing the sensor in one of its arms, moves out of balance the heater starts to operate. The temperature can be changed by varying the resistance in another arm of the bridge, which in effect requires another value of the sensor resistance for the balance condition.

Temperatures between 4.2 K - 1.3 K were obtained by reductions of the pressure over liquid helium.

3.1.7 Evaluation of Mössbauer spectral parameters

The interpretation of a Mössbauer spectrum requires the derivation of certain parameters from the spectrum. The number and type of parameters depends on the particular spectrum in question and evaluation of these parameters is done by fitting the spectrum to a number of Lorentzian or pseudo-Lorentzian lines using a least-squares fitting procedure.

In the present work a computer program, provided by Dr Price, Solid State Physics Department, A.N.U., performs a least-squares fit of a spectrum to a sum of analytical functions which define the parameters that are to be determined or in reverse calculate the spectra from the supplied parameters.

The least-squares fitting procedure provides an optimum description of the data by minimisation of the weighted sum of squares of the deviations of the data points from the fitting function. This is achieved by minimisation of a quantity called the goodness of fit parameter which is defined as:

$$\chi^2 = \sum_{i=1}^N [Y_i - Y(X_i, \underline{a})]^2 W_i \quad (3.1)$$

where Y_i are the data points, $Y(X_i, \underline{a})$ denotes the fitting function, X_i and $\underline{a}$ define the values of the fitting function corresponding to Y_i , W_i is the weight ascribed to the i^{th} data point and N is the number of data points. The process of γ -ray emission is a random event hence, W_i is the inverse of the square of the standard deviation of the i^{th} point (i.e. $W_i = 1/Y_i$). Y_i represents the number of γ -photons counted at a known channel number X_i , which is related to the Doppler velocity. The components of the M -dimensional vector $\underline{a}$ represent M parameters which define $Y(X_i)$ and which are to be determined. The parameters a_m do not all occur linearly in the fitting function and thus minimisation of χ^2 cannot be achieved by solving equation (3.2) analytically with respect to a_m .

$$\begin{aligned}
 \frac{\partial \chi^2}{\partial a_m} &= \frac{\partial}{\partial a_m} \sum_{i=1}^N [Y_i - Y(X_i, \underline{a})]^2 \frac{1}{Y_i} \\
 &= -2 \sum_{i=1}^N [Y_i - Y(X_i, \underline{a})] \frac{1}{Y_i} \frac{\partial Y(X_i, \underline{a})}{\partial a_m} = 0 \quad (3.2)
 \end{aligned}$$

where $m=1,2, \dots M$.

Expansion of $Y(X_i, \underline{a})$ in a Taylor series with respect to increments in a_m enables equation (3.2) to be solved with respect to the linear parameters δa_m (viz. the increment in a_m). The minimisation of χ^2 now consists of solving equation (3.2) with respect to δa_m iteratively to obtain successively better values of a_m .

The fitting procedure is iterative in the non-linear parameters, for example line widths, line positions and initial estimates of the parameters have to be supplied. Linear parameters, for example peak areas, however, are calculated exactly for each set of values of the non-linear parameters and no initial estimates are required for them. Further details of the fitting procedure can be found in Price⁶⁵.

3.2 Preparation of potassium trisoxalatoferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$

Potassium trisoxalatoferrate(III) trihydrate was prepared from ^{57}Fe (in order to achieve significant absorption without having too large a physical thickness). Enriched iron foil (90% ^{57}Fe) was dissolved in minimum amount of hydrochloric

acid. The solution was evaporated to dryness on water bath. The residue of ferric chloride was dissolved in a few drops of water and oxidized by a few drops of hydrogen peroxide; the subsequent procedure followed the method described by Johnson⁶¹. This method involved the addition of ferric chloride solution to a hot solution of potassium oxalate according to the equation



The bright green products crystallised on cooling in the ice bath. The products were washed with a small volume of ice cold water and air dried. The yield was 80-85%.

Chemical analysis (found: C, 14.70; H, 1.20; Fe, 11.33.

Calc. for $\text{C}_6\text{H}_6\text{FeK}_3\text{O}_{15}$: C, 14.66; H, 1.22; Fe, 11.37%).

3.3 Preparation of potassium trisoxalatoaluminate(III) trihydrate, $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$

This method was described by Bailar and Jones⁶². Aluminium hydroxide was added to the solution of potassium hydrogen oxalate, which can be prepared by addition of a 1:1 molar ratio of potassium oxalate and oxalic acid. The stoichiometric equation is



The white products formed immediately upon addition with 90% yield.

Chemical analysis (found: C, 16.02; H, 1.25; Al, 5.91.

Calc. for $\text{C}_6\text{H}_6\text{AlK}_3\text{O}_{15}$: C, 15.57; H, 1.30; Al, 5.83%).

All starting materials used in preparation of the above complexes were A.R. grade reagents.

3.4 Preparation of dilute solid-solution absorbers

All complexes prepared in 3.2 and 3.3 were recrystallised before preparation of solid solutions.

3.4.1 Powdered samples

The powdered samples were prepared by dissolving the required amount of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ in as little water as possible and transferring the solution dropwise into a tube containing liquid nitrogen. After all liquid nitrogen had evaporated off, the frozen solution was pumped to dryness on a vacuum line. This process took about 2-5 days depending on the amount of solid solution. This method produced puffy powdered samples with greater homogeneity than the usual method of precipitation from alcohol. This is because there is a significant difference in solubilities resulting in preferential precipitation.

Powdered sample absorbers were prepared by mixing the powdered sample with boron nitride and then placing the mixture in a brass sample holder between Mylar sheets.

Dimensionless effective thickness parameters which are extremely useful in the determination of the optimum thickness of a source and an absorber can be defined, for sources and absorbers in which the resonant nuclei are randomly distributed by

$$T_s = f_s n_s a_s \sigma_0 t_s$$

$$T_a = f_a n_a a_a \sigma_0 t_a$$

where the subscripts s and a indicate the following source and absorber quantities

f = probability of resonance absorption without recoil

n = number of atoms per unit volume

a = fractional abundance of atoms which can absorb resonantly

t = thickness

σ_0 is the resonance absorption cross-section of the Mössbauer nuclei.

The quantity of a sample used in a particular powder absorber and the thickness of a single crystal absorber were defined by the criterion that the effective thickness of the absorber, T_a , should be less than unity. If this condition is satisfied then, assuming that the effective thickness of the source, T_s , is $\gg 1$, the transmitted peak has a Lorentzian shape and a full width at half height which is the sum of the emission and absorption peak widths⁶³.

The non-resonant absorption factor is also significant in determining the appropriate thickness of dilute absorbers; to obtain good absorption spectra the thickness of samples should be restricted to $t_a < \frac{1}{\mu}$ where μ is the non resonant absorption coefficient.

3.4.2 Single crystal samples

The single crystals were prepared by growing them from saturated aqueous solutions of known mixtures of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ and $K_3[Al(C_2O_4)_3] \cdot 3H_2O$. The crystals were

collected when the largest plane (010) was between 0.1-0.5 cm² in area. The crystals were then embedded in epoxy resin and sliced off on a saw to the appropriate thickness (1-2 mm) to be used as absorbers.

The thickness of single crystal absorbers was somewhat difficult to regulate because the mixed crystal was very brittle.

3.5 Preparation of frozen solution samples

The frozen solution samples were prepared by dissolving the $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ complex in an appropriate solvent to make up the concentration required. Then the solution was transferred into a polythene container and rapidly frozen by immersing in liquid nitrogen. Because the container was very thin (~ 1 mm) thermal equilibrium was obtained within one minute.

All preparations were carried out with minimum exposure to light because of the photo-sensitivity of the iron complex.

3.6 Analysis and quality control of samples

3.6.1 Chemical analysis: functional groups were characterised by infrared spectroscopy of KBr discs using a UNICAM SP200 spectrometer. The assignments of the infrared absorption bands were based on calculation by Nakamoto et al.⁶⁴ The purity of the samples was determined by microanalysis of the elemental composition by the Microanalytical Unit, A.N.U.

3.6.2 Physical analysis: structures of prepared samples were checked routinely by x-ray powder diffraction method.

The Phillips diffractometer (PW 1050) with a wide angle goniometer using CuK_α radiation was used. The data were compared to the data from ASTM powder diffraction file 1965.*

Single-crystal solid solutions were examined with a polarised light microscope and the space group of one mixed crystal ($x = 0.005$) was determined by the crystallographic group in the Research School of Chemistry, A.N.U., which indicate that it was isostructural with $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$. The unit cell dimensions are presented below

Unit cell dimension	$\text{K}_3[(\text{Al}_{0.095}\text{Fe}_{0.005})(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}^{**}$
a	7.72	7.66
b	19.53	19.87
c	10.23	10.27
β	$108^\circ 15'$	$105^\circ 6'$

* See Appendix B

**Data reproduced from reference 6

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Spectra of solid solutions at various concentrations

The spectra of a number of powdered and single crystal samples in the solid solution series $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ have been obtained. The usual temperature at which the spectra were accumulated was 4.2K (in order to minimize spin-lattice relaxation rate). The effect of temperature on the resolution of hyperfine structure is clearly evident from a comparison of the spectra of Figures (4.1) and (4.2). The spectral behaviour of powdered samples as the concentration of iron is reduced is discussed in the following paragraph and the spectra are shown in Figure (4.3).

For $x = 0.25$ the powdered sample yielded a spectrum showing extensive but incomplete resolution of the hyperfine structure. The four outer lines are resolved to give broad peaks but the two inner ones remain obscured by the strong relaxation-broadened absorption of this complex. When x has decreased to 0.05 the central absorption had disappeared, indicating that the Fe(III) ions are sufficiently far apart for the spin-spin relaxation rate to be long enough to produce a static hyperfine field at the nucleus ($\tau_s \gg 5 \times 10^{-8}$ sec). However the spectrum is smeared; six lines are discernible but they are very broad. At $x = 0.03$ the lines have sharpened considerably as a result of a further decrease in the spin-spin relaxation rate with increasing dilution, but two additional

low intensity absorptions have appeared and there are indications of two more. At higher dilution, $x = 0.008$, the spectrum is sharper with the additional absorptions becoming more clearly defined because of the longer spin-spin relaxation time. At this stage, the hyperfine spectrum consisted of sharp lines indicating that we have achieved condition $\tau_s \gg \omega_L^{-1}$. This indicates that the hyperfine structure of this complex is not a simple sextet. Therefore the zero-field splitting parameter D must be rather small with consequent significant population of all Kramers' doublets at temperature as low as 4.2 K.

