

SOME PROPERTIES OF FERRIMAGNETIC SPINELS
AND THEIR DETERMINATION WITH THE MÖSSBAUER EFFECT

A thesis

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ABSTRACT

In this thesis we report the results of a Mössbauer effect and magnetic moment study of several ferrimagnetic spinels. By determining the area ratio of the tetrahedral (A) and octahedral (B) site lines for Fe_3O_4 and YIG as a function of temperature we have determined the ratio of recoilless fractions $\frac{f'_B}{f'_A}$ for Fe^{57} in A and B sites. At room temperature we find $\frac{f'_B}{f'_A} = 0.94$ and at 0° K we find $\frac{f'_B}{f'_A} = 0.99$. A method is described for determining the cation distribution among crystallographically inequivalent sites without knowledge of the ratio of recoilless fractions.

The temperature dependence of the hyperfine coupling constant is determined by comparing hyperfine field data obtained for Fe_3O_4 to the sublattice magnetization as measured by neutron diffraction over a 500° K temperature interval. It is found that the hyperfine coupling constant changes by less than 1% over the 500° K temperature interval for both Fe^{57} in A and B sites.

The determined ratio of recoilless fractions is used in conjunction with Mössbauer spectra in high applied fields to determine the cation distribution of NiFe_2O_4 , CoFe_2O_4 and MnFe_2O_4 . NiFe_2O_4 is found to be inverse, the cation distribution of CoFe_2O_4 is found to be dependent on the heat treatment. The cation distribution determined for MnFe_2O_4 is the same as that determined by neutron diffraction experiments.

The magnetic moment of CoFe_2O_4 is determined as a function of the cation distribution. The contribution to the magnetic moment of a Co^{2+} ion in a B site is found to be $3.1 \leftrightarrow 3.2$ Bohr magnetons per ion. This value is discussed in terms of an orbital contribution to the magnetic moment, covalency effects and a reduction in the spin contribution due to spin orbit coupling.

Experimental evidence is presented which indicates the absence of any Fe^{2+} in MnFe_2O_4 . The low magnetic moment of MnFe_2O_4 is discussed in terms of a proposed spin arrangement which requires only the B site Mn magnetic moments to make a substantial angle with the A site Mn magnetic moments. This spin arrangement is consistent with the absence of a $\Delta m = 0$ transition in the Mössbauer spectrum in a high magnetic field.

A model is proposed which explains in good detail the broad asymmetrical absorption lines found for Fe^{57} in B sites of CoFe_2O_4 and MnFe_2O_4 . The model is based on the assumption that the temperature dependence of an Fe^{57} B site hyperfine field depends on the kind and distribution of nearest neighbor A site ions. The temperature dependence of the various B site hyperfine fields are determined for CoFe_2O_4 and MnFe_2O_4 . Using a simple extension to the molecular field theory we have found the $\text{Fe(A)} - \text{Fe(B)}$, $\text{Co(A)} - \text{Fe(B)}$ and $\text{Mn(A)} - \text{Fe(B)}$ superexchange interactions by comparing theoretical calculations to the experimental data. The ratio of the $\text{Co(A)} - \text{Fe(B)}$ and $\text{Mn(A)} - \text{Fe(B)}$ superexchange interactions to the $\text{Fe(A)} - \text{Fe(B)}$ interaction is found to be 0.68 and 0.66 respectively.

Mössbauer spectra taken at low temperatures indicate a distribution in hyperfine fields at Fe^{57} B site nuclei at 0°K for MnFe_2O_4 and CoFe_2O_4 . This distribution in hyperfine fields is discussed in terms of super-transferred hyperfine fields which seems to explain the observed effects at least qualitatively.

A possible correlation between super-transferred hyperfine fields and superexchange interactions is discussed and is displayed using published hyperfine field data for the orthoferrites.

The various contributions to the hyperfine fields including covalency and overlap effects. The difference in the A and B site hyperfine fields is discussed in terms of covalency effects. It is found that both the isomer shifts and hyperfine fields can be explained at least qualitatively by including the ligand to metal 4s transfer.

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CHAPTER 1

Introduction

1.1 General

Ferrimagnetic spinels have been of interest to chemists, physicists and engineers since their discovery. The main reasons for the interest in these materials are their magnetic and electrical properties and the fact that these properties can be varied over a wide range by simply varying the kind of cations in the material. Materials like $\gamma\text{Fe}_2\text{O}_3$ and combinations of Mn, Ni and Zn ferrites are commonly used materials in magnetic tapes and in ferrite core computer memories. Although many of the macroscopic properties of ferrimagnetic spinels have been studied and explained in part there are numerous properties which are not fully understood. Since the discovery of the Mössbauer effect the interest in ferrimagnetic spinels and garnets has been renewed. The Mössbauer effect provides a new means for investigating the submicroscopic properties of these materials and with the use of the Mössbauer effect we hope to gain a better understanding of their properties.

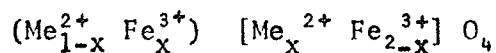
1.2 Spinel Structure

Since the spinel structure has been reviewed in detail in numerous publications (1-4), I will only briefly describe the structure as related to the work presented here.

The general chemical formula for the ferrimagnetic spinels which are reported on here is $\text{Me}^{2+} \text{Fe}^{3+} \text{O}_4$, where Me refers to various possible divalent cations. In the spinel structure the oxygen ions form a cubic close packed framework which provides for two types of "holes" for the cations. There are thirty-two holes of octahedral symmetry per unit cell of which sixteen are usually occupied by cations. These "holes" or sites will be referred to as B sites. There are sixty-four "holes" of tetrahedral symmetry per unit cell of which eight are usually occupied by the cations. These are referred to as A sites.

The size of one unit cell of the oxidic spinels is usually between eight and nine $\text{\AA}^3$. It should be noted that the cation-oxygen distance for the A sites is considerably less than that for the B sites. These distances are given by $a(\frac{1}{8} + \delta) \sqrt{3}$ and $a\sqrt{\frac{1}{16} - \frac{\delta}{2} + 3\delta^2}$ respectively (3). δ denotes the slight deviation of the oxygen positions from the ideal structure. The fact that the A site hole is smaller than the B site hole has important consequences when one is attempting to explain the difference in the hyperfine fields and isomer shifts for Fe^{57} nuclei in the two sites.

Since the magnetic properties of the spinels depend on the cation distribution over these two types of sites we will write the chemical formula as



where the round brackets refer to cations in the A sites and the square brackets to those in the B sites.

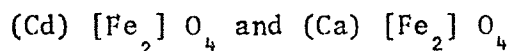
There are 3 classes of spinels which differ in the distribution of the divalent and trivalent cations over the two sites.

These are :

1. $x = 0$ i.e. all the divalent cations are in the A sites.

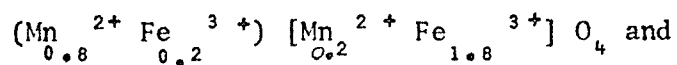
This is generally referred to as a normal spinel.

Examples of these are :



2. $0 < x < 1$ i.e. both sites contain some trivalent and some divalent cations.

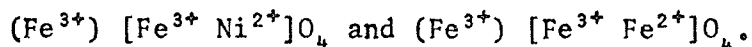
Examples of these are :



$(\text{Mg}_{1-x} \text{Fe}_x) [\text{Mg}_x \text{Fe}_{2-x}] \text{O}_4$. In these materials one can usually vary the cation distribution by heat treating the sample.

3. $X = 1$ i.e. All the divalent cations are in the B sites.

Examples of these are referred to as inverse spinels :



The particular class that a material belongs to depends on the site preference of the cations involved. Dunitz, Orgel (5) and McClure (6) have calculated the site preference of various transition metal ions using a purely ionic bond and a one electron model. The site preference is calculated from the cubic crystal field stabilization which is due to the crystal field splitting of the d orbitals into a doublet (e_g) and a triplet (t_{2g}). The site preference then depends on the splitting of the e_g and t_{2g} levels in the A and B sites. The results of this calculation are that the octahedral site preference increases in the order : Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} .

Blasse (3) has done calculations using molecular orbital theory and found that the octahedral site preference of these ions increased in the order :-

Mn^{2+} , Co^{2+} , Mg^{2+} , Ni^{2+} . This is in better agreement with experimental results.

Besides the cubic crystalline field the spinel structure also provides for a trigonal field with the [111] axis as the axis of trigonal symmetry. This has important consequences as far as the magnetic anisotropy and the orbital contribution to the magnetic moment are concerned. The trigonal field splits the ground state t_{2g} orbital triplet into a lower

lying doublet plus a singlet of higher energy. This effect together with spin-orbit coupling has been used to calculate the magnetic anisotropy (7), (8) and orbital contribution to the magnetic moment for a Co^{2+} ion in a B site.

1.3 Ferrimagnetism

The materials to be discussed belong to a class called ferrimagnets. Ferrimagnetism has been reviewed in many publications (2-4, 9-11) so I will only present a brief description as related to the materials we are studying. This is a class of materials where the dominant super-exchange interaction is the antiferromagnetic intersublattice super-exchange interaction.

In the case of the spinels one finds that the A-B antiferromagnetic super-exchange interaction is usually the dominant one. That is to say the A-A and B-B super-exchange interactions are usually much less than the A-B interactions. This can be justified by considering the A-O-B, A-O-A and B-O-B bonding angles and relative distances. All the possible angles and distances have been shown in a paper by Gorter (2). From these considerations one can also come to the conclusion that the B site ions have six nearest neighbour A-site ions for favourable super-exchange and that A-site ions have twelve such nearest neighbour B-site ions. The temperature dependence of the A- and B-site magnetizations can be described at least qualitatively by the molecular field approximation. In the special case where the A- and B-site ions are the same and the A-A and B-B interactions can be neglected we can write;

$$H(B) = N_{AB} M_A$$

$$H(A) = N_{AB} M_B$$

where $H(B)$ and $H(A)$ are the molecular fields acting on the A and B sites respectively and N_{AB} is the molecular field coefficient corresponding to the A-B super-exchange interaction. M_A and M_B refer to the magnetizations of the A and B site ions respectively. At 0°K $M_B = 2M_A$ if all the available sites are occupied, so it is easy to see that the B site magnetization will decrease more rapidly than that of the A site. To show this experimentally, can of course not be done by bulk magnetization measurements but it can be done by methods like neutron diffraction, Mössbauer effect and N.M.R. The more complicated case where A-B and B-B interactions are taken into account can be found in Néels paper (9), books by Smart (11) or Morrish (10). Also in these works is given the relation between the long range magnetic ordering temperature and the various molecular field coefficients.

In the case where B-B or A-A antiferromagnetic super-exchange interactions are comparable to the A-B super-exchange interaction, the spin arrangement may be different from the simple collinear Néel type spin arrangement. It has been shown by Wafet and Kittel (12) that one can get triangular type spin arrangements in the case where the intrasublattice exchange interactions are comparable to the intersublattice interactions. This for example could happen if one substituted diamagnetic ions for the magnetic ions in one of the sublattices. We will show that for $MnFe_2O_4$ a non-collinear spin arrangement may be an explanation for the low magnetic moment of this material.

The magnetic moment of the ferrimagnetic spinel with the chemical formula given by $(\text{Me}_{1-x}^{2+} \text{Fe}_x^{3+}) [\text{Me}_x^{2+} \text{Fe}_{2-x}^{3+}] \text{O}_4$ will be $x M_{\text{Me}}(\text{B}) + (2 - x) M_{\text{Fe}}(\text{B}) - (1 - x) M_{\text{Me}}(\text{A}) - x M_{\text{Fe}}(\text{A})$ per unit chemical formula, at 0° K if the spin arrangement is of the Néel colinear type. M refers to the magnetic moment of the ion of type Me or Fe in the (A) or (B) sites. The Fe^{3+} ion is an S state ion, that is the 3d shell is half full giving it a net spin of $\frac{5}{2}$ and a magnetic moment of $5\mu_B$ where μ_B is the Bohr magneton. In the materials we have studied Me is either Mn^{2+} or Ni^{2+} or Co^{2+} or Mg^{2+} or Fe^{2+} . Of these Mg^{2+} has a filled shell, therefore the spin and orbital contribution will be zero. Mn^{2+} is isoelectronic to Fe^{3+} therefore it has a magnetic moment of $5\mu_B$. For Co^{2+} , Ni^{2+} or Fe^{2+} one will have in addition to the spin contribution also a contribution from the orbital angular momentum.

Measurements of the magnetic moment once the cation distribution is known gives information about the orbital contribution of ions like Co^{2+} , Ni^{2+} or Fe^{2+} or for Mn^{2+} or we can obtain information about the spin arrangement.

1.4 Mössbauer Effect

The basic principles involved and the many uses as a research tool of the Mössbauer effect have been reviewed in numerous articles and books (13-16). I will only present the reasons why it is useful in the study of ferrite spinels and use this section also to define many of the symbols which will be used throughout the thesis.

With the Mössbauer effect one can measure the effects of the interaction of the nucleus with its surroundings. If the properties of the nucleus are known as most of them are for Fe^{57} , we can use the nucleus to probe its surroundings. The nucleus has a charge Ze , a quadrupole moment Q and a magnetic dipole moment given by $g\mu_n I$. For Fe^{57} we measure effects of S-electron density, electric field gradient and magnetic field on the energy difference between the first excited state of energy 14.419 Kev, $I = \frac{3}{2}$, and the ground state 0 Kev, $I = \frac{1}{2}$. The Hamiltonian of a nucleus in these effective fields is given by :

$$= g\mu_n I \cdot H + Q \cdot \nabla E + \frac{2\pi}{5} Ze^2 |\psi(0)|^2 R^2,$$

where g is the nuclear g factor. μ_n is the nuclear magnetic dipole moment, I is the nuclear spin, H is the magnetic field at the nucleus, Q is the nuclear quadrupole moment ∇E is the electric field gradient at the nucleus, $-Ze$ is the nuclear charge, $|\psi(0)|^2$ is the electron density at the nucleus, and R is the nuclear radius.

If the quadrupole interaction is small compared with that of the magnetic dipole interaction and if the electric field gradient is axially symmetric with the symmetry axis making an angle θ with respect to H , then the energy levels will be given as follows for $I = \frac{3}{2}$ and $I = \frac{1}{2}$, i.e. the excited and ground states of Fe^{57} :-

$$E^{\frac{3}{2}} = -g_{ex} \mu_n H M_{I_{ex}} + (-1)^{|M_I|} + \frac{1}{2} \frac{e^2 q Q}{4} \frac{3 \cos^2 \theta - 1}{2}$$

$$+ \frac{2\pi}{5} Ze^2 |\psi(0)|^2 R_{ex}^2.$$

[1]

$$E^{\frac{1}{2}} = g_g \mu_n H M_{I_g} + (0) + \frac{2\pi}{5} Ze^2 |\psi(0)|^2 R_g^2.$$

The quadrupole interaction energy for $I = \frac{1}{2}$ is zero because of the presence of a term like $[3M_I^2 - I(I+1)]$. The energy separation of the ground and excited states is then :-

$$E_{M_{Iex}} - E_{M_{Ig}} = -\mu_n [g_{ex} M_{Iex} - g_g M_{Ig}] + (-1)^{|M_I|} + \frac{1}{2} \quad [2]$$

$$\frac{e^2 q Q}{4} \frac{3 \cos^2 \theta - 1}{2} + 2 \frac{\pi}{5} Z e^2 (R_{ex}^2 - R_g^2) [|\psi(0)|^2]$$

Here q is the axial component of the electric field gradient.

The more complicated examples where the electric field gradient is not axially symmetric or where the quadrupole interaction is comparable to the magnetic dipole interaction can be found in the literature (13,17,18).

The various origins of the magnetic field H have been discussed in numerous publications (19-22). The main contribution in the case of Fe^{3+} in a magnetically ordered material is from the spin polarization of the s electrons by the 5 unpaired $3d$ electrons (19), which gives rise to the Fermi contact term. Some of the other contributions will be discussed later.

Eg[2] gives rise to eight possible transitions, two of which corresponding to $\Delta M = \pm 2$ are forbidden transitions and can only be observed if the quadrupole interaction is comparable to the magnetic dipole interaction. The intensities of the other six transitions and their dependence on the γ -ray polarization are given in table 1.1 (3).

Table 1-1

Intensities of the six allowed first excited to ground state transitions for Fe^{57} and the dependence on γ ray polarization.

<u>Transitions</u>	<u>Δm</u>	<u>Total</u>	<u>Angular dependence</u>
$\frac{3}{2} \rightarrow \frac{1}{2}$	-1	3	$\frac{3}{4}(1 + \cos^2\theta)$
$-\frac{3}{2} \rightarrow -\frac{1}{2}$	+1		
$\frac{1}{2} \rightarrow \frac{1}{2}$	0	2	$3 \sin^2\theta$
$-\frac{1}{2} \rightarrow -\frac{1}{2}$	0		
$-\frac{1}{2} \rightarrow \frac{1}{2}$	+1	1	$\frac{3}{4}(1 + \cos^2\theta)$
$\frac{1}{2} \rightarrow -\frac{1}{2}$	-1		

The last term in eq (2) is called the isomer shift. This term merely shifts the center of the spectrum. There is another term which is not present in eq (2) which also shifts the center of the spectrum. This is the second order doppler shift (23) given by

$$\frac{\Delta E}{E_0} = \frac{1}{2} \frac{\langle v^2 \rangle}{c^2}$$

where ΔE is the energy shift, E_0 is the γ -ray energy and v is the velocity of the nucleus bound in a crystal. From the temperature dependence of the shift we can obtain information about the vibrational kinetic energy of the nucleus.

It was mentioned previously that with the Mössbauer effect we can probe the surroundings of a nucleus. The important thing is that we can do this on an atomic scale. In the ferrites the nucleus can be situated in either an A or B site. The nuclei in these two sites have different immediate surroundings and thus have in general different energy levels. Since for Fe^{3+} the main contribution to the hyperfine field comes from the contact term and since the relaxation time of the electronic spins is much smaller than nuclear precession time (see section 4) the hyperfine field will be proportional to $\langle S_z \rangle$ where S_z is the z component of the electronic spins. By measuring the temperature dependence of the hyperfine field we can find the temperature dependence of the magnetization for both the A and B sites. As pointed out previously this information cannot be obtained by macroscopic magnetization measurements.

It will also be shown in a later section that with the Mössbauer effect we can determine the relative number of ions in the two sites from which we can determine the cation distribution. The cation distribution as pointed out before is extremely important in attempting to describe the macroscopic magnetic properties of ferrites.

To find the relative amount of iron in the two sites of ferrites one must be able to measure the intensity ratios of the Mössbauer lines corresponding to Fe^{57} in the two sites. In order to do this the lines corresponding to Fe^{57} in the two sites must be well separated. If they are not well resolved as is frequently the case, a large external magnetic field can be used to separate them. This happens because of the antiferromagnetic alignment of the spins in the two sites. Since the hyperfine field (H_{hpf}) is antiparallel to the electronic magnetic moment the applied field will add to the H_{hpf} at the nuclei in A sites and subtract from H_{hpf} for nuclei in B sites. In this way the spectra can be resolved. This was first reported by us in the case of $\gamma\text{-Fe}_2\text{O}_3$. (24).

1.5 Analysis of the Mössbauer Spectra

The recoilless γ -ray absorption lines have ideally a Lorentzian line shape given by :

$$Y(v) = Y_0 \left[1 - \frac{\alpha}{\left(\frac{v-v_j}{.5\beta} \right)^2 + 1} \right] \quad [1]$$

where $Y(v)$ is the number of counts at a velocity v , Y_0 is the off resonance

counting rate, α is the fractional absorption at the peak position given by v_j and β is the full width at half height. A complete Mössbauer spectrum may consist of the sum of several such peaks and in some cases Y_0 may also be a function of the velocity. In this case equation [1] must be modified as follows :

$$Y(v) = Y_0 \sum_{i=0}^m k_i (v-v_0)^i \left[1 - \sum_{j=1}^N \frac{\frac{\alpha_j}{2}}{\left(\frac{v-v_j}{.5\beta_j} \right)^2 + 1} \right] \quad [2]$$

where $Y_0 \sum_{i=0}^m (v-v_0)^i$ is just the polynomial describing the off resonance

counting rate as a function of the velocity. α_j , v_j , β_j are the parameters of the Lorentzian corresponding to peak j . A computer program was obtained from Argonne National Laboratories (25) which does a least square fit by variable metric minimization to an equation like [2] where n and m can range from 1 to 8. In this program initial guesses for the parameters and errors in the parameters were input requirements. Since the program requires a lot of core storage it was possible to use only 200 data points at one time. This required us to fit one spectrum in sections containing one or more Lorentzians.

On numerous occasions we wanted to fit several Lorentzians to a line which showed some structure or asymmetrical broadening but where the separate Lorentzians were not well resolved. In this case it is possible to put constraints on one or more of the parameters. The constraints chosen may be based on a theory or model which one is attempting to justify. Since the program requires initial guesses for the parameters

we frequently used the final parameters obtained with the constraints imposed as the initial guesses for a fit without constraints to see if the goodness of fit would improve. The goodness of fit is found in all cases and is given by :

$$F = \sum_{i=1}^{NP} \frac{(Y_{exp}^i - Y_{calc}^i)^2}{Y_{calc}^i}$$

For a good fit we should have $F < 1.5 NP$ where NP is the number of data points.

CHAPTER 2

Apparatus

2.1 Magnetic Moment Measurements

The magnetic moment measurements were carried out using a vibrating sample magnetometer made by P.A.R. (26). The measurements were carried out in an applied field of up to 18 KOe. The field was supplied by an electromagnet manufactured by Magnion (27).

The magnetic field measurements were made with a rotating coil gauss meter which was accurate to $\pm 1\%$ gauss. The magnetometer was calibrated with a nickel sample for which we used a magnetic moment of 55.07 e mu/g (29) at room temperature extrapolated to zero applied field from the high field values.

The magnetic moment measurements at 4.2° K and 77° K were carried out using a variable temperature cryostat built by Andonian (30). This cryostat uses a variable flow of liquid helium or liquid nitrogen plus a heater coil to vary the temperature in the sample chamber. The measurements were carried out either on pellets of sintered materials or powdered samples. The pellets were mounted on a sample holder by using ordinary glue. The powder samples were encapsulated in either an aluminum or epoxy resin sample holder. The aluminum was used for low temperature work in order to ensure that the sample and the sample chamber were at the same temperature. Temperature measurement was carried out using a copper-constantan thermocouple mounted on the walls of the sample chambers. At LHe temperatures we used a thermistor to measure temperature.

To obtain the magnetic moment at 0° K we used the relation

$$\sigma(0, 4.2) = \lim_{H_i \rightarrow \infty} \frac{\sigma(H_i, 4.2^\circ)}{1 - C/H_i} \quad [1]$$

where $\sigma(H_i, T)$ is the magnetic moment per gram, H_i is the internal field and T is the temperature.

We then got measurements of σ_i at various field and 4.2° K and extrapolated these results to $\frac{1}{H_i} \rightarrow 0$. Equation [1] is correct in the case of low temperatures compared to the magnetic order-disorder transition temperature and for fields much less than the molecular field.

In order to use equation [1] we are required to know H_i the internal field produced by both the applied field and the demagnetization field produced by the material itself. This requires knowledge of the samples. We can, however, get a reasonable estimate of H_i as follows. First we assume that the sample is uniformly magnetized. We can then write that $H_i = H_a - DM\rho$ where D is the demagnetization constant, H_i is the applied field, ρ is the density and M is the magnetic moment. For low values of H_a that is in a region H_a below the approach to saturation we will have a region where $H_i \ll H_a$ so that $H_a \approx DM\rho$. From the slope of the straight line in a plot of M vs H_a we can determine H_i for high applied fields.

The magnetization will usually be given in terms of μ_B /formula.

2.2 Mössbauer Apparatus

The Mössbauer effect spectrometers were purchased from Elron. (31). One of these spectrometers was operated at constant velocity and the other at constant acceleration. The block diagrams for the two systems are shown in figures 2.1 and 2.2 respectively. Both systems used an electromechanical drive, which consists of a central cylinder moving in a magnetic field produced by permanent magnets. The motion is produced by coils mounted on either end of the cylinder. One coil is used as the driving coil while the other serves as a velocity sensing device. The signal from the sensing coil is compared to a reference voltage supplied by scaler 1 and a digital to analog converter. The difference signal is amplified and fed into the driving coil. The velocity is then directly proportional to the number appearing in scaler 1. In the constant velocity mode, the velocity is kept constant until the moving member activates a limit switch at which time a flyback signal is supplied to the driving coil which causes the moving cylinder to return to a second limit switch. The process is then repeated. During the flyback period the gate to scaler 2 is closed.

This process is repeated for from 100 - 300 secs live time at which time a printer prints out the values of scaler 1 and 2 and scaler 1 is advanced to the next number. In this way the whole velocity scale from - v_{max} to + v_{max} is swept through in up to 1000 steps.

FIGURE 2-1

Block diagram of the constant velocity Mössbauer
effect spectrometer

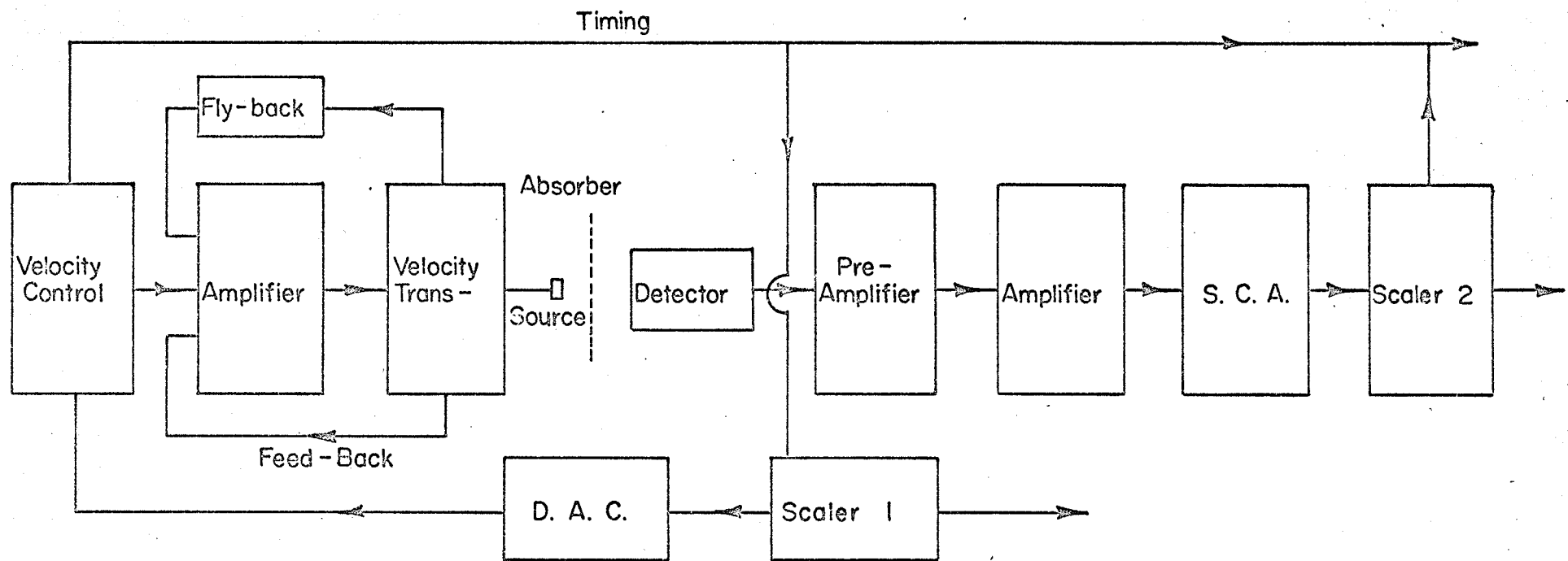
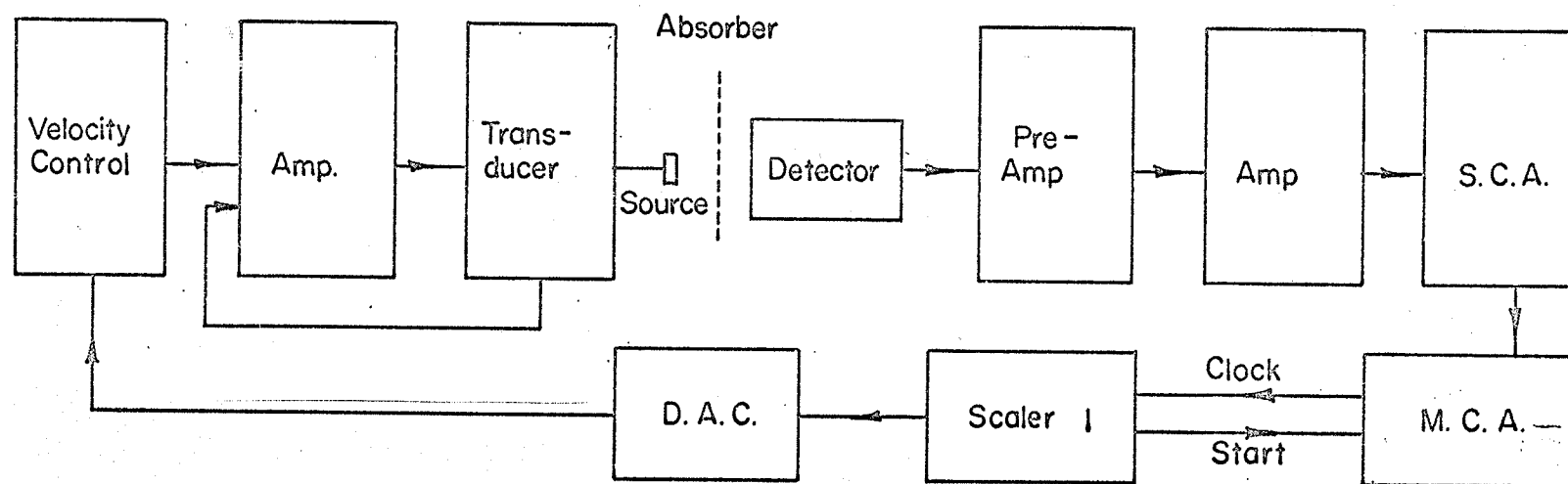


FIGURE 2-2

Block diagram of the constant acceleration
Mössbauer effect spectrometer



The constant acceleration system works in conjunction with a ND 2200 1024 channel analyser (32). Clock pulses advance the M.C.A. at the same rate as scaler 1. In this way the velocity is constant while the M.C.A. is at a particular location with a velocity proportional to the number on scaler 1. When the moving member reaches the limit switch, scaler 1 is set to zero and the scanning of the M.C.A. and the scaler 1 is started. The advantage of the constant acceleration system is that one does not require as good long term stability in the radiation detection system as one needs for the constant velocity mode.