The spectra of solid solutions in the form of single crystals were also measured to detect any distortion of the environment of the Fe(III) ions arising from the method of preparing the powdered samples. The use of a single crystal served to confirm the material as the truly desired crystal and greatly reduced the loss of water of hydration to the air. Some single crystals were grown and spectra were recorded with the 010 plane perpendicular to γ -ray beam. Figure (4.4A) shows that at $x = 0.05$ the spectrum consisted of predominantly six broad lines. The breadth of the lines indicated that the spin-spin relaxation time is still not long enough to achieve the condition $\tau_s \gg \omega_L^{-1}$. At $x = 0.015$ the spectrum is sharper but the baseline is curved, as shown in Figure (4.4B). The center of the spectrum still shows evidence of significant spin-spin relaxation. Comparison with the powdered sample with $x = 0.03$ suggests that the crystal actually contains more iron than

expected from the composition of the crystallising liquor. However the spectrum of the single crystal for $x = 0.005$, Figure (4.4C), and of the powder for $x = 0.008$ are very similar. The Mössbauer results from single-crystal solid solutions indicates that our method of preparing powdered solid solutions is an effective one.

We noticed that the broad singlets at room temperature, Figure (4.1) and Figure (4.2A), are slightly asymmetric suggesting differences between the relaxation times of the Kramers' doublets.

Figure (4.2) shows that the spin-spin relaxation rate in the solid solution with $x = 0.005$ is comparable in magnitude to the spin-lattice relaxation rate; consequently the effect of temperature on the line shapes of the spectra can be observed.

For none of these spectra can a comparison be made between the absorption intensities as the samples were not comparable in thickness. No quantitative use of experimental linewidths have been made in the consideration of relaxation times. The reasons for this are

- (a) In the very broad line cases, linewidth has no relevant meaning because the line shapes are not Lorentzian
- (b) For the fairly sharp hyperfine spectra, variable amounts of broadening make it impossible to rely on the observed linewidths as a quantitative measure of relaxation broadening

(c) The unresolved background out of which individual peaks arise makes it impossible to determine accurately the width at half maximum for most of the peaks.

4.2 Spectra of powdered samples in applied magnetic fields

Spectra of powdered samples with $x = 0.005$ and 0.002 in applied magnetic fields were also obtained. External magnetic fields of up to 1 kOe were applied to the samples with the field direction perpendicular to the direction of γ -ray propagation. The application of a small magnetic field results in more distinctive peaks for the low intensity absorptions possibly due to decoupling between electronic spin of Fe(III) ions and nuclear spin of neighbouring ^{27}Al nuclei, particularly for the $\pm 1/2$ doublet as shown in Figures (4.5) and (4.6). The better resolution in the central region of the spectra is immediately seen.

4.3 The interpretation of experimental spectra

A comparison of calculated spectra and experimental spectra at zero field has been made and the assignments are shown in Figure (4.5C). The spin Hamiltonian used in producing the theoretical spectra is

$$\mathcal{H} = \mathcal{H}_{CF} + \mathcal{H}_M + \mathcal{H}_Q$$

where $\mathcal{H}_{CF} = D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2)$

$$\mathcal{H}_M = AI_zS_z + \frac{1}{2}A(S_+I_- + S_-I_+)$$

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}\{3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 - I_-^2)\}$$

assuming that EFG tensor and A has same principal axes and coincide with crystal field axes. The unusually strong absorption of line 4, due to overlapping of $\pm 1/2$ and $\pm 5/2$ transitions, and line 5 due to overlapping of $\pm 3/2$ and $\pm 5/2$ transitions, destroyed the symmetry of the resolved hyperfine spectra. This lack of symmetry increases as the concentration of iron are lowered. This is clearly observed in the spectra of solid solutions for various concentrations at 4.2 K, Figures (4.3) and (4.4).

Comparison of calculated and experimental spectra yields the following best values for the various parameters at 4.2 K, table (4.1).

Zero-field splitting parameter D	$+0.20 \pm 0.05 \text{ cm}^{-1}$
$\lambda = E/D$	0.05 ± 0.01
Asymmetry parameter η^*	0.15 ± 0.03
Associated hyperfine field $ H $	$540 \pm 5 \text{ kOe}$ or 216 kOe/spin
Quadrupole interaction energy $\frac{1}{2}e^2qQ$	0.05 mm sec^{-1}

Table (4.1) Experimentally determined parameters for Fe(III) ion in $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ at 4.2 K.

*The parameter η could not be very well determined independently as it had little effect on the spectra; η was taken to be equal to 3λ . Much smaller or much larger values of η gave spectra that were in noticeably worse agreement with experiment.

From the parameters obtained from this work, it is evident that the site symmetry of Fe(III) ion is not axial since $\lambda \approx 0.05$ and therefore there is some mixing of the wavefunctions of the Kramers' doublets. The hyperfine field at the Fe(III) nucleus is 540 kOe which is the usual value for an octahedrally-coordinated high-spin Fe(III) complex with slight covalency effects^{23,72}. The magnitude of quadrupole splitting, $\Delta E_Q \approx 0.10 \text{ mm sec}^{-1}$, of this complex rules out the possibility that the Fe(III) oxalate complex intermediate doublet with $\Delta E_Q = 0.7 \text{ mm sec}^{-1}$ arises simply from potassium trisoxalatoferrate(III) with modified relaxation. The magnitude and sign of the zero-field splitting parameter, $D = +0.20 \pm 0.05 \text{ cm}^{-1}$ (0.29 K) indicates that the $S_z = \pm 1/2$ state is the lowest Kramers' doublets, the next $\pm 3/2$ and the highest $\pm 5/2$. The separation between $\pm 1/2$ and $\pm 5/2$ states is $\approx 1.2 \text{ cm}^{-1}$ (1.74 K), so that at 4.2 K the three crystal-field states are almost equally populated.

4.4 Further investigations

4.4.1 Application of magnetic field to single crystal sample

External fields up to 1 kOe were applied to a single crystal sample with $x = 0.005$; the resulting spectra are shown in Figure (4.7A,B). The spectra were recorded with the 010 plane perpendicular to the γ -ray beam and hence the magnetic field was parallel to the 010 plane. According to the crystal structure⁶, the trigonal axis of the Fe(III) ion is approximately parallel to the crystal a axis. Further experiments

should be done with the magnetic field parallel to the trigonal axis. At this stage a detailed interpretation of the behaviour of the ionic levels in an external magnetic field is made difficult by the uncertainty in the orientation of the field with respect to the trigonal axis. It will be sufficient to note that less than 1 kOe produces an electronic Zeeman splitting larger than the hyperfine interaction but smaller than the crystal field splitting.

4.4.2 Measurement of resolved spectra at 1.3 K

The resolved spectra of powdered samples $x = 0.008$ and 0.25 and single crystal samples with $x=0.005$ and 0.015 were obtained at 1.3 K in an attempt to observe any temperature-dependent behaviour. Figure (4.8) shows that the intensities of the two outer peaks and two inner peaks have diminished considerably and peak 2 and 5 to a lesser extent, while there has been a slight broadening of the low intensity absorption peaks between the main peaks. For clarity Figure (4.4C) and Figure (4.8D) were reproduced in Figure (4.8.1). A similar observation was found in the spectrum of a single crystal sample with $x = 0.005$ in an applied magnetic field of 1 kOe at 1.3 K, as shown in Figure (4.7C).

The phenomenon of reduction of intensity and broadening of the Mössbauer absorption spectrum at lower temperature is not encountered in the preceding spectra. The selectivity of the reduction of intensities and broadening of lines rules out the possibility of line broadening due to experimentation such as vibration from pumping system.

The phenomenon of broadening of magnetic hyperfine spectra at lower temperatures is not common because the spin-lattice relaxation rate will decrease with decreasing temperature and the spin-spin relaxation rate is essentially temperature-independent. At lower temperatures the Mössbauer spectrum should be sharper or at least stable (if $\tau_s \gg \omega_L^{-1}$ already) because of the longer relaxation times and also the larger recoil-free fraction of the Mössbauer transitions. However, Blume has shown that a temperature-dependent spin-spin relaxation will occur in special cases, as exemplified by ferric hemin⁴⁶ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ^{78,79,80}.

The prominent features of the hyperfine spectra of, solid solutions, $\text{K}_3[(\text{Al}_{1-x}\text{Fe}_x)(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ observed at 1.3 K is the broadening of lines indicating a faster relaxation rate so a relaxation mechanism must be found which becomes faster as the temperature is lowered.

The essential features of the proposed explanation of these phenomenon are the following:

- (a) The D value of the crystal field splitting must be positive which results in $S_z = \pm 1/2$ Kramers' doublet being the lowest.
- (b) The total separation of the Kramers' doublets ($\approx 6D$) must be larger than 1.3 K.
- (c) At temperature 1.3 K the excited Kramers' doublets $\pm 5/2$ and $\pm 3/2$ become depopulated resulting in the reduction of intensities of lines, especially the two outer and two inner lines arise from $\pm 5/2$ highest Kramers' doublet.

(d) The depopulation of $\pm 5/2$ and $\pm 3/2$ Kramers' doublets results in an increase in population at the $\pm 1/2$ ground Kramers' doublet. The intralevel spin-spin relaxation within $\pm 1/2$ Kramers' doublet becomes faster while the $\pm 1/2$ level becomes more populated. Consequently the broadening of lines at lower temperature will be observed.

The theoretical explanation for temperature-dependent spin-spin relaxation has been put forward by Blume⁴⁶ and the essential outlines will be presented below.

Spin-spin relaxation causes the ion to make transitions between the different sublevels, and these transitions will produce a randomly time-dependent magnetic-field at the nucleus. The Hamiltonian for the nucleus, assuming that EFG is axially symmetric and has its major principal axis parallel to the magnetic hyperfine field, can be presented by

$$\mathcal{H}(t) = \mathcal{H}_Q + g_N \beta_N I_z h f(t) \quad (4.1)$$

$$\text{where } \mathcal{H}_Q = \frac{e^2 q Q}{4I(2I-1)} (3I_z^2 - I^2)$$

$h = 220$ is the hyperfine field per spin expectation value as in Equation (2.13) and $f(t)$ is a random function of time which can only take on the six values $\pm 1/2$, $\pm 3/2$ and $\pm 5/2$. To specify the function $f(t)$ completely, the matrix of the transition probabilities per unit time between the various values which $f(t)$ can take on must be constructed. Following

Blume, it is assumed that the transitions are due to dipole-dipole interaction between the ion containing the Mössbauer nucleus and the other ions in the sample. This interaction is proportional to

$$(r_j^3)^{-1} \{ (\vec{S} \cdot \vec{S}_j) - 3(\vec{S} \cdot \hat{r}_j)(\vec{S}_j \cdot \hat{r}_j) \} \quad (4.2)$$

where $\hat{r} = \vec{r}/r$ and the transitions, in first order, will be induced by term of the form

$$(r_j^3)^{-1} (1 - 3\cos^2\theta_j) (S_+ S_{j-} + S_- S_{j+}) \quad (4.3)$$

i.e. (4.2) has been truncated to restrict transitions to angular momentum conserving ones. Using the golden rule, it is seen that transition probabilities are of the form

$$W(M_i \rightarrow M_j) = |\langle M_j | S_{\pm} | M_i \rangle|^4 \cdot c \cdot n(M_j) \quad (4.4)$$

The fourth power of the matrix elements enters because the golden rule involves the square of the matrix element of the interaction, and in order for one ion to make a transition from M_i to M_j , another must make a transition from M_j to M_i . For the same reason the Boltzmann factor

$$n(M_j) = e^{-E_M/KT} / \sum_M e^{-E_M/KT}$$

for the level M_j enters. The constant c is proportional to

$$\sum_j (1 - 3\cos^2\theta_j)^2 / r_j^6$$

and is dependent on the distance between Fe(III) ions. Calculation of the matrix elements in Equation (4.4) gives

$$\begin{aligned} W(\pm 1/2 \rightarrow \mp 1/2) &= 81 \cdot c \cdot n(\pm 1/2) \\ W(\pm 1/2 \rightarrow \pm 3/2) &= 64 \cdot c \cdot n(\pm 3/2) \\ W(\pm 3/2 \rightarrow \pm 5/2) &= 25 \cdot c \cdot n(\pm 5/2) \end{aligned} \quad (4.5)$$

where $n(\pm 1/2) = 1/z$, $n(\pm 3/2) = e^{-2D/KT}/z$ and $n(\pm 5/2) = e^{-6D/KT}/z$ with $z = 2(1 + e^{-2D/KT} + e^{-6D/KT})$.

It can now be seen how the temperature dependence of the spin-spin relaxation arises. In order for one ion to make a ground state transitions from $+1/2$ to $-1/2$, say, a neighbouring ion must make a transition from $-1/2$ to $+1/2$. At low temperature, only the $\pm 1/2$ levels are occupied so there will be a very large probability that a neighbouring ion is in the right state for flipping. At temperature large compared with D , however, all three Kramers' doublets will be equally populated, and consequently the transition probability for the same $+1/2$ to $-1/2$ transition is reduced by a factor of three.

In addition, expression (4.5) shows that the relaxation times in the excited states will be longer than those in the ground states. Hence at high temperatures ($T \gg D$) as the excited levels are populated, the spectrum becomes asymmetric since it consists of a superposition of asymmetric spectra of ions in the more slowly relaxing excited states and the spectrum from ions in the ground state. In this calculation Blume imagined

a small magnetic field along the z axis to be present which lifts the degeneracy of the $\pm 1/2$ levels, so that the hyperfine structure of these levels can also be represented by an effective magnetic field at the nucleus. This should not change the qualitative picture greatly.

These experiments at 1.3 K confirm that the value of the zero-field splitting parameter D is rather small ($1.3 \text{ K} < 6D < 4.2 \text{ K}$) and positive. This also agrees with the results obtained from Mössbauer experiments with solid solutions at 4.2 K.

4.4.3 Experiments with frozen solutions

The spectra of frozen solutions were recorded for comparison with the spectra of solid solutions in the expectation that frozen solutions would behave like powdered solid solutions because of the random orientation of molecules and that the electronic state of the Fe(III) ion would be determined predominantly by the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ complex ion.

The spectrum of a frozen solution with a concentration of iron approximately equivalent to $x = 0.002$ in solid solutions*, using water as solvent, consisted of a broad singlet as shown in Figure (4.9A). This is inconsistent with the spectral behaviour of solid solutions since we observed hyperfine structure for solid-solution samples even at concentrations as high as $x = 0.25$. Formation of crystallites is very unlikely to occur at this low concentration so the ions should be well-separated. Therefore we suspected that

* Based on numbers of iron ions per unit volume

the water dipoles could play some role in the electronic relaxation⁷⁷. However the frozen solution of approximately equivalent to $x = 0.00008$ in solid solution yielded hyperfine spectra Figure (4.9B) but the spectrum is statistically very poor since there is too small a quantity of iron in this sample.

We tried to reduce the effect of water on electronic relaxation by using a less polar solvent. Ethyleneglycol is viscous and a good glass-forming solvent but the solubility of the iron complex is too low to give sufficient iron in the solution. However the solubility in ethyleneglycol : water = 1:1 is adequate to prepare a solution containing an amount of iron approximately equivalent to $x = 0.0004$ in solid solution but the hyperfine spectrum, Figure (4.9C) is also very poor.

A frozen solution in ethyleneglycol : water = 1:2 approximately equivalent to $x = 0.001$ in solid solution, yielded a sharper hyperfine spectrum in reasonable counting time. The spectra of this sample at 1.3 K and in the presence of various magnetic fields are shown in Figures (4.10) and (4.11). The zero-field and low-field hyperfine spectra of the frozen solutions are slightly different from those of the solid solutions but as the external magnetic field increases from 60 Oe to 500 Oe the hyperfine structure of the frozen solution is almost identical with that of the solid solutions (except for the curved background due to the solid-angle effect which was caused by the motion of the source). The spectrum at 1.3 K, Figure (4.10B), showed the selective reduction of intensities and broadening of lines similar to that observed in solid solutions at 1.3 K.

We can conclude that:

- (1) The difference between the Fe(III) hyperfine interactions in frozen solution and solid solution in zero-field is very small since a small magnetic field, $\sim 60-500$ Oe, can produce an electronic Zeeman splitting sufficient to overcome the difference. The small difference in hyperfine interaction simply reflects the difference in the environment of the Fe(III) ions. In one case the nearest neighbours are the trisoxalatoaluminate(III) complex ions, $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ and the trisoxalatoferrate(III) complex ions, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ packed in an ordered lattice, while in the other case there are ethyleneglycol and/or water molecules as neighbours in a random solid array. The small differences could therefore be due to strains or distortions of the complex ion in each case or to other interaction (e.g. magnetic dipolar) with the environment. This also confirms that the solid solutions prepared in this project are good solid solutions, i.e. truly representative of the $\text{K}_3[(\text{Al}_{1-x}\text{Fe}_x)(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ system.
- (2) The results from frozen solutions confirms the results from solid solutions that the crystal field splitting between the Kramers' doublets must be between 4.2 K and 1.3 K with the $\pm 1/2$ Kramers' doublet lying lowest.

4.5 Conclusion and Prospect

A qualitatively satisfactory explanation of the Mössbauer spectra of high-spin Fe(III) ion in solid solutions,

$K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ at 4.2 K has been proposed. Additional experimental work would be necessary to determine in detail the validity of the approximations made. In particular, the zero-field splitting parameter D might more accurately be obtained using electron paramagnetic resonance. In fact a preliminary study by Dr A. Edgar⁸¹ on EPR spectra of a single-crystal solid solution of $K_3[(Al_{0.095}Fe_{0.005})(C_2O_4)_3] \cdot 3H_2O$ at room temperature gave an estimate of the magnitude without sign of the zero-field splitting parameter $|D|$ to be approximately 0.198 cm^{-1} . This is in good agreement with the value $D = +0.20 \pm 0.05 \text{ cm}^{-1}$ obtained from our Mössbauer experiments.

The selective reduction of intensities and broadening of lines in the paramagnetic hyperfine spectra of $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ at 1.3 K arising from temperature-dependent spin-spin relaxation show conclusively that the sign of the zero-field splitting parameter D is positive. The above phenomenon also give an insight into the magnitude of the zero-field splitting between Kramers' doublets. The results are in good agreement with the results from solid-solution experiments at 4.2 K.

Additional experiments carried out in frozen solutions of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ in appropriate solvents at 4.2 K and 1.3 K suggest that the Fe(III) ion environments in solid solutions and frozen solutions are essentially identical. Thus there is a strong basis for the assumption that Fe(III) ion in solid solutions, $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ is truly representative

of Fe(III) ion in $K [Fe(C_2O_4)_3] \cdot 3H_2O$ which is the compound of interest. In due course we would wish to extend our interpretation of the behaviour of dilute solid solutions to the non-diluted compound.

Although the structural unit in the $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ is octahedral complex ion, $[Fe(C_2O_4)_3]^{3-}$, with three planar oxalate ligands, a value of λ ($\lambda = E/D$) differing from zero might be expected because the oxygen atoms around the central iron(III) ion form a slightly-distorted octahedron. The λ value of 0.05 ± 0.01 obtained from this project, reflects this slight distortion. The high degree of uncertainty associated with λ and D values obtained here results from the model of the crystal field Hamiltonian used in the calculation since

$$\mathcal{H}_{CF} = D\{S_z^2 - 1/3S(S+1)\} + E(S_x^2 - S_y^2)$$

assumes that the crystal field splitting is large compared with the electronic Zeeman term. Therefore in the system with small crystal field splitting, a more complicated crystal field Hamiltonian which includes the cubic term should be used. In fact a more complete program is now being developed to compute the spectra using the crystal field Hamiltonian in Equation (2.2.3).

Further Mössbauer experiments on oriented single-crystal solid solution in applied magnetic field of higher strength would be very desirable in obtaining more accurate spin Hamiltonian parameters.