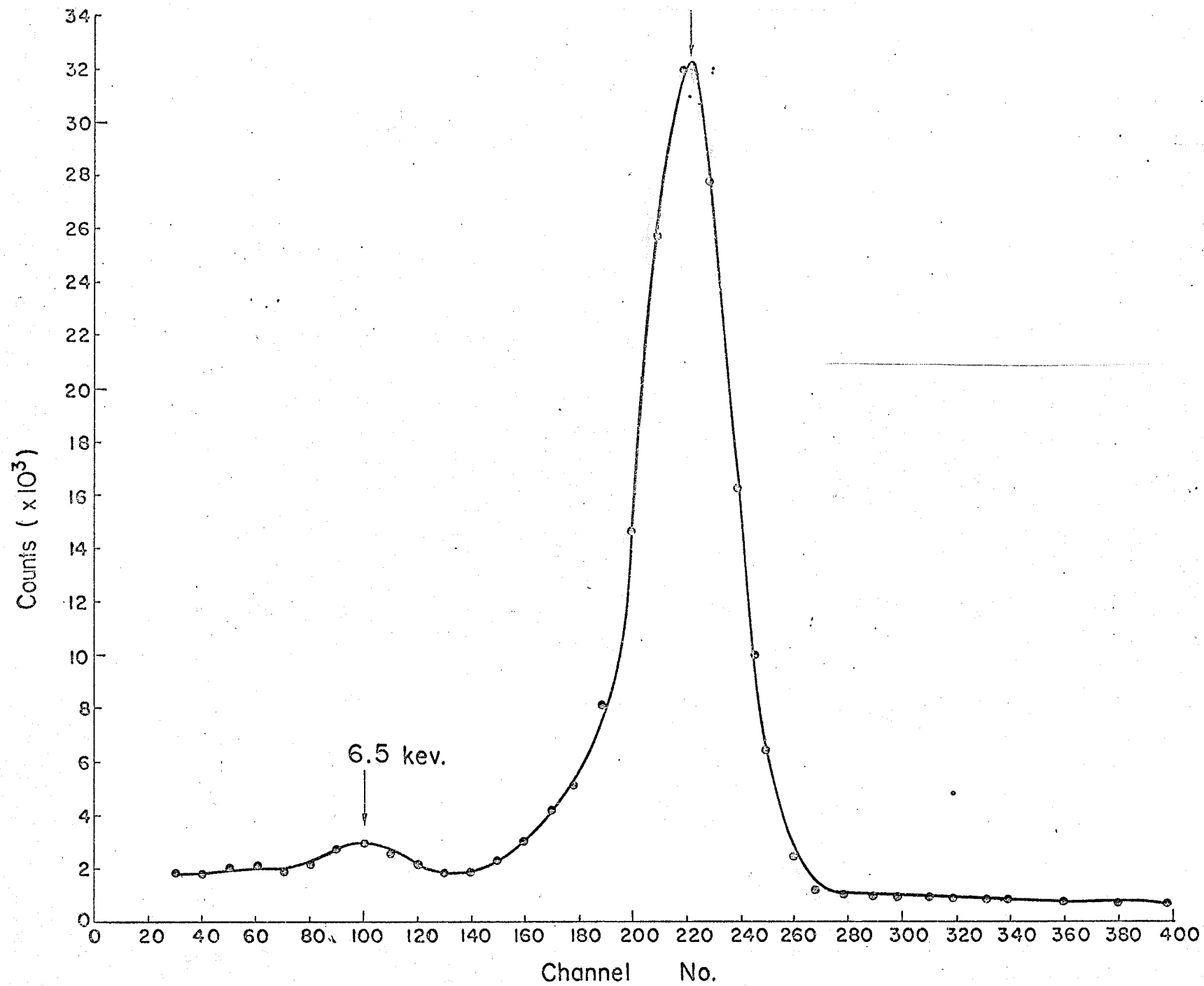
The radiation detection and selection system consisted of a sealed Ar 10% Methane proportional counter manufactured by Twentieth Century Electronics (33). A high voltage power supply, pre amp, amplifier, a single channel analyser and scaler 2, A spectrum obtained using a Co^{57} source in a Cr matrix is shown in figure 2.3. The six Kev x-rays have been virtually eliminated with Al foil and Mylar. The S.C.A. is set to accept about two times the full width at half height of the 14 Kev peak.

The advantage of using a proportional counter instead of Na I(Tl) scintillation counter is that the proportional counter has much better resolution and also is insensitive to the 120 Kev γ -rays which if one wants to work with reasonable counting rates causes pile up when using the scintillation counter. The proportional counter cannot however be used with high counting rates when operating in the constant velocity mode because of quite serious drifts in the counting rate. We usually operated between 1000 and 1500 counts per second. Another disadvantage of using a

FIGURE 2-3

γ ray spectrum of a Co^{57} source using

an Ar 10% methane proportional counter



proportional counter is that it has a life time of only about one month to a year depending on the counting rating used.

We also tried a flow through counter but found that it was quite unstable. This instability was found to be due to fluctuations in atmosphere pressure since we did not use a pressure regulated system.

The Mössbauer sources used were 5 m.c. Co^{57} in Pd and 10 m.c. Co^{57} in Cr. The Cr source is more suitable than the Pd source because of the presence of a 22 Kev x-ray from the Pd.

To calibrate the spectrometer we used absorbers of $\alpha\text{Fe}_2\text{O}_3$ and Fe foil. A Mössbauer spectrum of $\alpha\text{Fe}_2\text{O}_3$ is shown in figure 2-4 together with the full widths at one half max of the various peaks. From the separation of the peaks the spectrometer can be calibrated using the known values listed in the Mössbauer effect data Index (34). The linearity of the system was checked by using an Fe foil absorber. In the case of Fe the separation of the lines i.e. Δ_{72} , Δ_{23} , Δ_{45} , Δ_{56} should be equal. The values we obtained are 56.8, 57.0, 57.0, 56.9 channels respectively.

Figure 2-4

Mössbauer spectrum of $\alpha\text{Fe}_2\text{O}_3$, ΔV indicates the line width in cm/sec.

Counts ($\times 10^3$)

58 60 62 64 66 68 70 72 74

$\Delta v = .031 \text{ cm/sec}$

$\Delta v = .028 \text{ cm/sec}$

$\Delta v = .023 \text{ cm/sec}$

$\Delta v = .023 \text{ cm/sec}$

$\Delta v = .028 \text{ cm/sec}$

$\Delta v = .031 \text{ cm/sec}$

2.3 Furnace and Cryostat

For the temperature dependent measurements we used a furnace and cryostat designed and built at the University of Manitoba. The designs were very similar to those reported by Sharon and Treves (35), except that the furnace and cryostat were built separately. In figures 2-5 and 2-6 is shown a diagram of the furnace and cryostat.

The furnace consists of an outer cylinder 1 made of stainless steel with three access ports marked 2, 3 and 4. The cylinder is closed at the top and bottom with removable stainless steel discs 5 and 6 and vacuum sealed using O rings. The holes in the center of these two discs are sealed with .005" mylar windows which are glued on with epoxy resin. Two stainless steel cups marked 7 and 9 fit into the outer casing and are separated from it and from each other with three stainless steel legs. These cups have removable covers marked 8 and 10 the first of which screws into 7 and the second fits into 9 using a pressure fit. Four .001" Al radiation shields cover the holes in the bottom and top of these cups. Two concentric s.s. cylinders connected with an s.s. ring 11 fit snugly into the s.s. cup 10. These cylinders support a 0.032" lava cylinder 12 which is used as electrical and thermal insulation. A heater wire 13 thermocoax N.C. -10 is counter-wound around the copper core 14. This assembly fits snugly into the lava cylinder 12. The copper core has two holes in the sides for two thermocouples. One thermo-

FIGURE 2-5

Furnace used for high temperature

Mössbauer experiments Scale 1:1

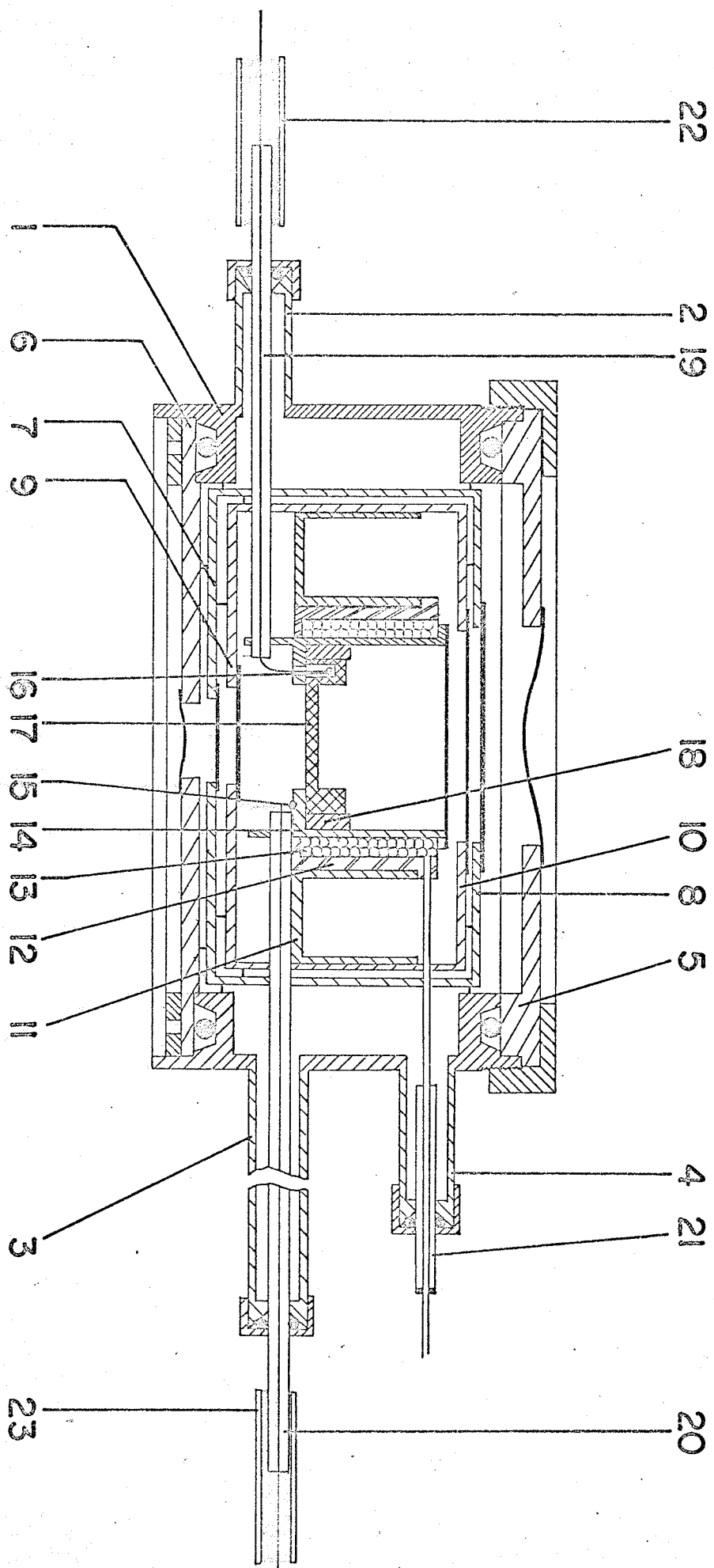
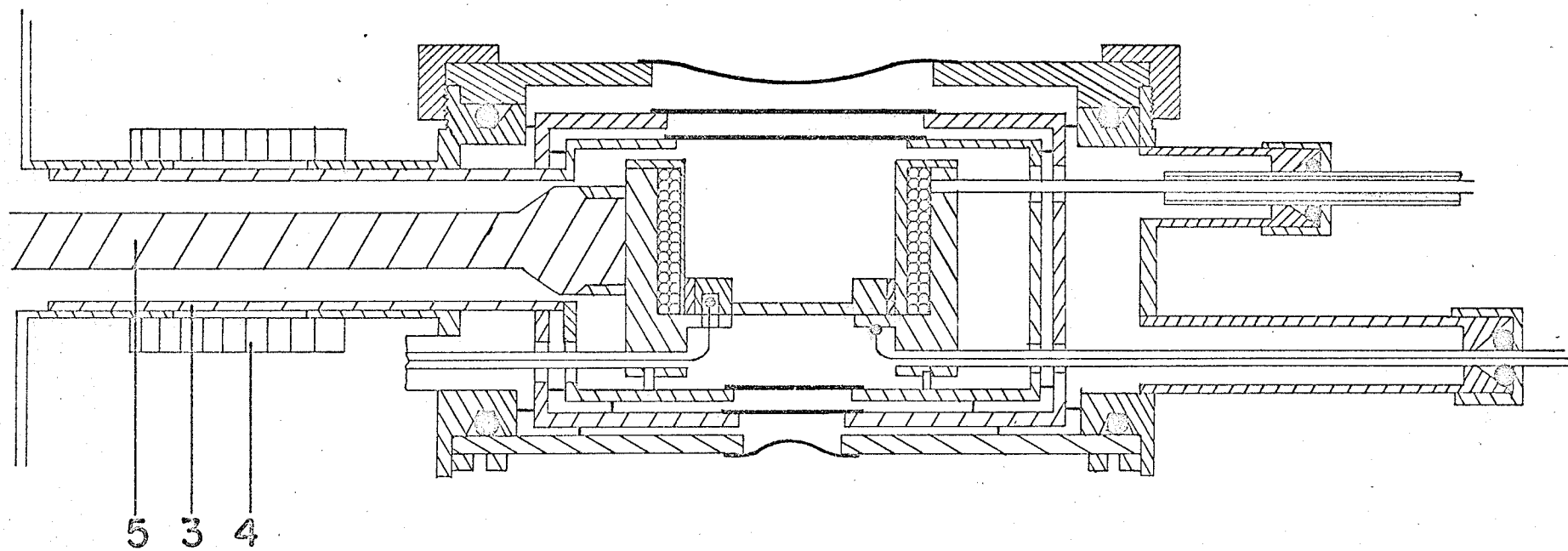


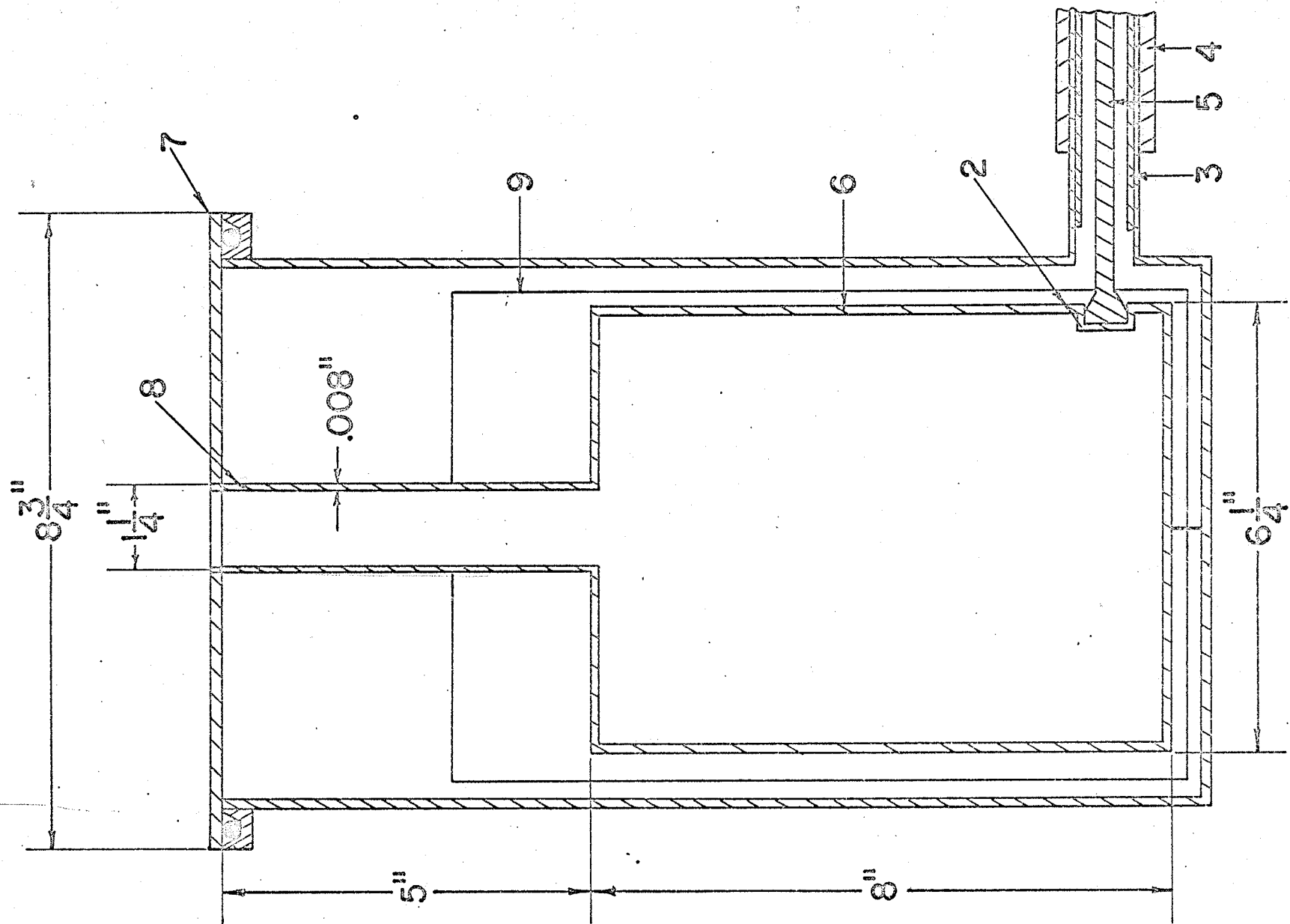
FIGURE 2-6

Liquid nitrogen cryostat and storage tank

Scale is 1:1 for the cryostat and 1:2 for

the storage tank





couple 15 is glued into the copper core with ceramic cement and electrically insulated from the copper with a thin coat of ceramic cement. Another thermocouple 16 is silver soldered into a small copper cup which fits snugly into a small hole at the bottom of a graphite dish 17. The graphite dish fits snugly into a copper ring 18 which fits snugly into the copper core. The thermocouples used are chromel and alumel. These pass through two double holed alundum tubes (19 and 20). The alundum tubing used is grade "A" obtained from McDanel Refractory Porcelain Company. Some of the other alundum tubing tried was too porous to obtain a good vacuum. These tubes pass through the ports marked 2 and 3. An O ring vacuum seals the alundum tubes to the body of the furnace. The thermocouples are vacuum sealed to the alundum tubing using quartz wax. This method enables us to take the wires directly out of the furnace without making any connections. The port marked 3 is also used as a vacuum port. A Fore pump and cold trap are used to evacuate the system to about 10μ . The power required to operate the furnace at 800°K is about twenty watts. At this temperature the outer wall of the furnace is at about $40^{\circ}\text{C} - 50^{\circ}\text{C}$. At higher temperatures than this we used a cooling fan.