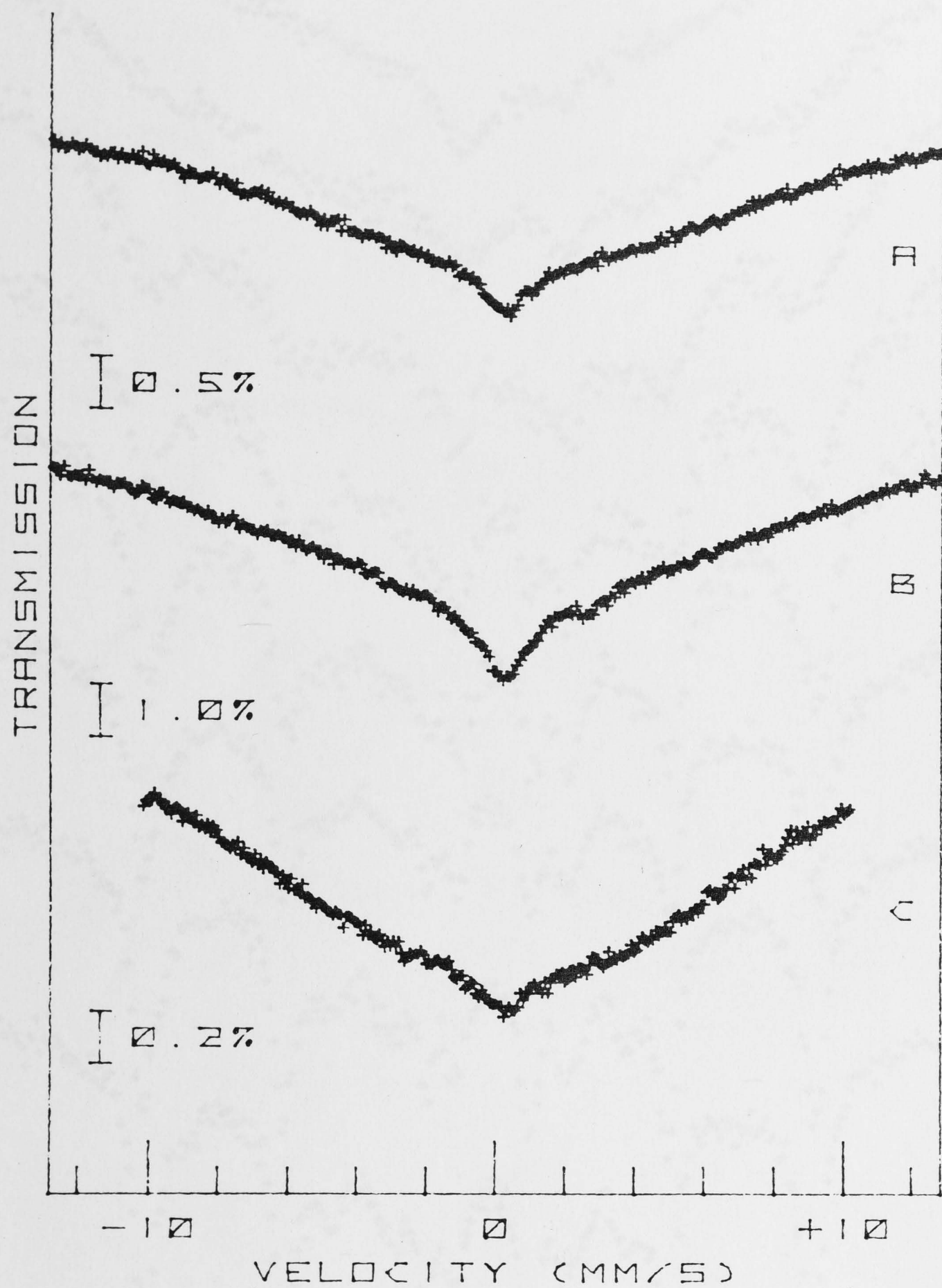


Figure (4.1) Mössbauer spectra of solid solutions, $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ at room temperature

- A) $x = 0.03$ powdered sample
- B) $x = 0.015$ single crystal sample
- C) $x = 0.008$ powdered sample

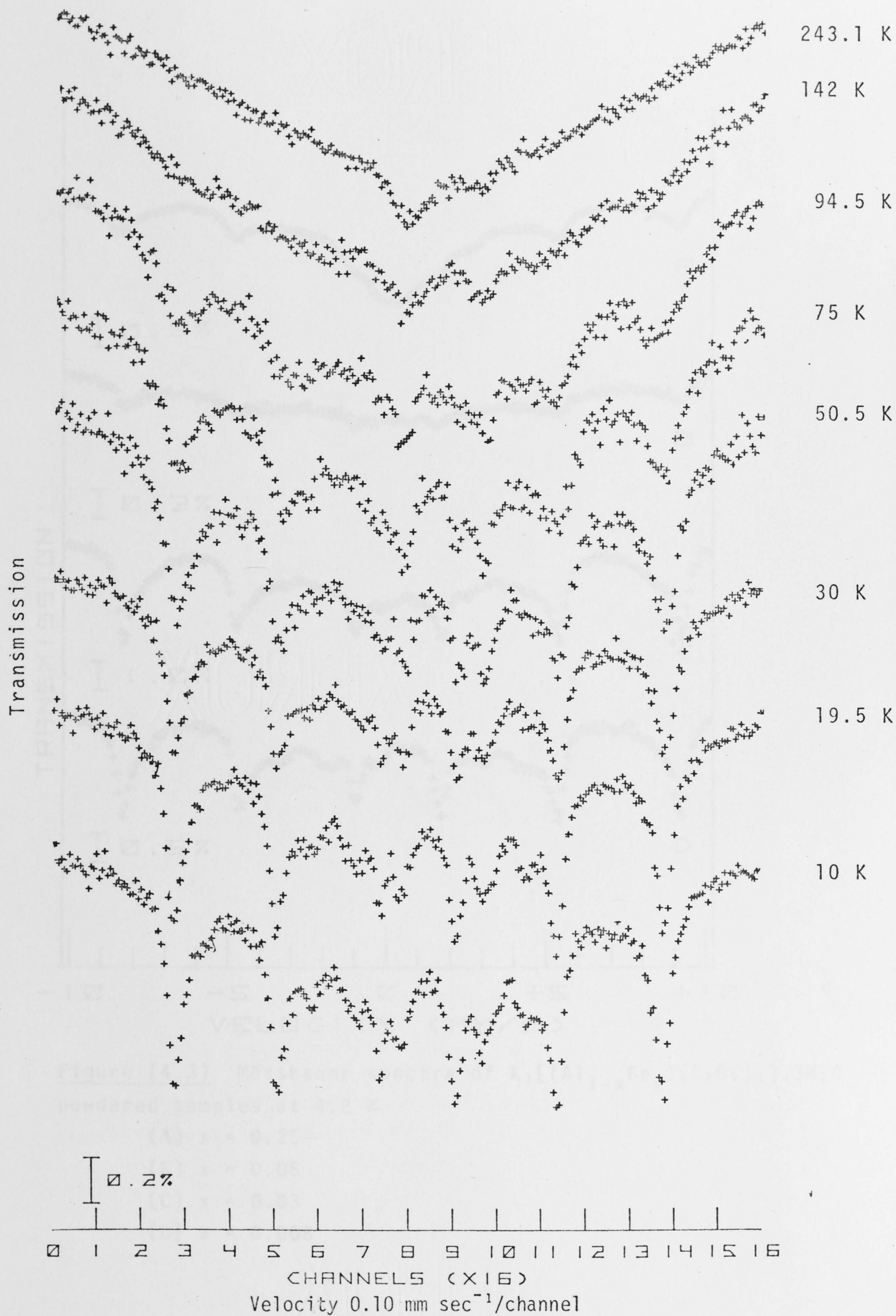


Figure (4.2) Mössbauer spectra of $K_3[(Al_{0.0095}Fe_{0.005})(C_2O_4)_3] \cdot 3H_2O$ powdered sample at various temperatures.

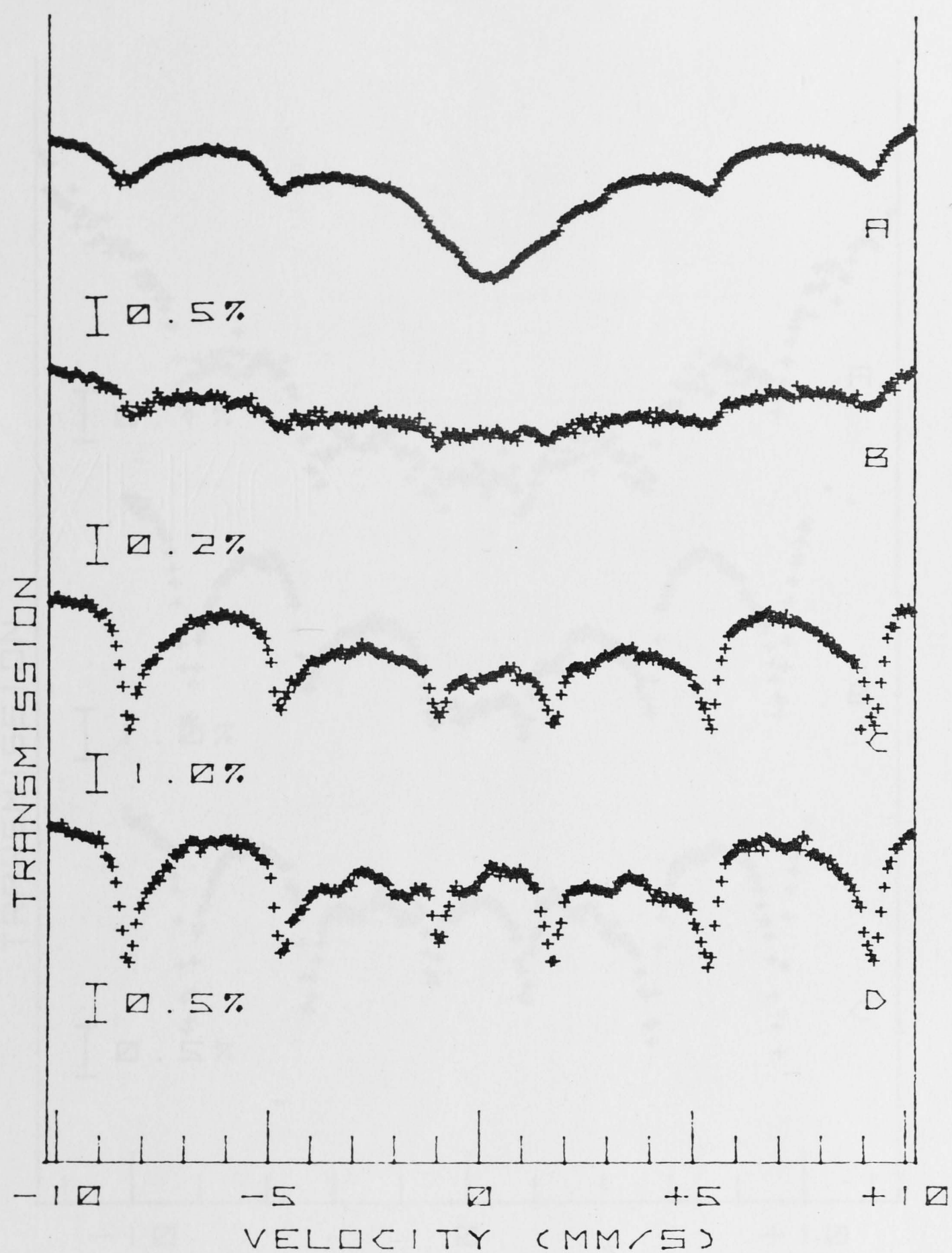


Figure (4.3) Mössbauer spectra of $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ powdered samples at 4.2 K