The two thermocouples were used too; one control and two to measure the temperature. The reference junction of the control thermocouple was placed in L.N. This provides for a good reference because the slope of the E.m.f.vs. temperature curve is quite small at L.N. so that even if the reference temperature changes by 0.5°K the furnace temperature will only change by 0.2°K at 300°K .

The temperature control electronics was designed and built by our electronics technicians. It consists of a reference power supply and difference amplifier. The difference signal is used to drive a continuously variable power supply which provides the heater current. The current is thus continuously variable depending on the difference signal. This is in contrast to the usually used on-off system. The temperature stability was better than $\pm 0.5^\circ \text{ K}$ depending on the time taken to collect a spectrum.

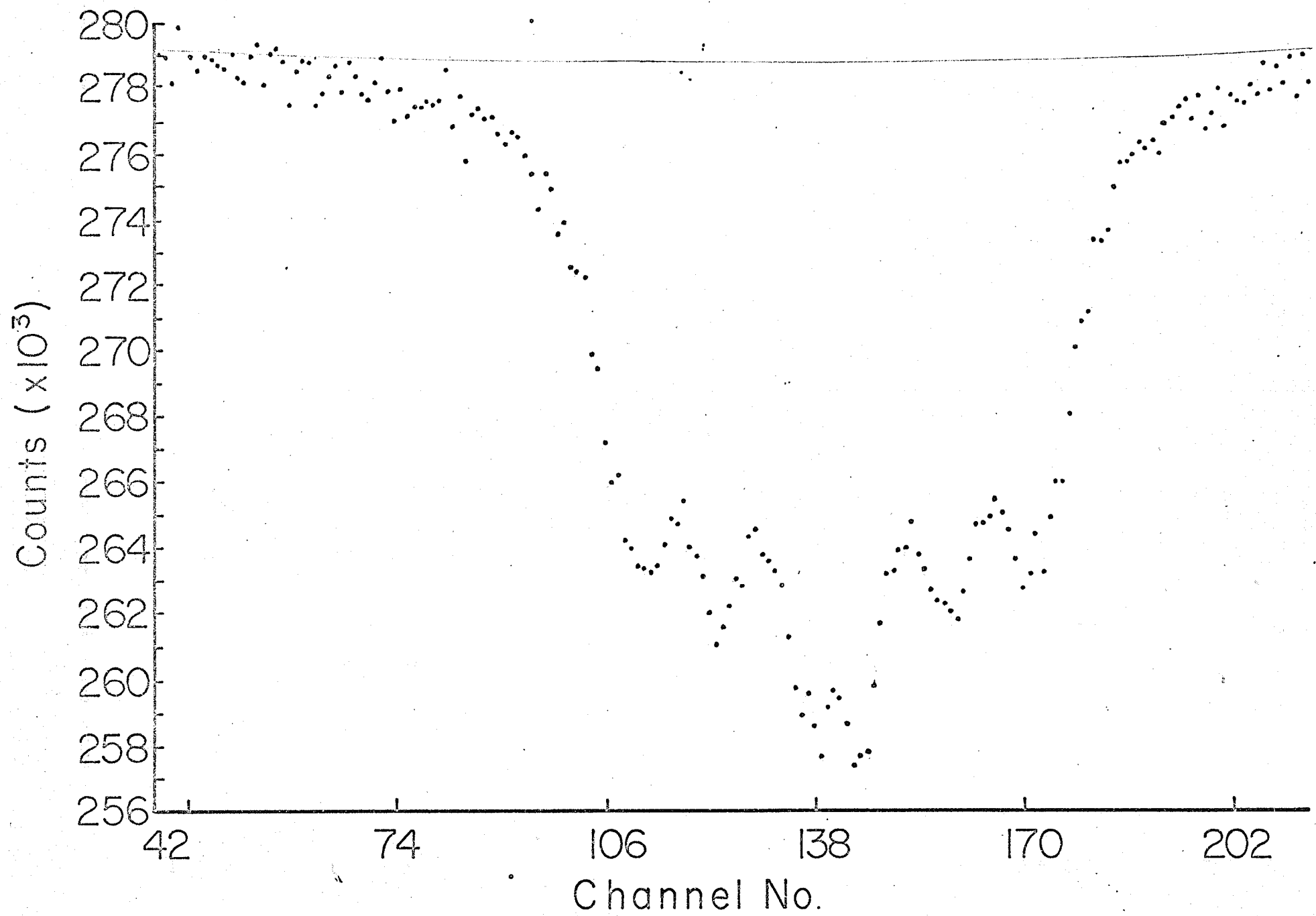
Temperature measurements were done using a Rubikon potentiometer and Tinsley Type MR4 galvanometer. The sensitivity of this system was 1 mm deflection on the galvanometer for 1 μv . volt change.

One of the difficulties in designing a furnace for Mössbauer effect experiments is the problem of temperature homogeneity. In order to get the temperature as homogeneous as possible we mixed our absorbers with graphite and packed this mixture firmly into the graphite dish. To check the temperature homogeneity we collected spectra of HoFeO_3 close to the Néel temperature. A spectrum taken within 2.5° K of the Néel temperature is shown in figure 2-7. Although there seems to be a paramagnetic peak in the center of the spectrum this peak is small compared to the area under the rest of the spectrum. An upper limit to the temperature gradient can be obtained by measuring the full width at half height of line one or line six of the six line spectrum as a function of temperature. Since the peak position of line one is given by

$$\frac{\partial x_j}{\partial H_{\text{hpf}}} = C$$

FIGURE 2-7

Mössbauer spectrum of HoFeO_3 taken
at 2.5°K below the Néel temperature



where x_j is the peak position H_{hpf} is the hyperfine field and C is a constant. Here we have neglected contributions from the isomer shift and quadrupole interaction. This equation can be written as

$$\frac{\partial x_j}{\partial T} = \frac{C \partial H_{\text{hpf}}}{\partial T}$$

where T is the temperature. A temperature gradient across the sample of ΔT will then lead to a line broadening ($\Delta \Gamma$) given by

$$\Delta \Gamma = \Delta x_j = \frac{C \partial H_{\text{hpf}}}{\partial T} \Delta T$$

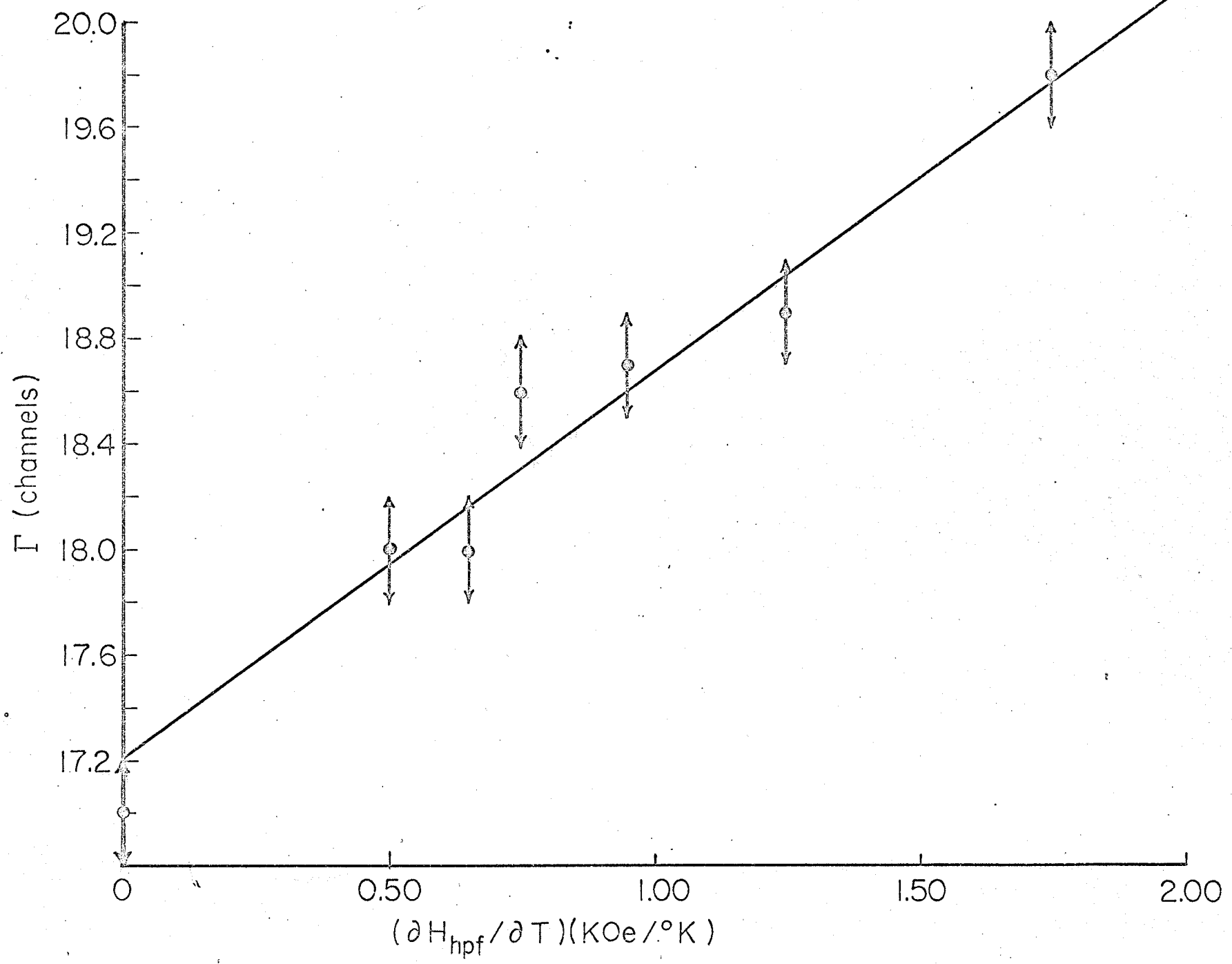
In figure 2-8 is shown a plot of Γ versus $\frac{\partial H_{\text{hpf}}}{\partial T}$. From the slope of the

line we obtain $\Delta T \approx 2.5^\circ \text{ K}$. This is of course an upper limit because relaxation effects and broadening caused by impurities have not been taken into account.

The cryostat is very similar in design to the furnace. The only difference being that the items marked 11, 12 and 14 in figure 2-5 have been removed. The copper heater core has been replaced by one of more mass. This core is supported by four stainless steel legs at the bottom.

FIGURE 2-8

Plot of line width (Γ) versus the
derivative of the hyperfine field with
respect to temperature ($\partial H_{\text{hpf}}/\partial T$)



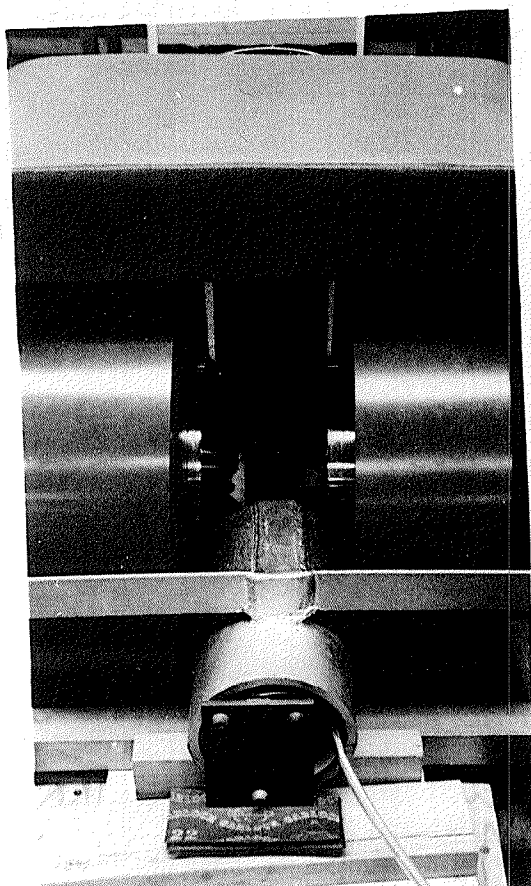
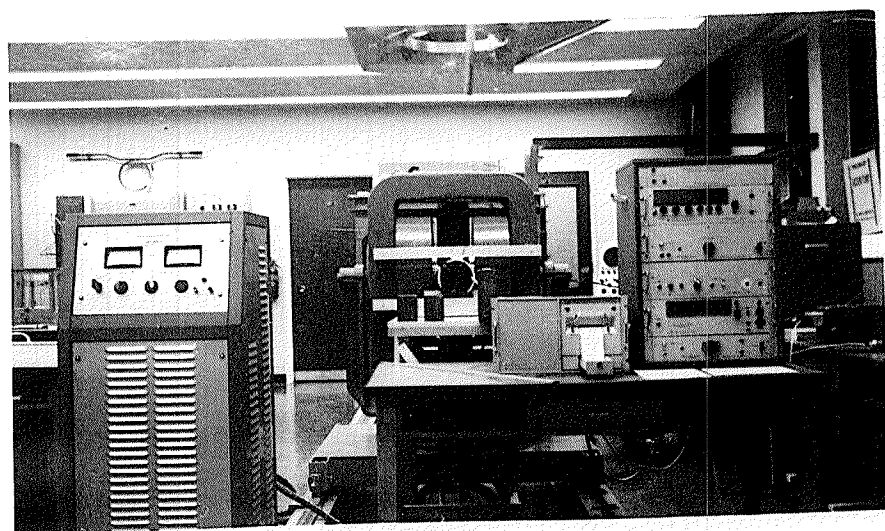
Also another large port has been added to accommodate the cold finger. The cold finger made of $\frac{1}{2}$ " copper rod is tapped at both ends and screwed into the copper core and also into a copper block 2 which protrudes into the L.N. storage tank. A radiation shield made of aluminized mylar wrapped around a lucite cylinder 3 is positioned between the cold finger and the outer wall. The vacuum connection between the cryostat and the L.N. storage tank is rubber tubing 4 which allows for expansion and contraction of the copper cold finger 5. The storage tank consists of an inner L.N. tank 6 made of stainless steel connected to the upper lid 7 by an 0.008" wall stainless steel tube 8. This tank is surrounded by a radiation shield 9. The thermocouples and heater wire are the same as those used for the furnace. With this system we could reach temperatures of 96° K which was satisfactory for our purpose. The L.N. lasted for 24 hours when operating at 96° K.

2.4 Magnetic Field

For experiments in the applied magnetic field we used the following arrangements (figure 2-9). A 20 K.G. electromagnet manufactured by Magnion (27) was used to supply the field. The pole tips are 6" in diameter and separated by 2". The absorber was a powder sample mixed with molten sealing wax and molded into a 2" diameter disc using a lucite mold. The absorber was taped firmly onto a lucite frame which was held in place between the pole tips with lucite plates. The lucite plates have vertical grooves in which the lucite frame can slide.

Figure 2-9

Picture of arrangement for Mössbauer
effect experiments in an applied field
of 17 KOe.



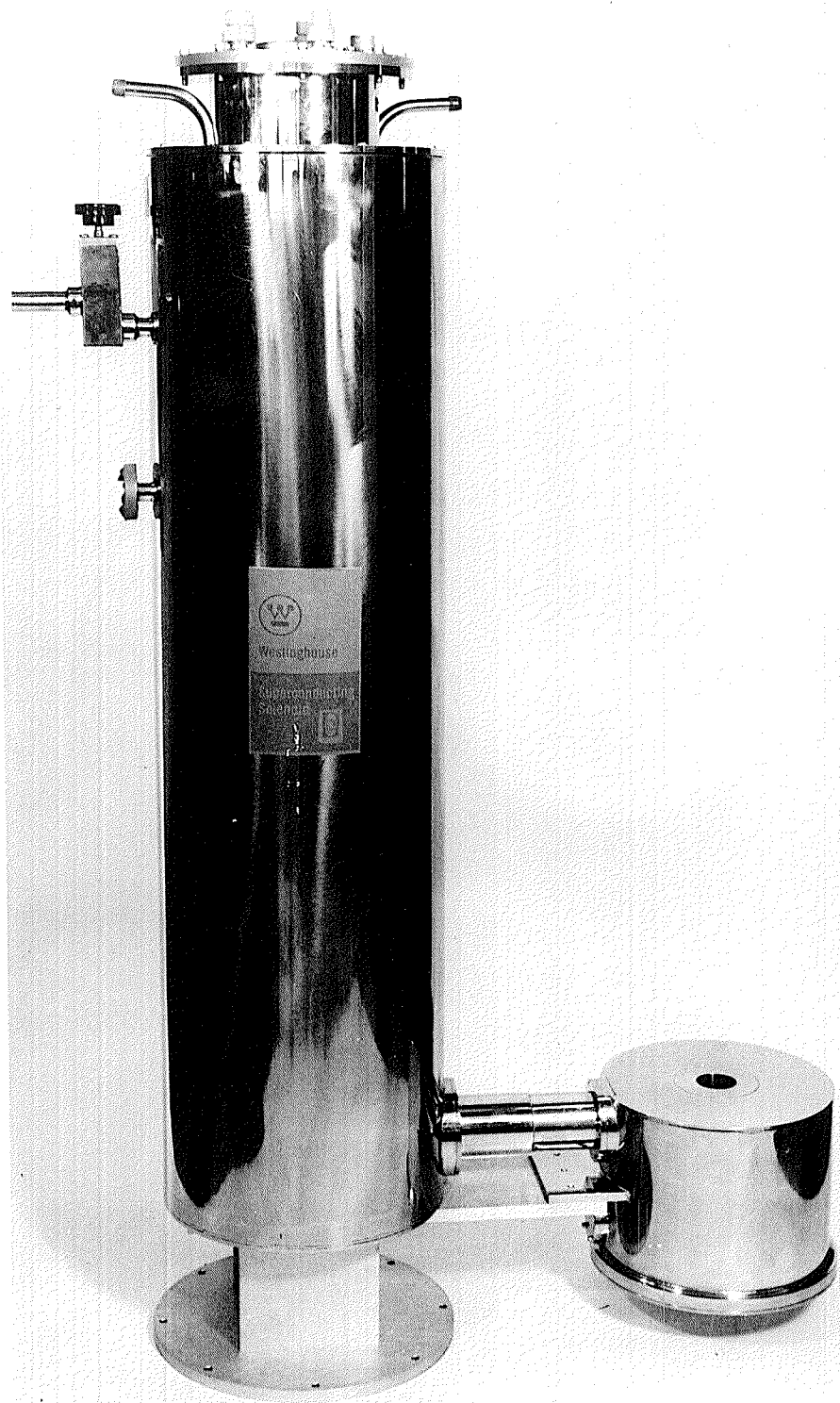
Since a magnetic field will broaden the source line and also affect the electromechanical drive we shielded these with a $\frac{1}{2}$ " thick soft iron cylinder closed at the end closest to the pole tips except for a $\frac{1}{2}$ " hole in the middle of the 1" thick soft iron plate. The transducer fit almost entirely into the cylinder. The field inside the cylinder was about 400 G which causes very little broadening. The proportional counter was protected also with a $\frac{1}{2}$ " wall soft iron cylinder 7" in diameter. A 2" by 3" hole was cut in the cylinder in line with the center of the magnet.

The geometry of this system was a problem. That is the source detector distance was 22" with only a 2" x 3" detector area. This usually meant that we had to run for three days in order to get sufficient statistics.

Many of the experiments run in a 55 KOe. field were done by the Mössbauer group in Thousand Oaks, California and I am very thankful for their cooperation in this matter. We have now obtained our own 55 KOe. super conducting solenoid manufactured by Westinghouse (36). A picture of this is shown in figure 2-10. The main features of the design are a $2\frac{1}{2}$ " diameter room temperature access, a liquid nitrogen and liquid helium access and the L shaped design so that the source detector distance is only approximately 12".

FIGURE 2-10

Picture of the 55 KOe, superconducting
magnet



Recoilless fraction ratios for Fe^{57} in octahedral
and tetrahedral sites of a spinel and a garnet

3.1 Introduction

The Mössbauer effect technique can be used to determine the relative amount of Fe^{57} in the A and B sites of spinels and garnets provided the ratio of the recoil free fractions for Fe^{57} in A and B sites is known. Numerous investigators (37-42) have determined the cation distribution by simply measuring the ratio of the areas under the peaks corresponding to A and B sites. It has been pointed out (43, 44) that the two recoil free fractions f'_A and f'_B need not be equal. In this case one is required to correct the area ratios found for this fact before relating the experimental results to the cation distribution. It is therefore of importance to know the ratio f'_B / f'_A .

To determine f'_A and f'_B we have recorded spectra of $(\text{Fe})[\text{Fe}_2]\text{O}_4$ and $\{\text{Y}_3\}(\text{Fe}_3)[\text{Fe}_2]\text{O}_4$. The first of these is the mineral magnetite which has the spinel structure and is known to be inverse. The second, commonly referred to as YIG has the garnet structure. Although this thesis is not directly concerned with the garnets these materials have a similar structure to the spinels in that the Fe^{3+} ions are located in tetrahedral (d) and octahedral (a) sites as indicated by the round and square brackets. The rare earth ions are located in dodecahedral sites. In this study we will change the notation commonly used for the garnets namely A, B, C, respectively. These materials are suitable for a study of the two recoil free fractions because (a) over a wide temperature range the hyperfine fields at the nuclei in the A and B sites differ

sufficiently for an accurate determination of the areas under the peaks.

(b) The distribution of the iron cations among the A and B sites is known for pure and stoichiometric samples.

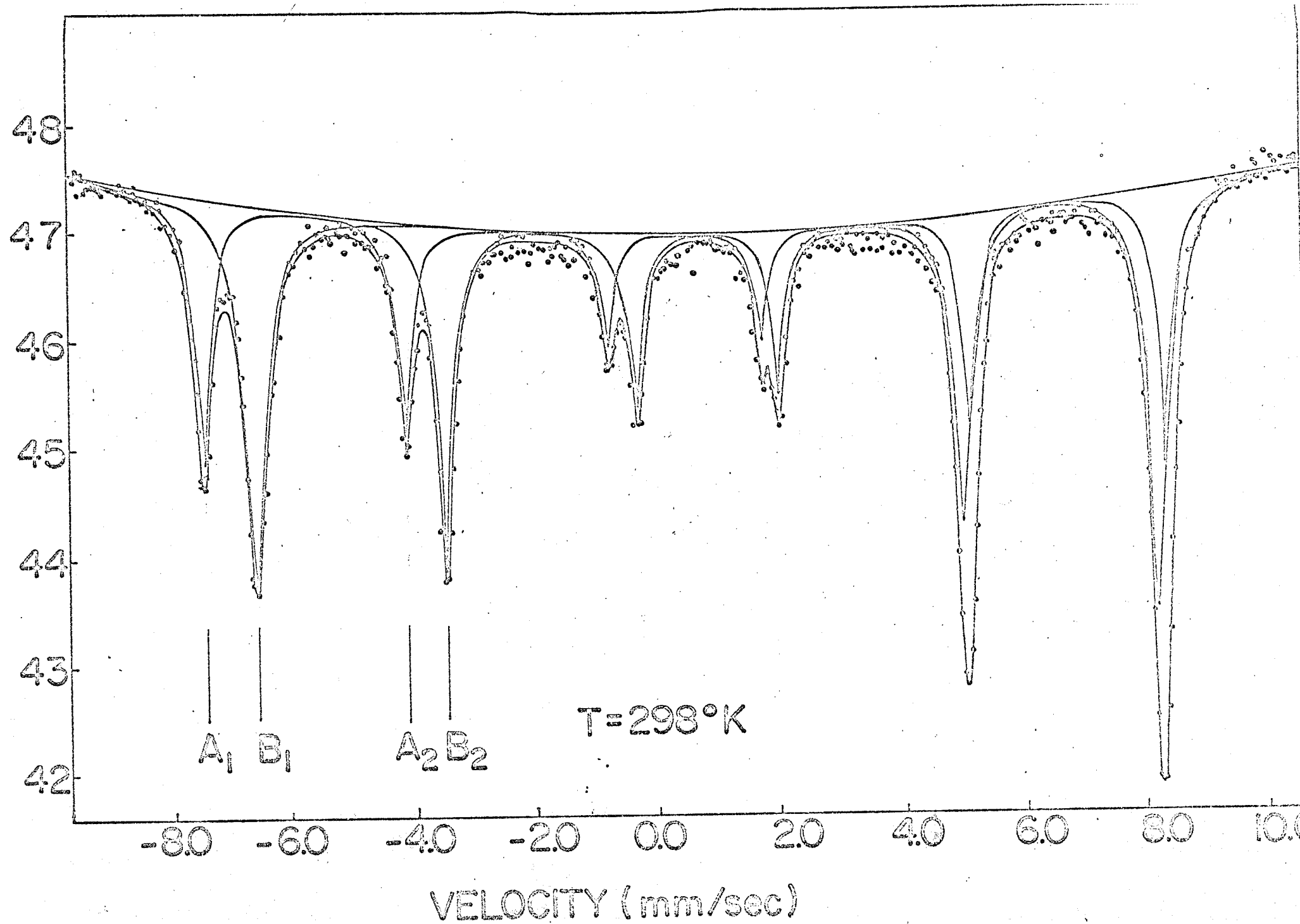
Experimental absorption Mössbauer spectra have been obtained for powdered samples of Fe_3O_4 and YIG using a 7 m.c. source of Co^{57} in a Cr matrix. The absorbers were crushed single crystals of the mineral magnetite and synthetically grown single crystals of YIG. The stoichiometry of the magnetite sample was better than 1% (45). The spectra were recorded using the constant acceleration system which has already been described. The furnace and temperature control electronics have also been described.

3.2 Results

Several absorption spectra of Fe_3O_4 have been recorded in the temperature range between 300° K and 800° K with absorber thickness of 25, 15 and 8 mg/cm². Some of the results obtained for magnetite will be discussed in a later section. All the spectra have been corrected for some absorption in the middle of the spectrum due to paramagnetic iron impurities in the beryllium window of the proportional counter and in the Al radiation shields in the furnace. The correction required was determined by recording spectra over the whole temperature range without any absorber. The spectrum obtained at 298° K for Fe_3O_4 is shown in figure 3.1. Below 119° K ferrous and ferric ions occupy the B sites. Above this temperature there is a rapid electron exchange between the ferric and ferrous ions which washes (46-49) out the difference between Fe^{2+} and Fe^{3+} . Consequently the

Figure 3-1

Mössbauer spectra of Fe_3O_4 at 298°K . A and B indicate the peak positions of the absorption lines from Fe^{57} in A and B sites. The solid lines drawn show both the envelope and the individual lines as obtained from a fit to the spectrum by the method of least squares.



Fe^{2+} and Fe^{3+} ions on the B sites feel the same field and the spectrum consists of the sum of 2 six line hyperfine patterns corresponding to Fe^{57} in A and B sites. A more careful investigation of the electron hopping and the nature of the transition has been reported by us and will not be dealt with here (49). The ratios of the areas $\frac{I_A}{I_B}$ under the peaks assigned to A and B sites can easily be determined from the spectra recorded between 300°K and 800°K . For a thin absorber this area ratio would be 0.50 if $f'_A = f'_B$. Above 800°K and above the ferrimagnetic Néel temperature (860°K) a considerable overlap of the peaks impedes an accurate determination of the area ratios.

The areas I_A and I_B as well as the ratio $\frac{I_A}{I_B}$ were determined by doing a least squares fit to the spectrum assuming Lorentzian line shape. The area is determined from the product of the full width at half height (Γ_{exp}) and the absorption at the peaks position (P_{exp}). Only the lines marked A_1 , A_2 , B_1 and B_2 in figure 1 were used. Lines A_1 and B_1 were used for determining I_A and I_B and $\frac{I_A}{I_B}$. This was done because lines A_2 and B_2 had considerably larger errors for P_{exp} and Γ_{exp} . These lines however were used to determine approximately what the errors were. The ratios $\frac{I_{A_2}}{I_{A_1}}$ and $\frac{I_{B_2}}{I_{B_1}}$ should be equal to 0.67. On table 3.1 are listed all the values of I_{A_1} , I_{B_1} , $\frac{I_{A_2}}{I_{A_1}}$ and $\frac{I_{B_2}}{I_{B_1}}$. In some cases the ratios $\frac{I_{A_2}}{I_{A_1}}$ and $\frac{I_{B_2}}{I_{B_1}}$ were quite far from the expected value of 0.67. These data have been rejected in the analysis of $\frac{I_{A_2}}{I_{B_1}}$. The average value of $\frac{I_{A_2}}{I_{A_1}} = 0.67$

TABLE 3-1

Tabulated absorption areas for lines 1 of Fe^{57}
in A and B sites and the ratio of the areas of line
2 to line 1 at various temperatures

<u>Absorber Thickness (mg/cm)</u>	<u>Temp (°K)</u>	<u>I_{A1}</u>	<u>I_{B1} *</u>	<u>$\frac{I_{A2}}{I_{A1}}$</u>	<u>$\frac{I_{B2}}{I_{B1}}$</u>
23	296	0.53	1.00	0.73	0.64
	369	0.52	0.93	0.67	0.64
	543	0.46	0.80	0.63	0.62
	636	0.38	0.63	0.64	0.73
23	296	0.54	1.00	0.63	0.60
	420	0.47	0.83	0.67	0.65
	472	0.45	0.77	0.64	0.68
	522	0.43	0.79	0.73	0.65
	575	0.39	0.72	0.60	0.68
	624	0.37	0.61	0.60	0.71
	720	0.32	0.56	0.67	0.72
	776	0.31	0.51	0.64	0.70
15	797	0.27	0.57	0.70	0.67
	296	0.53	1.00	0.71	0.65
	427	0.50	0.88	0.62	0.67
8	544	0.40	0.74	0.65	0.74
	296	0.53	1.00	0.67	0.63
	469	0.43	0.83	0.71	0.65
	600	0.36	0.66	0.66	0.71
	692	0.31	0.62	0.68	0.65
	774	0.34	0.55	0.73	0.69
Average =				0.67±0.04	0.67±0.03

* I_{B1} has been normalized to 1.0 at 296° K

and $\frac{I_{B_2}}{I_{B_1}} = 0.67$ are within the experimental error of 0.67. The error in $\frac{I_{A_1}}{I_{B_1}}$ is expected to be less than this because the errors in the parameters of lines 2 are about 2 times that of lines 1. We then estimate the error in $\frac{I_{A_1}}{I_{B_1}}$ to be about $\pm 5\%$. The areas I_{B_1} have been normalized to 1 at room temperature for each set of measurements.

Spectra of Fe^{57} in YIG were obtained in the temperature range 300°K to 775°K and for absorber thickness of 37, 34 and 17 mg/cm^2 . The spectra obtained at 298°K and 560°K are shown in figures 3-2 and 3-3. Below the ferrimagnetic Néel temperature the spectrum is complicated by the presence of two B site lines. The A site line is, however, well resolved from both of the B site lines for lines 1, 5 and 6 as seen in figure 3-2. The two B site lines are due to two possible angles $\theta = 0^\circ$ and 70° between the principal axes of the electric field gradient and the magnetic field. Since the quadrupole interaction depends on $3 \cos^2 \theta - 1$, two B site lines are expected. The area ratio of the two B site lines B' and B'' is expected to be 3:1 since the 70° angle occurs three times as often as the 0° angle (50,51).