- (A) $x = 0.25$
- (B) $x = 0.05$
- (C) $x = 0.03$
- (D) $x = 0.008$

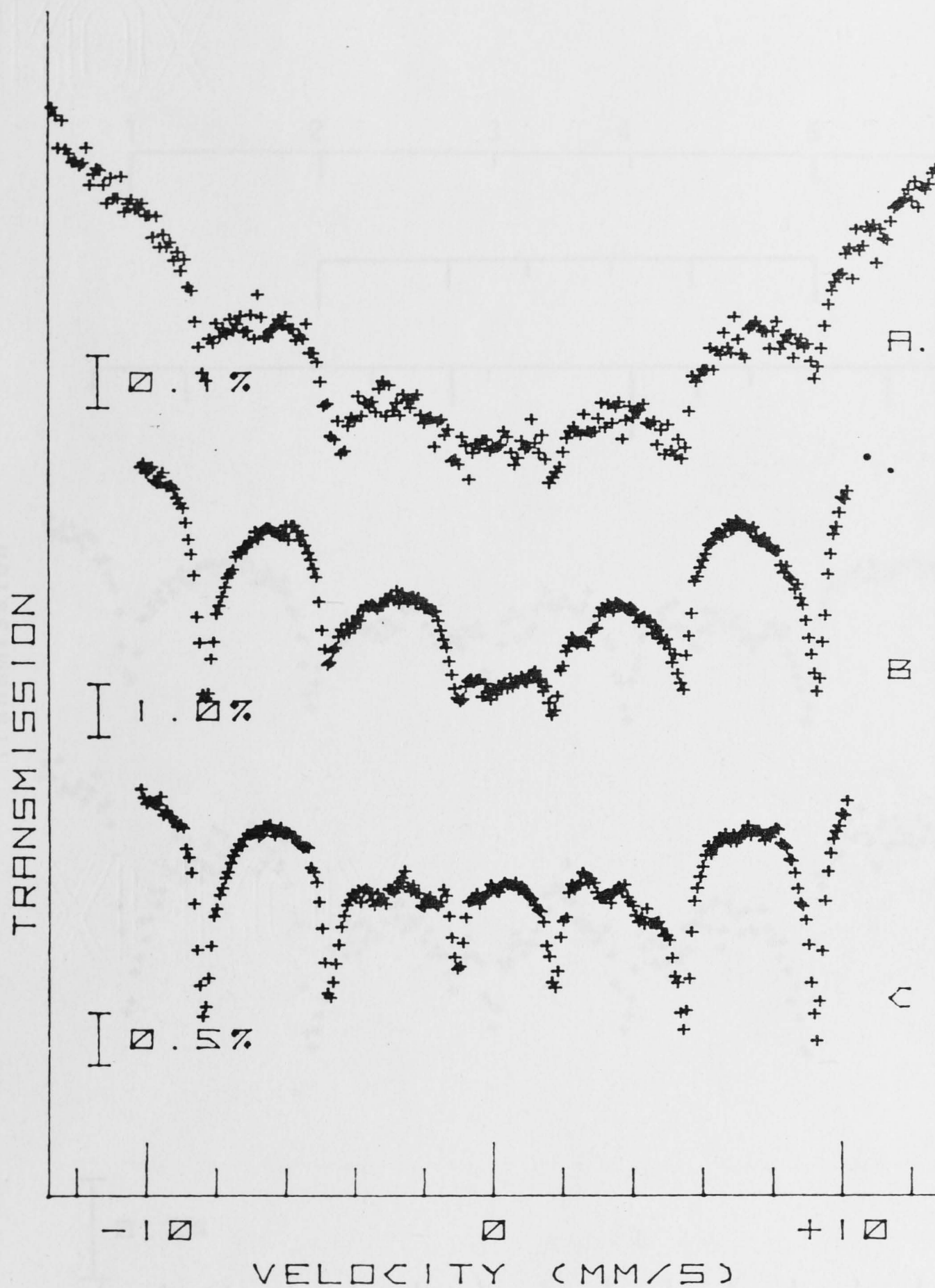


Figure (4.4) Mössbauer spectra of $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ single crystal samples at 4.2 K

(A) $x = 0.05$

(B) $x = 0.015$

(C) $x = 0.005$

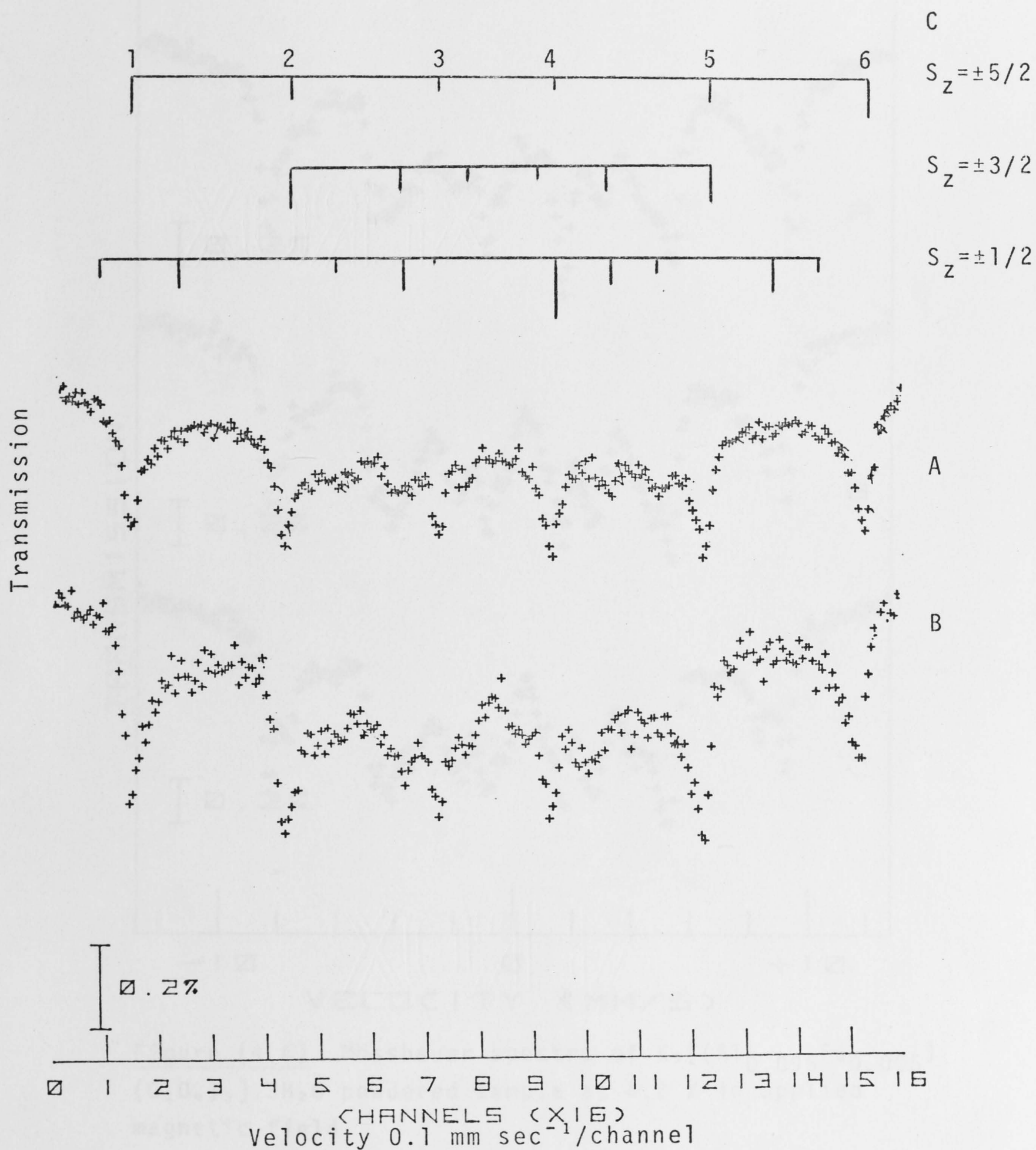


Figure (4.5) Mössbauer spectra of $K_3[(Al_{0.098}Fe_{0.002})(C_2O_4)_3] \cdot 3H_2O$ powdered sample at 4.2 K
 (A) $H = 0$ kOe
 (B) $H = 1$ kOe
 (C) Assignment of spectra from $S_z = \pm 1/2$, $\pm 3/2$, $\pm 5/2$ generated from data in Table (4.1)

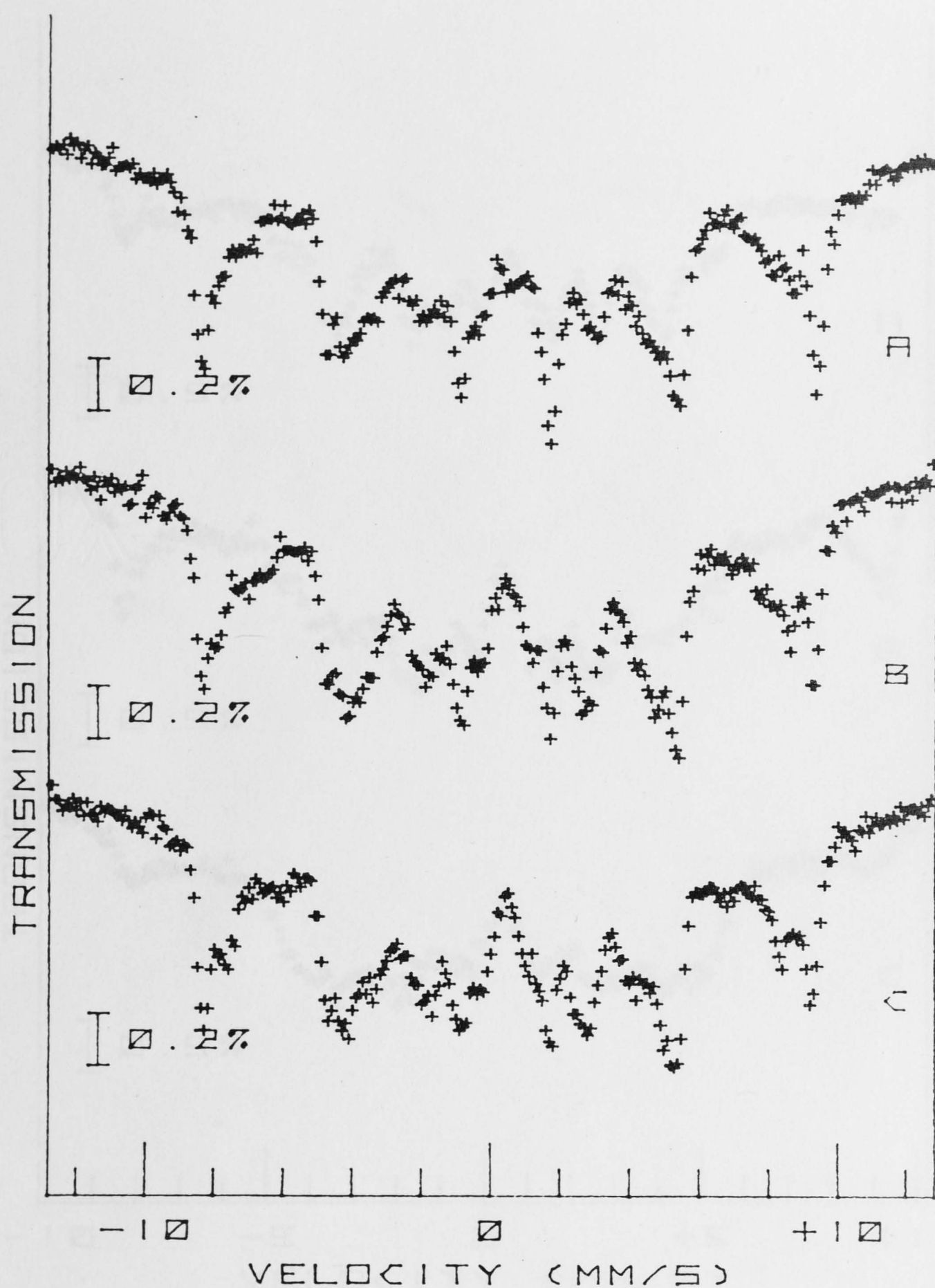


Figure (4.6) Mössbauer spectra of $K_3[(Al_{0.095}Fe_{0.005})(C_2O_4)_3] \cdot 3H_2O$ powdered sample at 4.2 K in applied magnetic field