A least squares fit was done to all spectra for $T < T_{FN}$ for lines 1, 2, 5 and 6. The fit was first done by imposing constraints that the area ratio $\frac{I_{B'}}{I_{B''}}$ was 3:1. The parameters obtained from this fit were then used as initial guesses for a fit without constraints. The area ratio $I_A / (I_{B'} + I_{B''})$ was insignificantly different for these two fits. The ratio $\frac{I_{B'}}{I_{B''}}$ was 2.5 ± 0.5 . Since the value of χ^2 (goodness of fit)

FIGURE 3-2

Mössbauer spectrum of YIG at room temperature
A and B indicate the peak positions of the
absorption lines from Fe^{57} in A and B sites.
The solid lines drawn show both the envelope
and individual Lorentzians as obtained from
a fit to the spectrum by the method of least
squares

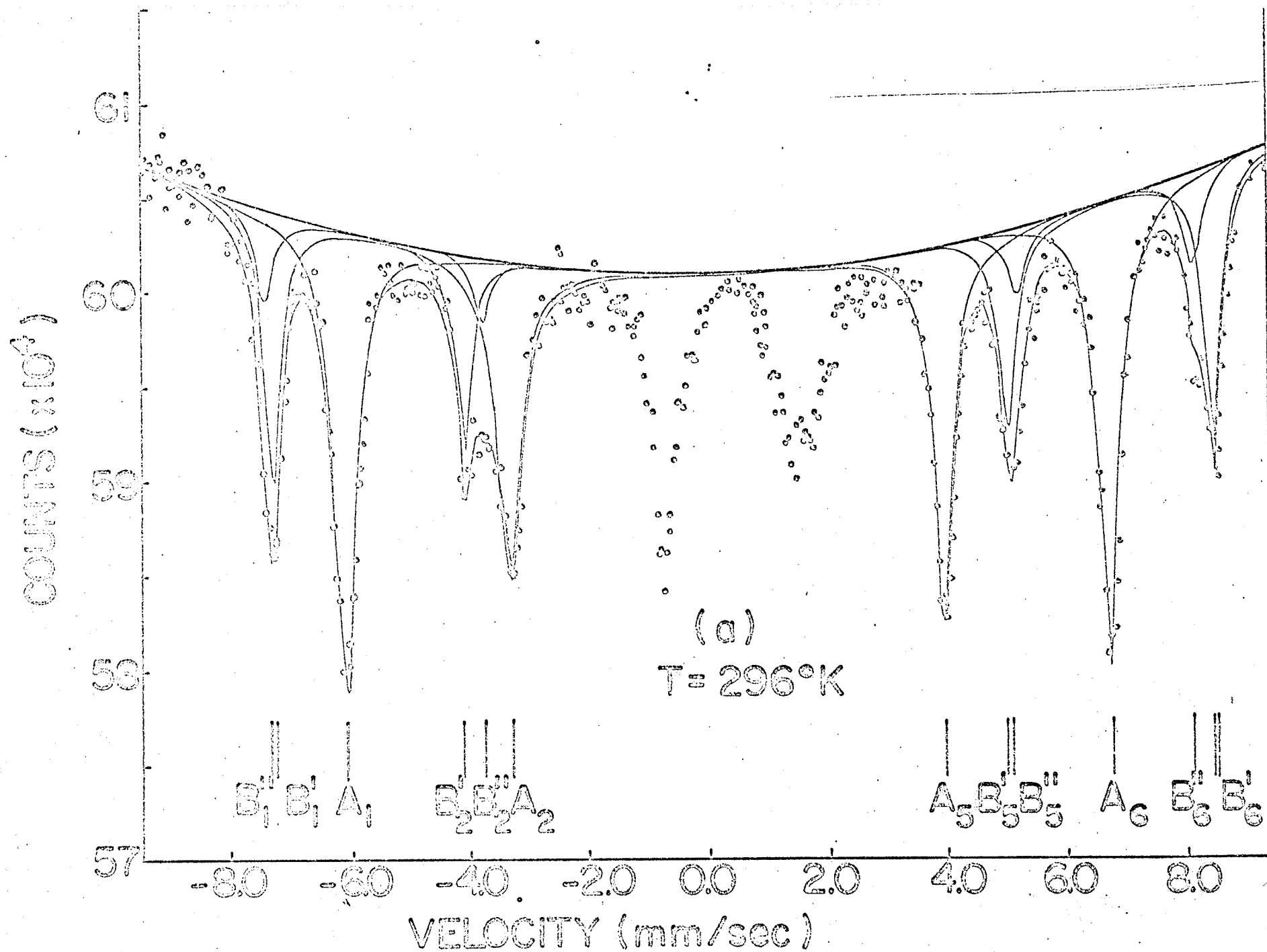


FIGURE 3-3

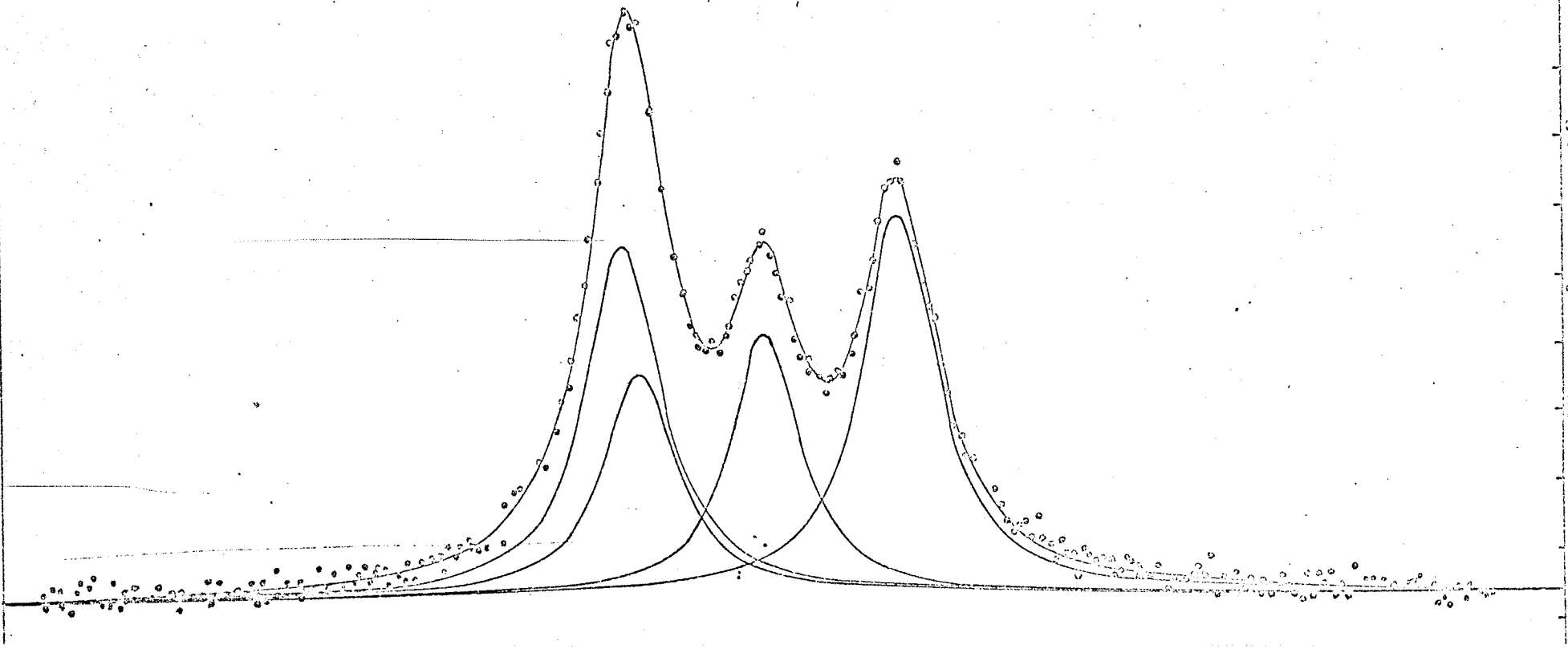
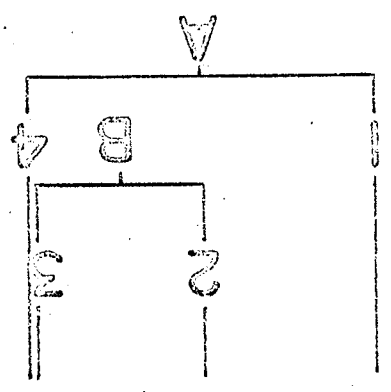
Mössbauer spectrum of YIG at 560° K. A and B indicate the peak positions of the absorption lines from Fe^{57} in A and B sites. The solid lines drawn show both the envelope and individual Lorentzians as obtained from a fit to the spectrum by the method of least squares

VELOCITY (mm/sec)

2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5

32
33
34
35
36
37
38
39

$T = 560^{\circ}\text{K}$
(b)



did not change appreciably for these two fits we conclude that the ratio

$\frac{I_B'}{I_B''} = 3$ is within the experimental error of our results. The large error in the value of $\frac{I_B'}{I_B''}$ i.e. ± 0.5 is due to the large amount of overlap

of these two lines. From here on we will use $I_B = I_B' + I_B''$ as the total

area. The ratio $\frac{I_A}{I_B}$ is expected to be 1.50 for a thin absorber if

$f_A' = f_B'$. Above T_{FN} the spectrum consists of 4 lines two of which

correspond to the A site and two for the B site. These spectra are

fit to the sum of four Lorentzians which are identified with the two

sites as shown in figure 3-3. It will be noticed that the peaks marked

3 and 4 in figure 3-3 have a slightly lower intensity than the peaks

marked 1 and 2. This is probably due to the large amount of overlap

between peaks 3 and 4 which increases the effective thickness of the

absorber. This fact can be used to check the thickness corrections

discussed below.

3.3 Corrections

Corrections for the finite thickness of the absorber can be made by using the following relation by Shirley (52) :

$$P_{\text{exp}} \Gamma_{\text{exp}} = n \sigma_m f f' \Gamma [1 - 0.24\tau] \quad \text{for } \tau < 4. \quad [1]$$

Here P_{exp} is the fractional absorption at the peak position. Γ_{exp} is the measured full width at half height and n gives the number of Fe^{57} nuclei/cm² on a particular site and in the correct hyperfine state. σ_m denotes the total cross-section for recoil-free absorption, and f and f' are the recoilless fractions for the source and absorber respectively. For all the recorded spectra the condition $\tau < 4$ was fulfilled where

$$\tau = n \sigma_m f' \frac{\Gamma}{\Gamma'} \quad [2]$$

In [2] Γ is the natural line width and Γ' is the absorber line width chosen so that $\Gamma_{\text{exp}} = (\Gamma' + \Gamma'_S) (1 + 0.35 \tau)$ and Γ'_S was adjusted to be consistent with all our data. Then in a particular absorption spectrum the ratio of the areas I_1 and I_2 of two lines denoted by 1 and 2 respectively is given by :

$$\frac{I_1}{I_2} = \frac{n_1 f'_1}{n_2 f'_2} \frac{1 - 0.24 \tau_1}{1 - 0.24 \tau_2} \quad [3]$$

and

$$\frac{n_1 f'_1}{n_2 f'_2} = \frac{I_1}{I_2} \frac{1 - 0.24 \tau_2}{1 - 0.24 \tau_1} \quad [4]$$

where

$$\frac{I_1}{1 - 0.24 \tau_1} \quad \text{and} \quad \frac{I_2}{1 - 0.24 \tau_2}$$

can be considered as the corrected areas under the peaks from which the ratio $\frac{f'_1}{f'_2}$ can be determined.

For the YIG sample of 37 mg/cm we get $\tau_A = 1.1 f'_A \frac{\Gamma}{\Gamma'_A}$, where

Γ is 2.4 channels and $2.4 < \Gamma'_S < 3.0$ channels which we found from experiments on α -Fe₂O₃ and Fe foil. Taking $\Gamma'_S = 2.6$ channels and at room temperature $\Gamma_{\text{exp}} = 11.0$ channels we get $\tau_A = 0.22$ where $f_A = 0.78$ is for $\theta_D = 400^\circ \text{ K}$. This means a correction of 5% is required for I_A for lines 1 and 6. For τ_B we get $\tau_B \approx 0.7 \tau_A \approx 0.15$ which corresponds to a correction of

about 3.5% to I_B for lines 1 and 6. The correction required for the area ratio amounts to only 1.5% and thus has been neglected. For the thinner absorbers the corrections required are still smaller. For the Fe_3O_4 samples the correction required for the area ratio is at most 2% for the thickest absorber i.e. 25 mg/cm². This correction has also been neglected.

For the YIG samples for $T > T_{FN}$ the corrections required are important. This is because the effective thickness is increased by a factor of 2 because the spectrum has collapsed to a four-line spectrum from a twelve-line spectrum, and also the line width is decreased which will increase the effective thickness. These corrections are especially important for the thick absorber, in which case $\tau_A \approx 0.9$ and $\tau_B \approx 0.7$. These corrections have been made taking into account that the τ values are temperature dependent due to the temperature dependence of f' and also Γ' . In figure 3-4 are plotted the corrected relative areas of the octahedral and tetrahedral peaks on a logarithmic scale as a function of temperature for both Fe_3O_4 and YIG.

3.4 Discussion

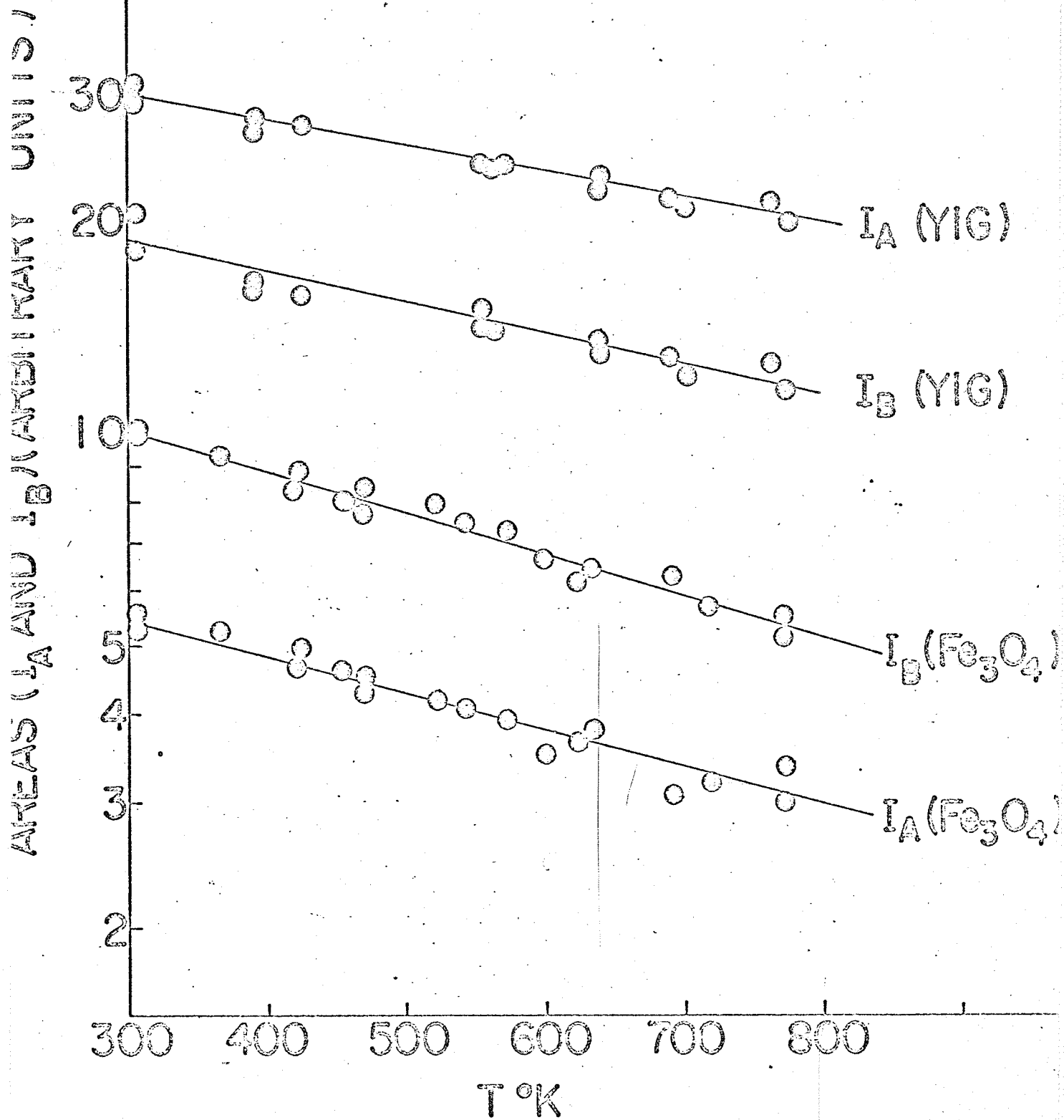
In the Debye approximation for lattice vibrations, the recoil-free fraction f' can be written as (54) :

$$f' = \exp[-2W] = \exp[-6E_T/k\theta_D^2] \quad [5]$$

for $T > \theta_D/2$. Here E_T is the recoil energy and k is the Boltzman constant. θ_D denotes the Debye temperature. Actually spinels and garnets have

Figure 3-4

Areas of the A and B site spectra for Fe_3O_4 and YIG plotted on a logarithmic scale versus temperature. The solid lines are fits to the data by the method of least squares.



structure which are too complicated for the Debye approximation. In order to correct in part for this we introduce two Debye temperatures θ_A and θ_B for A and B sites respectively. It is perhaps difficult to justify two Debye temperatures, but since this is the only variable in (5) we shall assume for the data analysis that this can be done. θ is a measure of the strength with which the ion is bound to its equilibrium position. In this way we have made the model more realistic. Because I is proportional to f' , the $\ln I$ versus T curve should be a straight line for $T > \theta/2$; hence θ_A and θ_B can be determined from the slope of the straight line. The drawn lines in figure 3-4 are the least squares fit to the data points. From this we find the Debye temperatures are :

$$\theta_A = 334 \pm 10^\circ \text{ K} \quad \theta_B = 314 \pm 10^\circ \text{ K for } \text{Fe}_3\text{O}_4$$

$$\text{and} \quad \theta_A = 406 \pm 15^\circ \text{ K} \quad \theta_B = 366 \pm 15^\circ \text{ K for YIG.}$$

The errors are calculated from the least squares fit and do not take into account the possible inadequacy of the Debye model. These Debye temperatures are much lower than those obtained by specific heat measurements. The values obtained from specific heat data range from 570° K to 660° K for Fe_3O_4 (54-56) and 454° K to 599° K for YIG (57-60). The large difference between our data and those obtained by specific heat measurements may be understood in the following way. The Debye temperature of these compounds as determined from specific heat measurements may refer mainly to the framework of cubic close-packed oxygen ions. We have shown that the octahedral ions have a lower Debye temperature than the tetrahedral ions. This would indicate that the framework of oxygen

ions could have a Debye temperature considerably different from that of the ions filling the holes in this framework.