- (A) $H = 0$ Oe
- (B) $H = 120$ Oe
- (C) $H = 1$ kOe

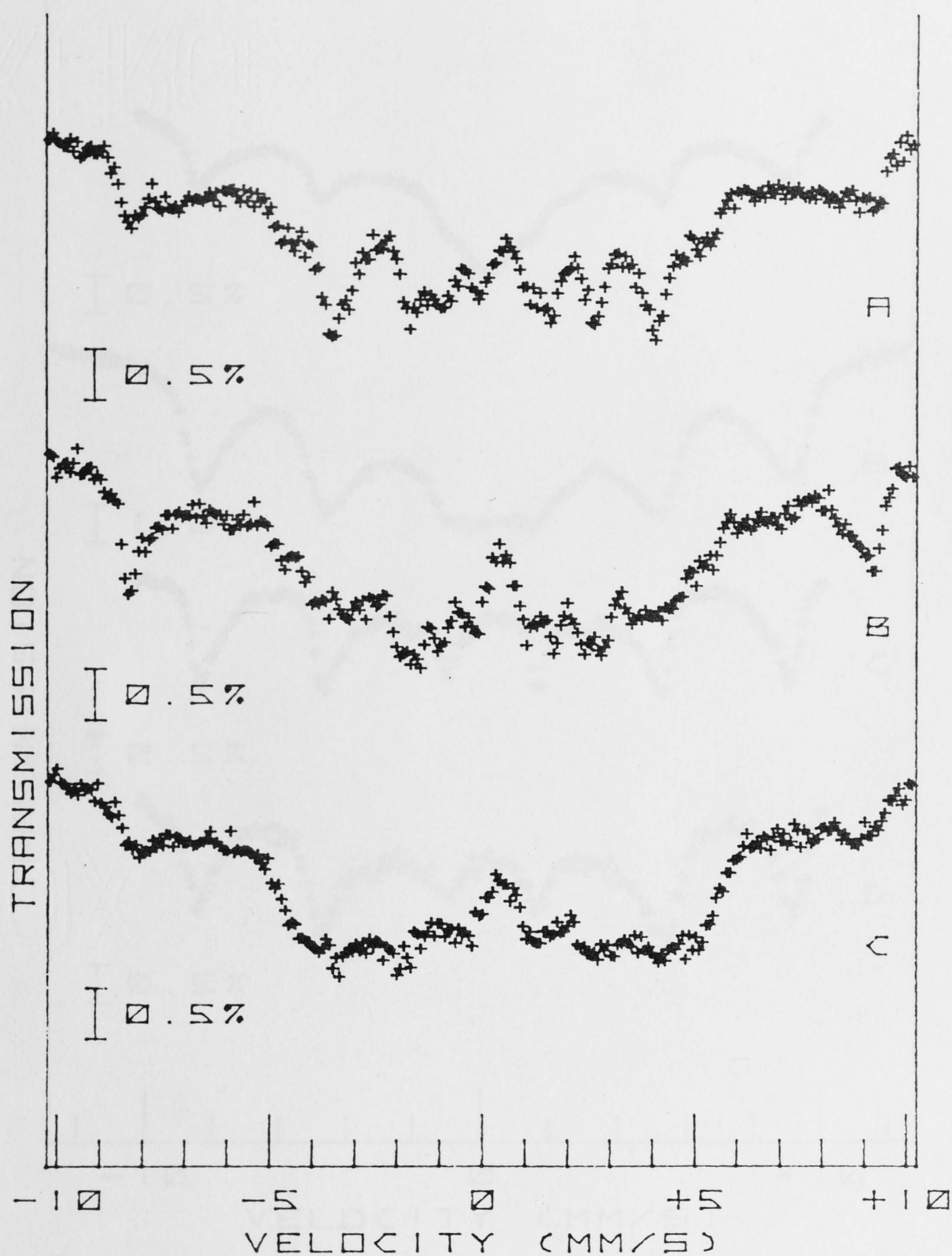


Figure (4.7) Mössbauer spectra of $K_3[(Al_{0.095}Fe_{0.005})(C_2O_4)_3] \cdot 3H_2O$ single crystal sample with 010 plane parallel to applied magnetic field

- (A) $H = 200$ Oe at 4.2 K
- (B) $H = 1$ kOe at 4.2 K
- (C) $H = 1$ kOe at 1.3 K

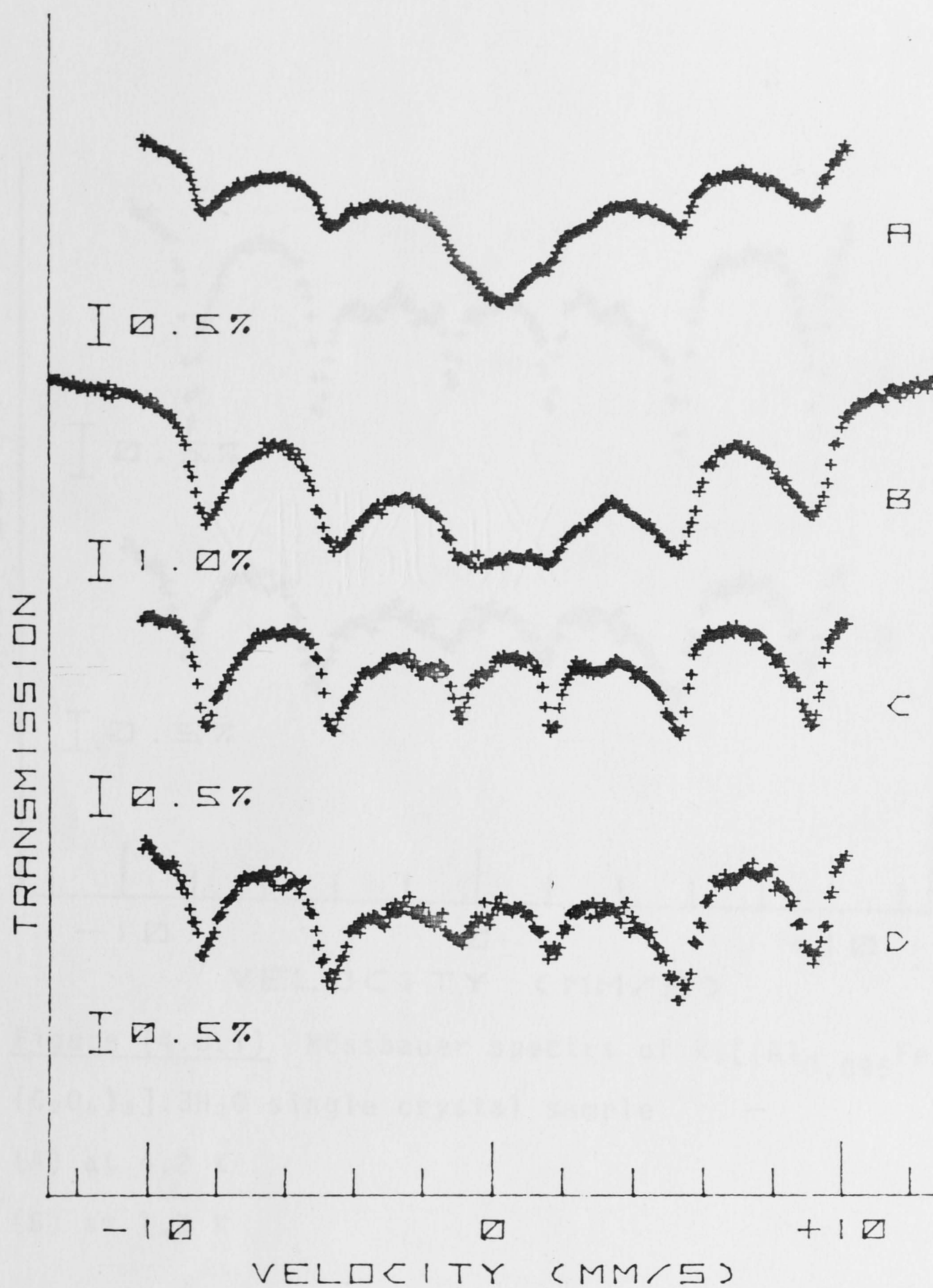


Figure (4.8) Mössbauer spectra of $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ solid solutions at 1.3 K

- (A) $x = 0.25$ powdered sample
- (B) $x = 0.015$ single crystal sample
- (C) $x = 0.008$ powdered sample
- (D) $x = 0.005$ single crystal sample