In figure 3-5 we have plotted the corrected values of the area ratios I_A/I_B for both Fe_3O_4 and YIG. At high temperature and in the Debye approximation this area ratio can be written as

$$\frac{I_A}{I_B} = \frac{n_A}{n_B} \exp \left[- \frac{6E_r T}{k} \left(\frac{1}{\theta_A^2} - \frac{1}{\theta_B^2} \right) \right] \quad (6)$$

which can be approximated by :

$$\frac{I_A}{I_B} \approx \frac{n_A}{n_B} \left[1 - \frac{6E_r}{k} \left(\frac{1}{\theta_A^2} - \frac{1}{\theta_B^2} \right) T \right] \quad (7)$$

The straight lines drawn in figure 3-5 are least square fits to eqn. 7 and from this we find $n_A/n_B = 0.508 \pm 0.015$ and

$\frac{1}{\theta_A^2} - \frac{1}{\theta_B^2} = -(1.4 \pm 0.2) \times 10^{-6}$ for Fe_3O_4 . For YIG we get

$n_A/n_B = 1.49 \pm 0.05$ and $\frac{1}{\theta_A^2} - \frac{1}{\theta_B^2} = -(1.5 \pm 0.2) \times 10^{-6}$. The values

of n_A/n_B are well within experimental error of the known values for

Fe_3O_4 (0.50) and for YIG (1.5). The values of $\frac{1}{\theta_A^2} - \frac{1}{\theta_B^2}$ are in good

agreement with those calculated from the previously determined values of

θ_A and θ_B . The two types of analysis, i.e. the determination of θ_A and θ_B

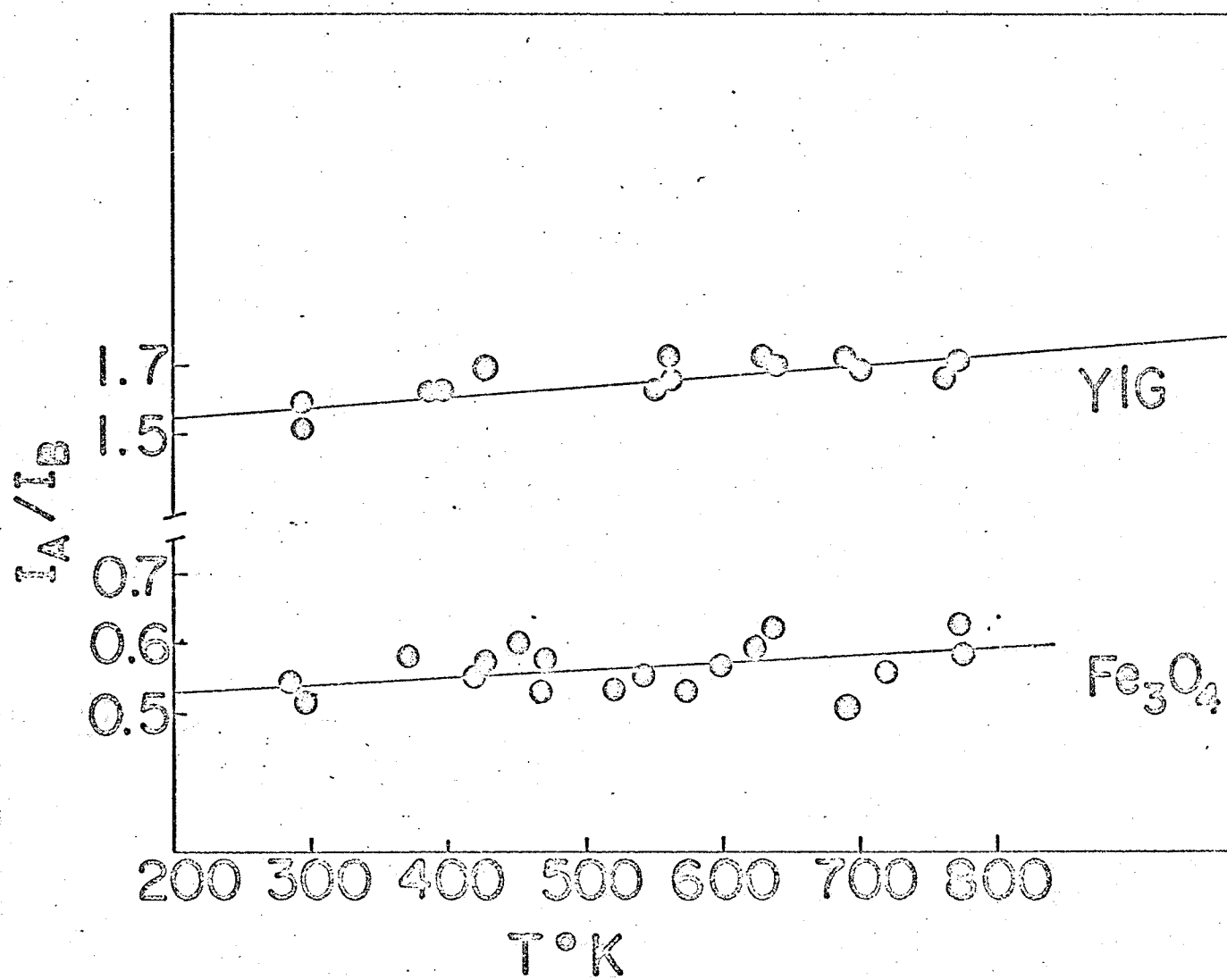
from the areas and the determination of n_A/n_B and $\frac{1}{\theta_A^2} - \frac{1}{\theta_B^2}$, involve

slightly different errors, especially for the cases where significant

thickness corrections are required. The area ratio is of course much less

FIGURE 3-5

Area ratio of the A and B site lines for
 Fe_3O_4 and YIG plotted versus temperature.
The solid lines are fits to the data by the
method of least squares



sensitive to thickness corrections than the area. It is gratifying to see that the two methods of analysing the data give the same results.

At room temperature the ratio of the recoilless fractions f'_B/f'_A determined from the intensity ratio is 0.94 ± 0.02 for Fe_3O_4 and 0.94 ± 0.02 for YIG. These values are much higher than the value of 0.85 reported by Van Leof for $\text{BaFe}_{12}\text{O}_{19}$ (43). It is, however, not known whether Van Leof made the necessary corrections. At 0°K the ratio of recoilless fractions can be calculated from

$$f'_B/f'_A = \exp \left[-\frac{3E_r}{2k} \left(\frac{1}{\theta_B} - \frac{1}{\theta_A} \right) \right] \quad (8)$$

by using the values determined for θ_A and θ_B we get $f'_B/f'_A = 0.99 \pm 0.01$ for Fe_3O_4 and 0.99 ± 0.01 for YIG. These values are in reasonable agreement with the ratio 0.96 ± 0.02 obtained by Grant et al for $\text{Ca}_2\text{Fe}_2\text{O}_5$ at 5°K (44).

3.5 Conclusions

From Mössbauer spectra of Fe_3O_4 and YIG the relative intensities of the peaks ascribed to Fe^{57} nuclei in tetrahedral and octahedral sites have been determined. From these results it has been shown that the recoil-free fractions of nuclei in the two sites are almost equal at 0°K . At room temperature the recoil-free fraction f'_B of octahedrally situated nuclei is 6% lower than f'_A of tetrahedral nuclei. This means that the relative occupation numbers cannot simply be determined from Mössbauer spectra of these materials at room temperature. However, the

information can be obtained by extrapolating from data taken at high temperatures over a wide temperature range.

3.6 Internal fields in YIG

Although the hyperfine fields, electric field gradients and isomer shifts of Fe^{57} as determined from the spectra obtained for YIG are not of immediate interest some of this data will be referred to later. In table 3-2 are tabulated the hyperfine fields, quadrupole interactions and isomer shifts at various temperatures. At room temperature the hyperfine field for B' and B'' spectra differ by 6 KOe. which is due to the difference in the dipolar fields. In figure 3-6 we have plotted the hyperfine field versus temperature. This data is in good agreement with that reported by Van Loef (51). The important point to notice is that the hyperfine fields for the A and B sites differ by 90 KOe., in reasonable agreement with the results of other investigators (50-51). This property of spinels and garnets will be discussed in a later section.

The quadrupole interaction for the A site and $T < T_{\text{FN}}$ is ≈ 0 which is in agreement with an angle $\theta = 55^\circ$ between the principal axes of the electric field gradient and the hyperfine field. The quadrupole interaction for the B' and B'' sites are :

$$\frac{e^2 q Q}{4} \frac{(3 \cos^2 \theta - 1)}{2} = 0.216 \pm 0.01 \text{ and } 0.057 \pm 0.01 \text{ mm/sec. respectively.}$$

The calculated ratio is $\frac{3 \cos^2(0^\circ) - 1}{3 \cos^2(70^\circ) - 1}$ is 3. The agreement is satisfactory.

TABLE 3-2

Tabulated values of the hyperfine field,
quadrupole interaction and isomer shift at
various temperatures.

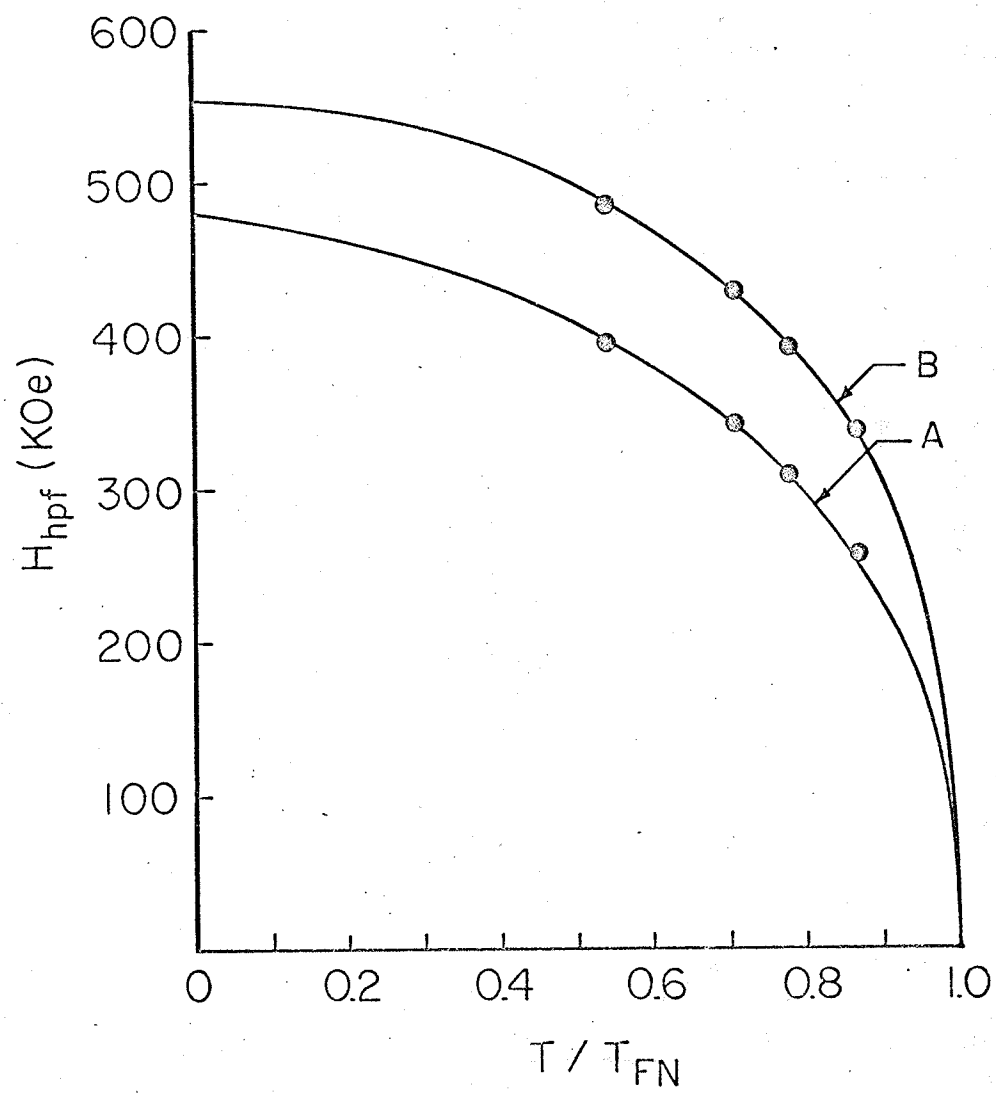
Temp. (°K)	$\frac{e^2qQ^*}{2}$ (mm/sec)			H_{hpf} (KOe.)			IS** (mm/sec)	
	A	B'	B''	A	B'	B''	A	B
296	-	0.34	0.43	396	488	483	0.33	0.55
388	-	0.38	0.42	343	433	427	0.28	0.50
427	-	0.36	0.40	308	396	390	0.25	0.46
477	-	0.25	0.43	255	330	324	0.21	0.45
553	0.98	0.41					0.12	0.32
561	0.98	0.44					0.12	0.33
562	0.97	0.44					0.11	0.33
639	0.97	0.44					0.06	0.27
640	0.97	0.44					0.07	0.28
702	0.96	0.44					0.02	0.23
763	0.97	0.44					-0.02	0.19
773	0.95	0.44					-0.02	0.19

* Taking $\theta = 70^\circ$ for B' and $\theta = 0^\circ$ for B''

** relative to Fe^{57} in Cr

FIGURE 3-6

Plot of the hyperfine field versus T/T_{FN} where T_{FN} is the ferrimagnetic Néel temperature