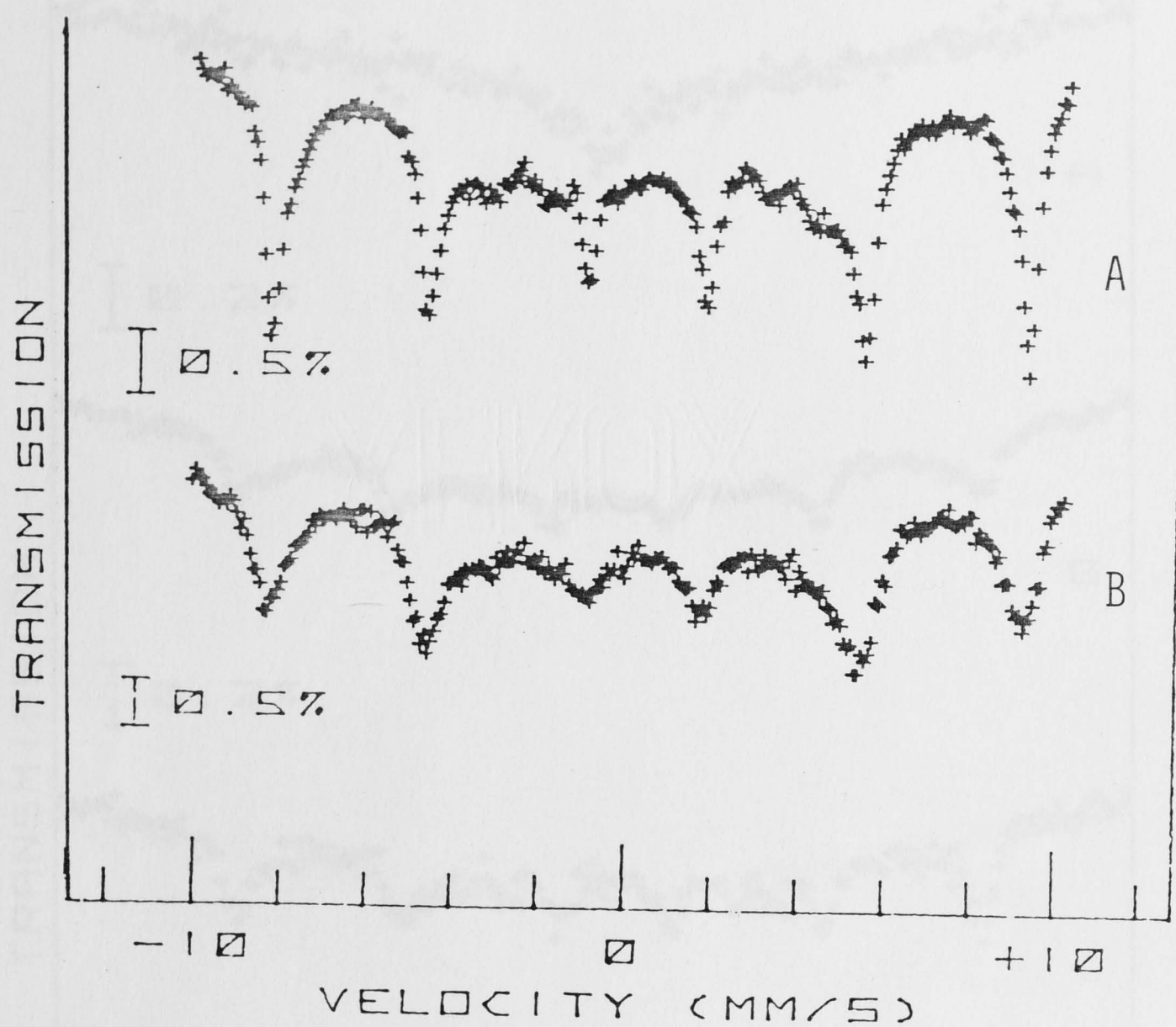


Figure (4.8.1) Mössbauer spectra of $K_3[(Al_{0.095}Fe_{0.005})(C_2O_4)_3].3H_2O$ single crystal sample

(A) at 4.2 K

(B) at 1.3 K

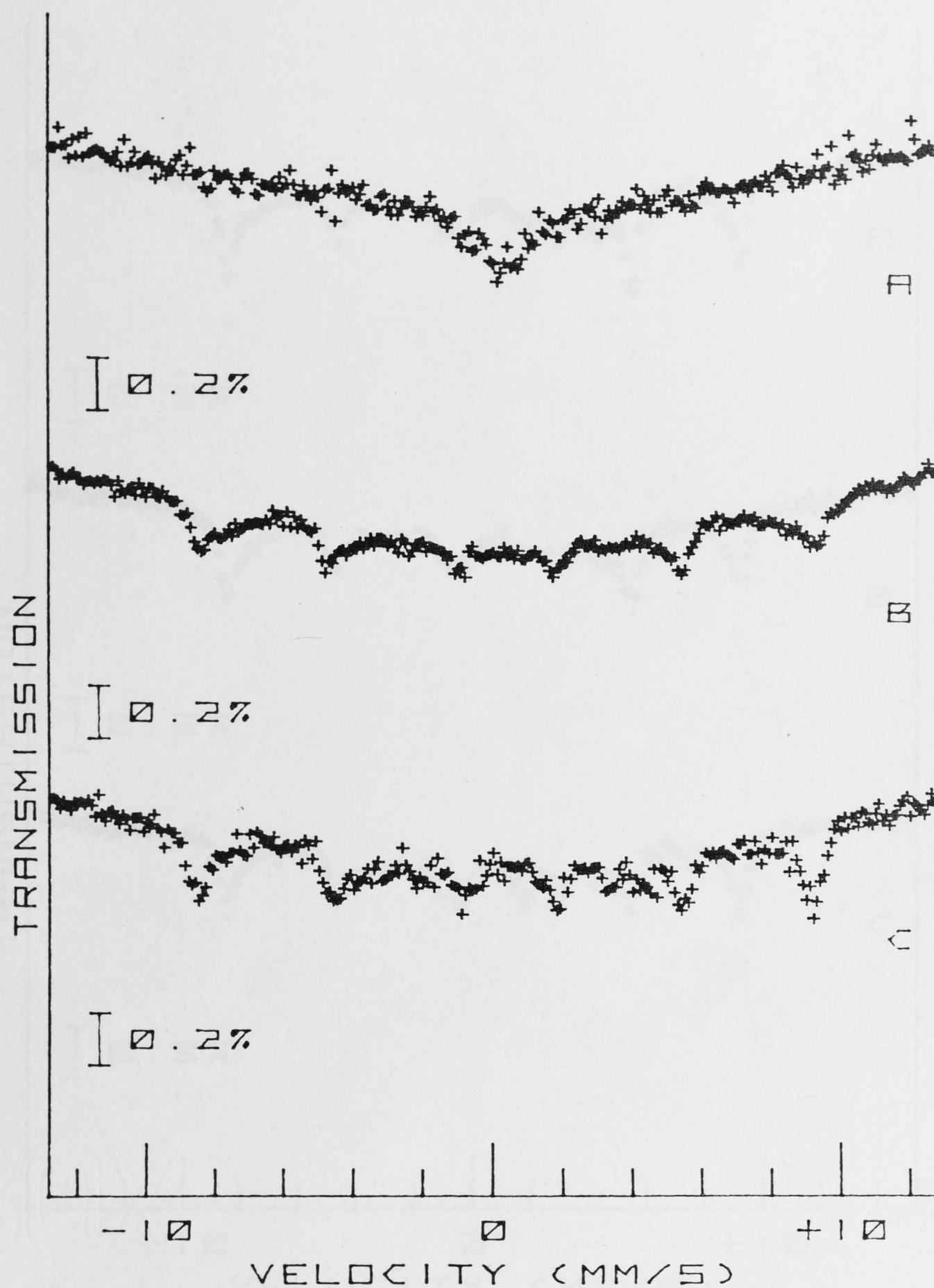


Figure (4.9) Mössbauer spectra of frozen solutions samples, at 4.2 K with concentration approximately equivalent to $K_3[(Al_{1-x}Fe_x)(C_2O_4)_3] \cdot 3H_2O$ in solid solution

(A) $x = 0.002$ in water

(B) $x = 0.00008$ in water

(C) $x = 0.0004$ in ethyleneglycol:water = 1:1

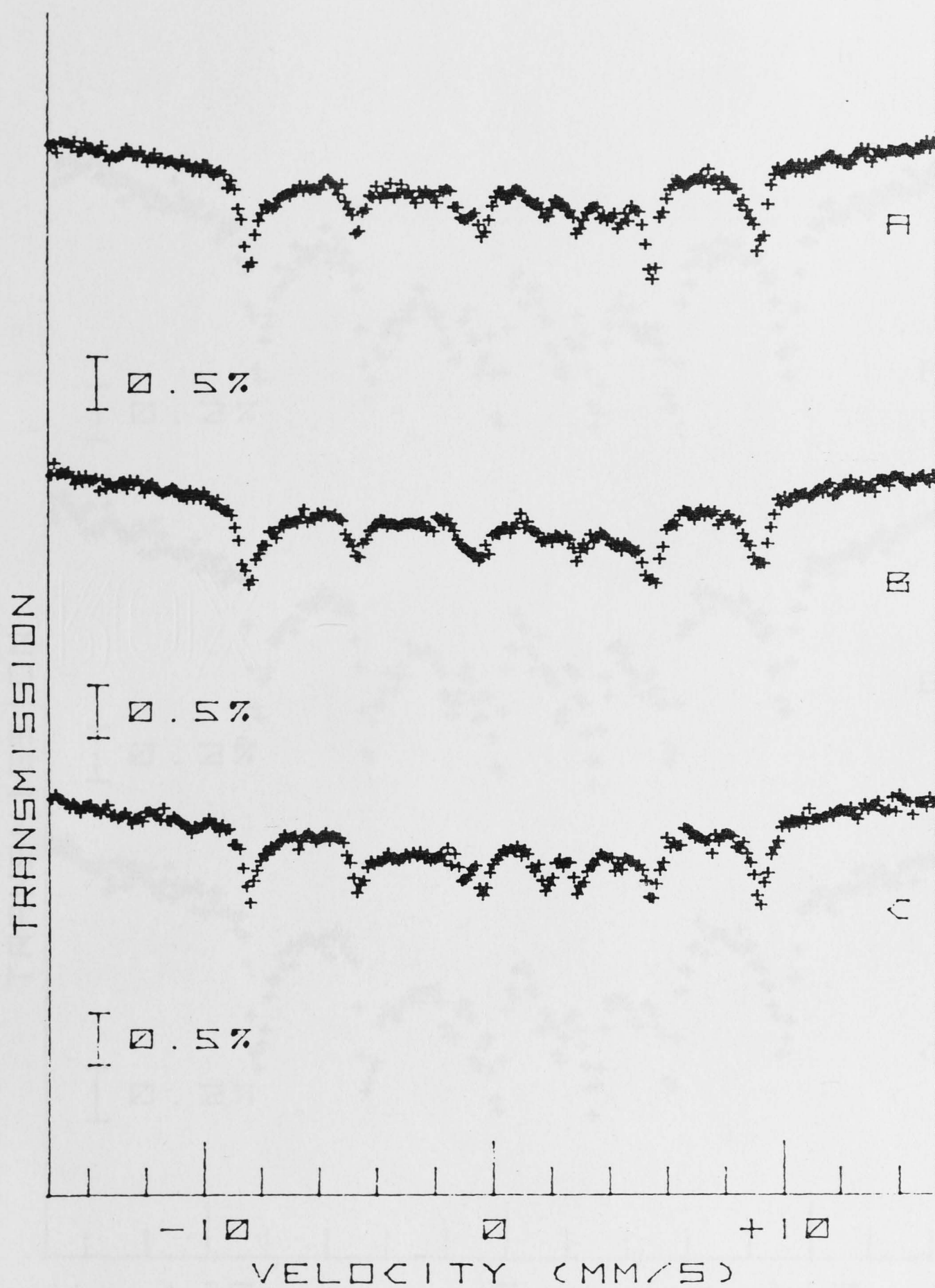


Figure (4.10) Mössbauer spectra of frozen solutions with concentration approximately equivalent to $K_3[(Al_{0.099}Fe_{0.001})(C_2O_4)_3] \cdot 3H_2O$ in ethyleneglycol:water = 1:2

(A) $H = 0$ Oe at 4.2 K

(B) $H = 0$ Oe at 1.3 K

(C) $H \approx 5$ Oe at 4.2 K

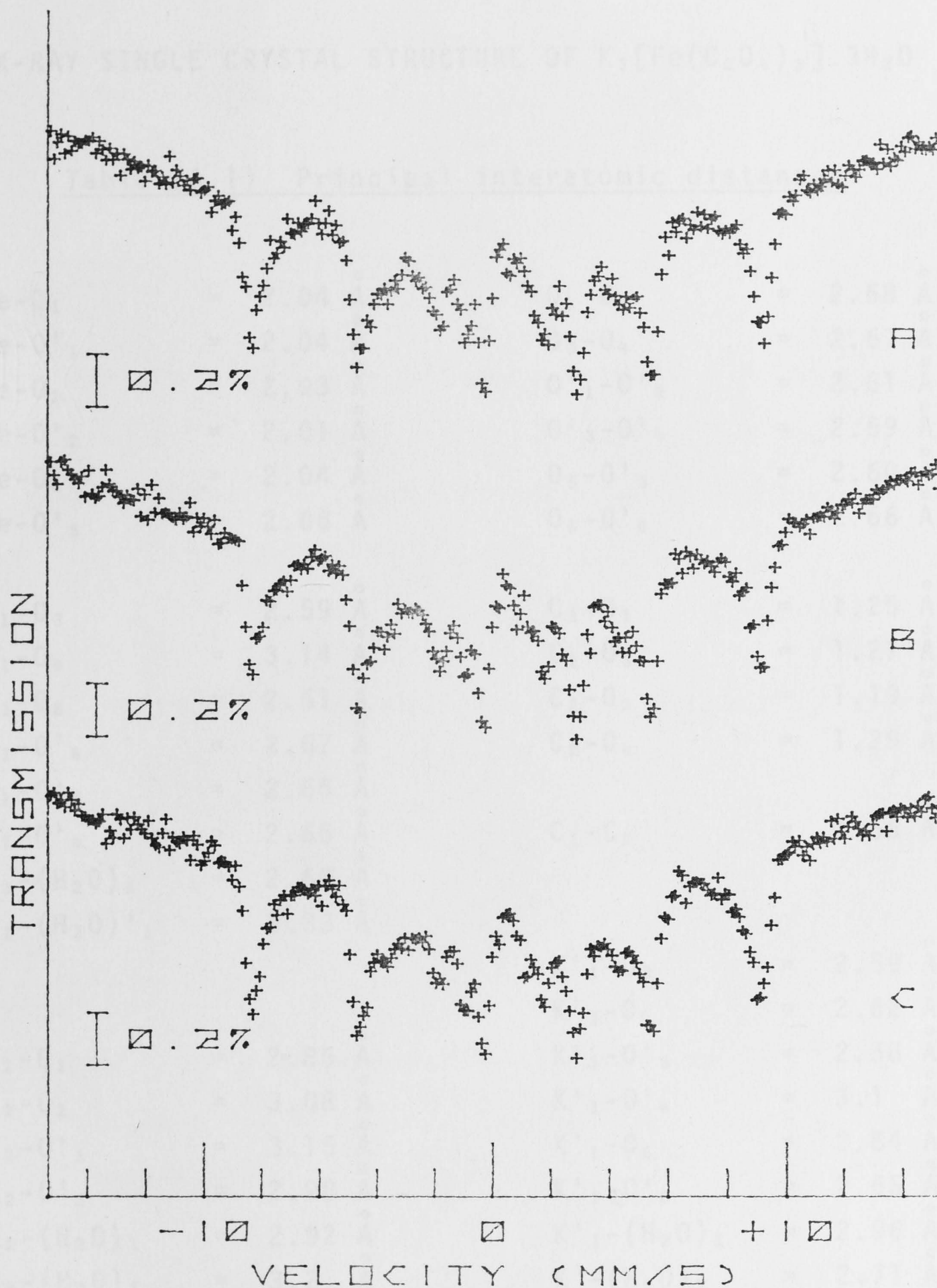


Figure (4.11) Mössbauer spectra of frozen solutions with concentration approximately equivalent to $K_3[(Al_{0.099}Fe_{0.001})(C_2O_4)_3] \cdot 3H_2O$ solid solution, in ethyleneglycol:water = 1:2

- (A) $H = 60.0e$
- (B) $H = 100.0e$
- (C) $H = 500.0e$

Table (A.2) Fe-Fe distances

From the atomic distances in table (A.1), we can calculate the Fe-Fe distances.

- (a) The shortest Fe-Fe distance is $6.95 \text{ \AA}$ between $\text{Fe}^{(1)}$ and $\text{Fe}^{(2)}$ where (1) corresponds to the base symmetry operation x, y, z and (2) corresponds to the base symmetry operation $x, \frac{1}{2}-y, \frac{1}{2}+z$.
- (b) The Fe-Fe distance is $7.66 \text{ \AA}$ between $\text{Fe}^{(1)}$ and $\text{Fe}^{(3)}$ where (3) corresponds to the base symmetry operation $1+x, y, z$.
- (c) The Fe-Fe distance is $10.27 \text{ \AA}$ between $\text{Fe}^{(1)}$ and $\text{Fe}^{(4)}$ where (4) corresponds to the base symmetry operation $x, y, 1+z$.
- (d) The Fe-Fe distance is $10.64 \text{ \AA}$ between $\text{Fe}^{(1)}$ and $\text{Fe}^{(5)}$ where (5) corresponds to the base symmetry operation $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

APPENDIX B

X-RAY POWDER DIFFRACTION PATTERN FOR $K_3[Fe(C_2O_4)_3] \cdot 3H_2O^*$

$d \text{ \AA}$	I/I_1	$d \text{ \AA}$	I/I_1
10.2	55	2.46	8
6.9	100	2.36	8
6.6	8	2.31	14
4.96	55	2.18	65
4.68	8	2.12	14
4.43	25	2.03	8
4.09	25	1.96	8
3.61	65	1.90	8
3.48	8	1.85	8
3.34	25	1.81	8
3.16	45	1.75	14
3.03	40	1.71	8
2.85	14	1.67	14
2.67	60	1.52	8
2.58	35	1.32	8
2.51	8		

* ASTM Powder Diffraction File 1965.

APPENDIX C

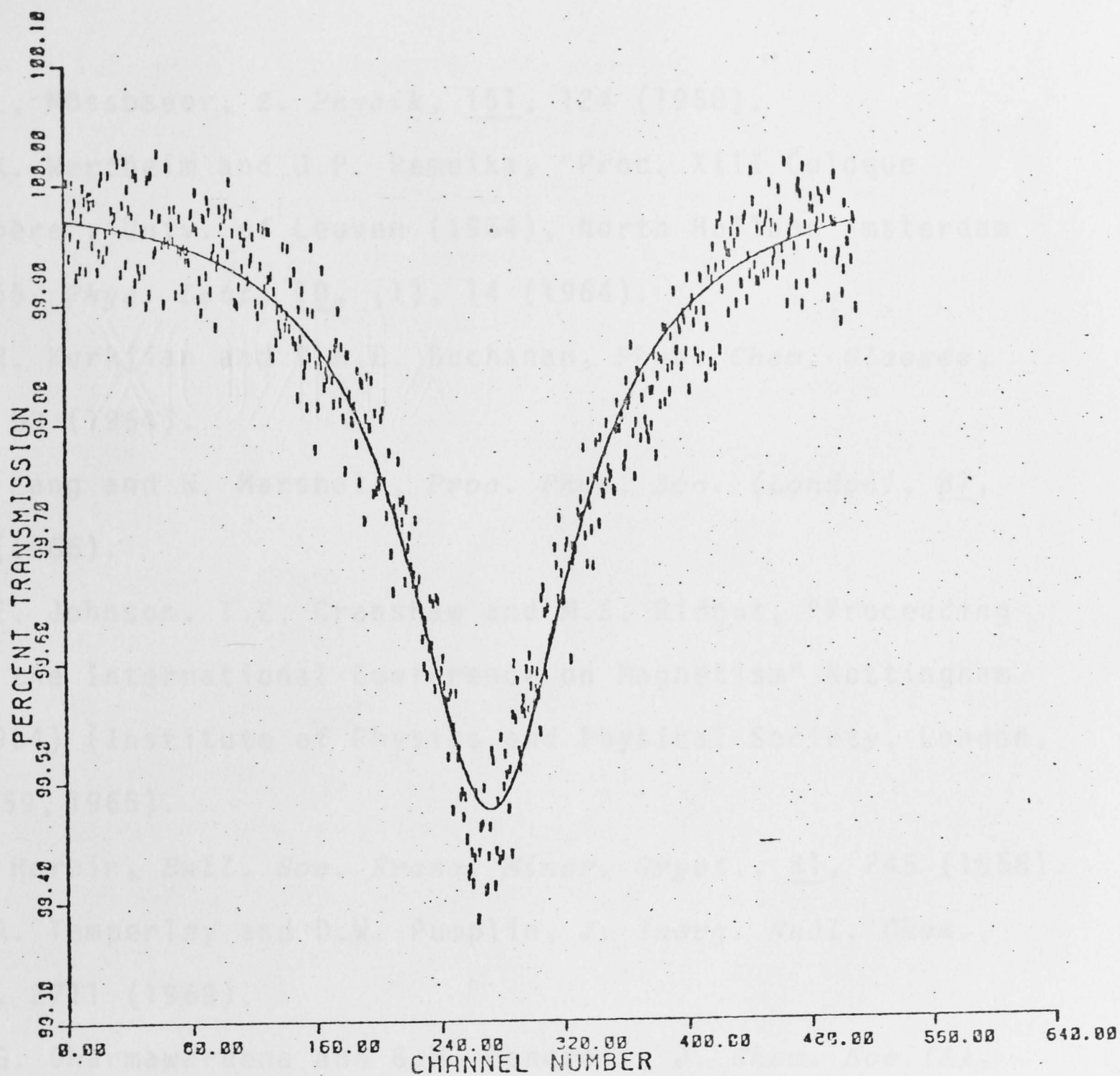


Figure (C.1) The Mössbauer spectrum of $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ at room temperature. A single-Lorentzian-line least square fit with isomer shift = 0.33 mm sec^{-1} , line width = 1.98 mm sec^{-1} .

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