Above T_{FN} the separations of the two doublets is given by $\frac{e^2qQ}{2}$. These values for the B site are in good agreement with those calculated for $T < T_{FN}$ using the relation

$$E_Q = \frac{e^2q_2Q}{4} \frac{(3 \cos^2 \theta - 1)}{2},$$

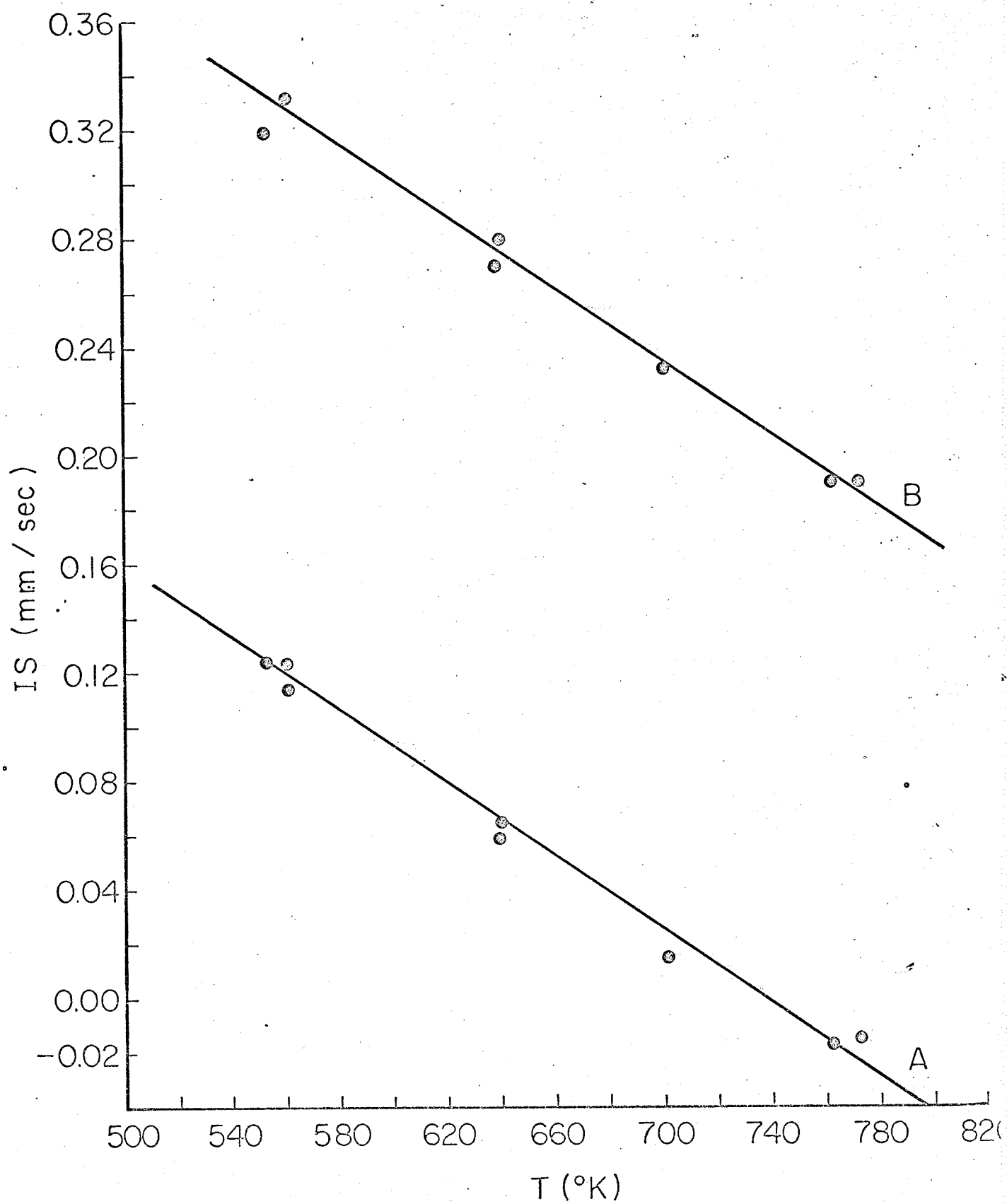
The A site quadrupole interaction is in fact quite large i.e. 0.98 mm/sec. which shows that for the A site the angle θ must be 55° in order for $E_Q (T < T_{FN})$ to be zero.

In figure 3-7 are plotted the isomer shifts for the two sites versus temperature for $T > T_{FN}$. Below T_{FN} the isomer shift determination is not very accurate i.e. ± 0.04 mm/sec. The slope of the two straight lines drawn through the data points is 6.7×10^{-4} mm/sec/ $^\circ K$ for the A site and 6.7×10^{-4} mm/sec/ $^\circ K$ for the B site. The error in these slopes is about $\pm 0.5 \times 10^{-4}$ mm/sec/ $^\circ K$. The surprising thing is that the slopes are nearly the same. This is not consistent with the results tabulated by Van Loef (61) which indicate that the slope for the A site ions is less than that for the B site ions. The difference in the isomer shifts to $T > T_{FN}$ is $IS(B) - IS(A) = 0.21$ mm/sec in agreement with the results tabulated by Van Loef (61).

FIGURE 3-7

Plot of the isomer shift versus temperature.

A and B refer to Fe^{57} in A and B sites.



Relation between the Hyperfine Magnetic Fields and Sublattice
Magnetizations in Fe_3O_4

4.1 Introduction

The Mössbauer effect (ME) technique has frequently been used to determine the temperature dependence of the hyperfine magnetic field H_{hpf} at nuclei in ferro-, ferri-, or antiferro- magnetic materials (62-68). Very often such a curve was assumed to be identical with the magnetization or a sublattice magnetization versus temperature curve. Since we will in later sections want to correlate the hyperfine field data with the sublattice magnetization we required detailed information about the relation between the hyperfine field and the magnetization.

A detailed study of the relationship between $H_{\text{hpf}}(T)$ and $M(T)$ has only been made for iron (69, 70). Except for approximate comparisons made by Van Loef (61), such studies have not been made for iron in ionic compounds. In view of the current interest in ferrimagnets and antiferromagnets, it is pertinent to make detailed investigations.

We have studied the inverse spinel Fe_3O_4 with the Mössbauer effect technique because accurate values of the sublattice magnetizations at temperature between 298° K and 860° K, obtained from neutron diffraction experiments by Riste and Tenzer (RT), are tabulated (71). For Fe_3O_4 , RT performed all the necessary corrections for extinctions and the Debye-Waller factor. The magnetization versus temperature curve, derived from these neutron-diffraction experiments agreed well with the magnetization data obtained by Pauthenet (ref. 5 in [78]). Our sample of

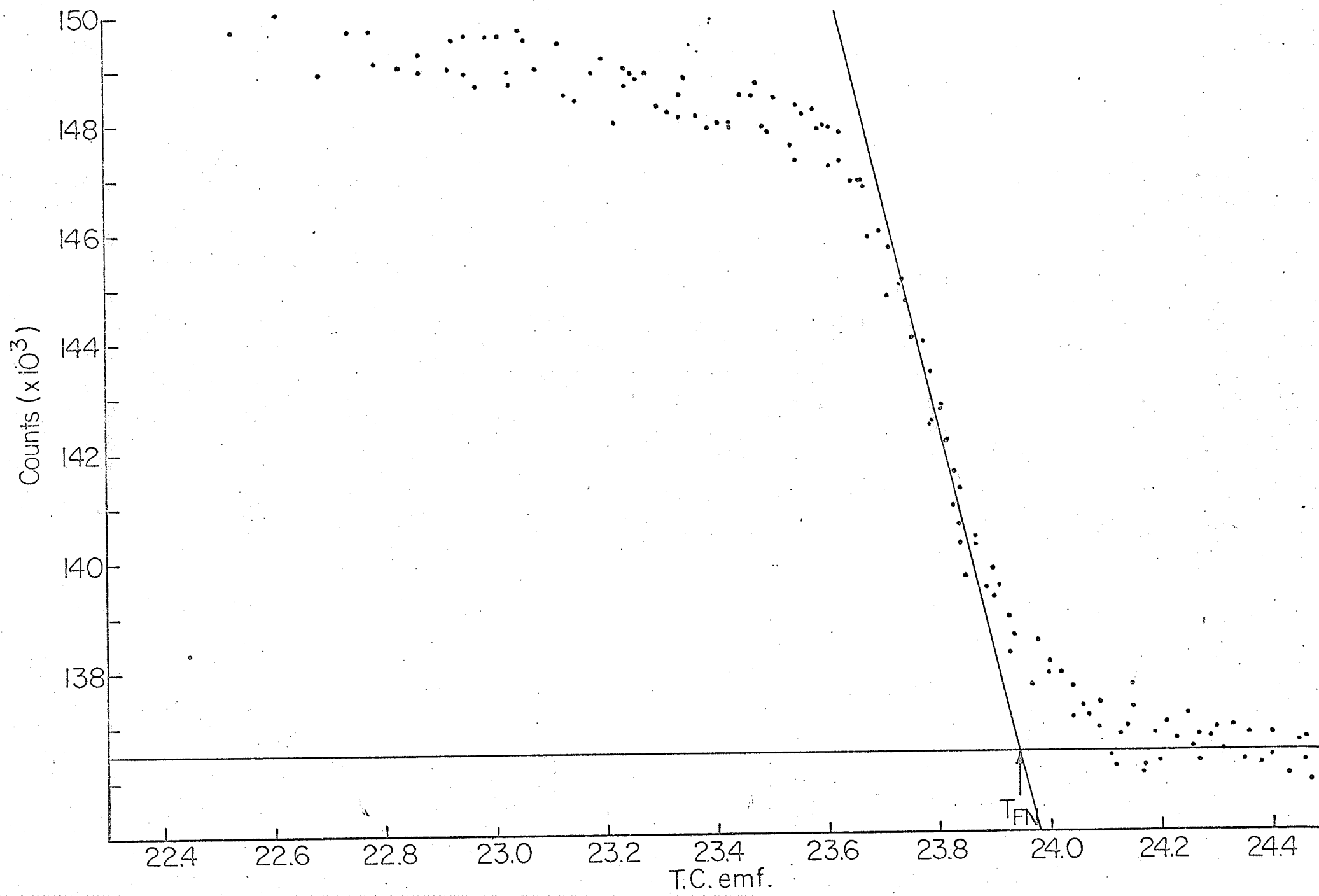
Fe_3O_4 as well as the material measured by RT is of natural origin and contained less than one percent impurities. Another advantage of Fe_3O_4 is that all the cations can be observed with the ME technique, because the material contains only iron cations. In addition, the splittings in these spectra can be determined accurately because the first three lines of the six line hyperfine pattern attributed to nuclei in tetrahedral (A) sites are well separated from those attributed to nuclei in octahedral (B) sites above room temperature.

4.2 Experimental

Mössbauer spectra were obtained by using a constant velocity drive (31) as described previously with about 50 channels per mm/sec. The source was 10 mC of Co^{57} in a chromium matrix. The vacuum furnace used has also been described. The single crystals of Fe_3O_4 were crushed and mixed with graphite. This mixture was placed into a graphite dish and pressed firmly in order to ensure temperature uniformity. The ferrimagnetic Néel temperature T_{FN} was measured by the thermal scanning technique. The counting rate is measured as a function of temperature with the velocity set at the peak position, of the paramagnetic line just above T_{FN} . This is shown in figure 4-1. The transition temperature is then defined as the intersection of the line drawn through the steepest part of the curve with the horizontal line drawn through the points well above T_{FN} . The transition temperature can then be found to within a relative accuracy of about 0.5° K . T_{FN} was found to be $850.0 \pm 0.5^\circ \text{ K}$ in good agreement with the values in the literature which range from 848° K to 858° K .

FIGURE 4-1

Plot of counting rate versus thermocouple e.m.f. with the transducer operating at a velocity corresponding to the peak position of the paramagnetic line. The intersection of the two straight lines drawn defines the ferrimagnetic Néel temperature (T_{FN}).



Typical Mössbauer spectra taken at temperatures ranging from room temperature to above the Néel point are shown in figure 4-2 to 4-5. A least squares fit, assuming Lorentzian line shapes, was made to all spectra with the IBM system /360 model 65 computer. From the least squares analysis, the relative error in the hyperfine field was less than 0.5% up to $0.9 T_{FN}$ and about 1% at $0.97 T_{FN}$.

The temperature dependences of the hyperfine magnetic fields experienced by Fe^{57} -nuclei in A- and B-sites respectively, as determined from Mössbauer spectra, are plotted in figure 4-6. The magnetizations as a function of the temperature for the A and B sublattices, as obtained by RT, are also plotted in the same figure. RT normalized the $M(T)$ data to the values 0.982 and 0.962 for $M(298^\circ K)$ of A- and B-sites respectively. For comparison we have chosen the same normalization values for $H_{hpf}(T)$ at room temperature. Since RT did not measure T_{FN} we estimated it by extrapolating the sublattice magnetization curves to zero. This left a large uncertainty in the value of T_{FN} ($T_{FN} = 858 \pm 2^\circ K$) used for the RT data. As can be seen from figure 4-6 there is very close agreement between the $H_{hpf}(T)$ versus T and the $M(T)$ versus T curves for A sites as well as for B sites. Above $0.9 T_{FN}$ the values for $M(T)$ drop below the $H_{hpf}(T)$ values. However, this may be due to the uncertainty in T_{FN} for the neutron diffraction data. The errors in $M(T)$ are not given by RT, but regarding the corrections that have to be made, we estimate this error to be about 1 percent for $T < 0.9 T_{FN}$. The differences between the normalized $H_{hpf}(T)$ and $M(T)$ values are less than 1 percent up to $0.9 T_N$. In view of the combined experimental error this difference

FIGURE 4-2

Mössbauer spectrum of Fe_3O_4 at room temperature.

A and B refer to Fe^{57} in A and B sites

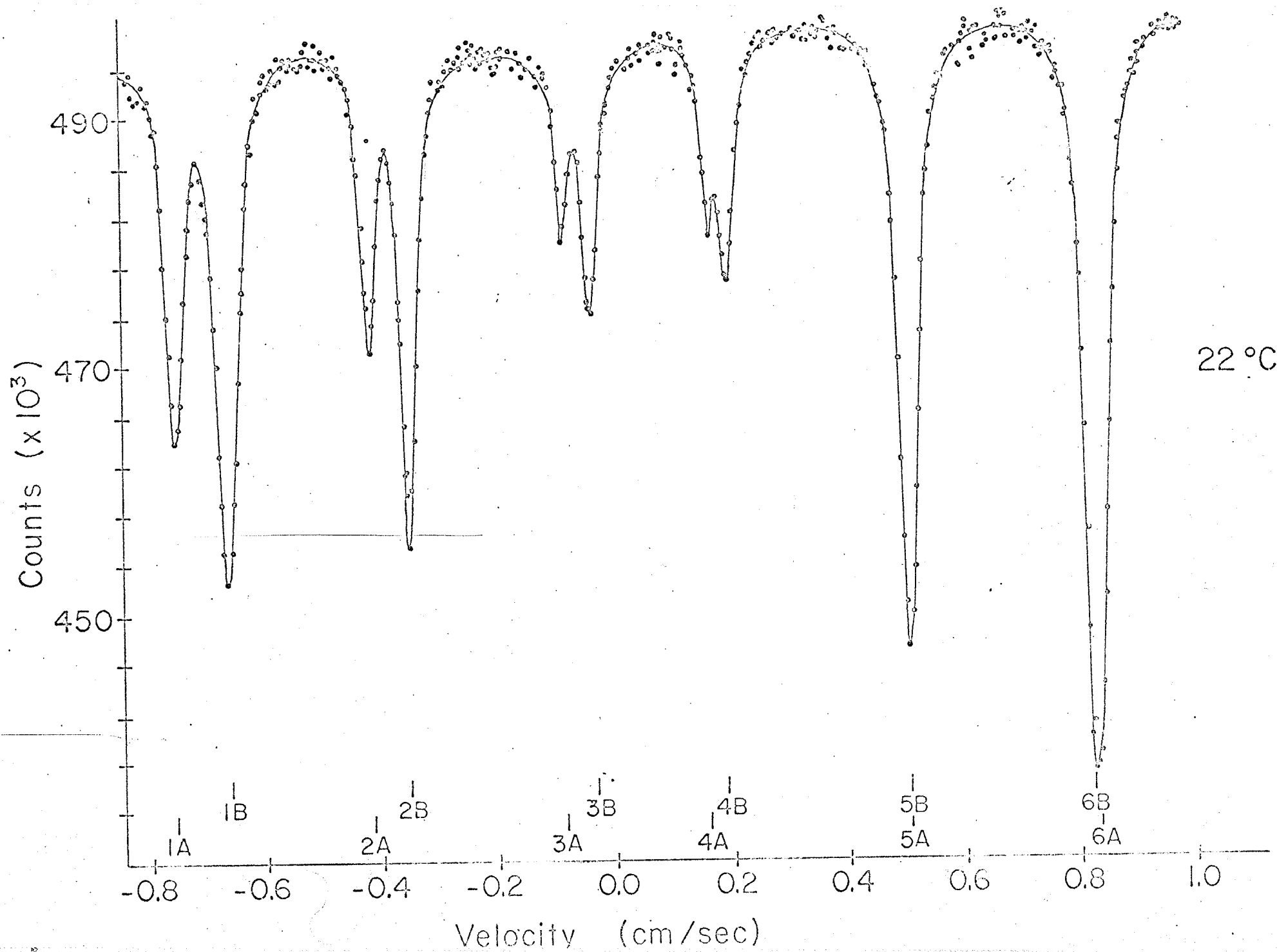


FIGURE 4-3

Mössbauer spectrum of Fe_3O_4 at 411.5°C . A and B refers to Fe^{57} in A and B sites

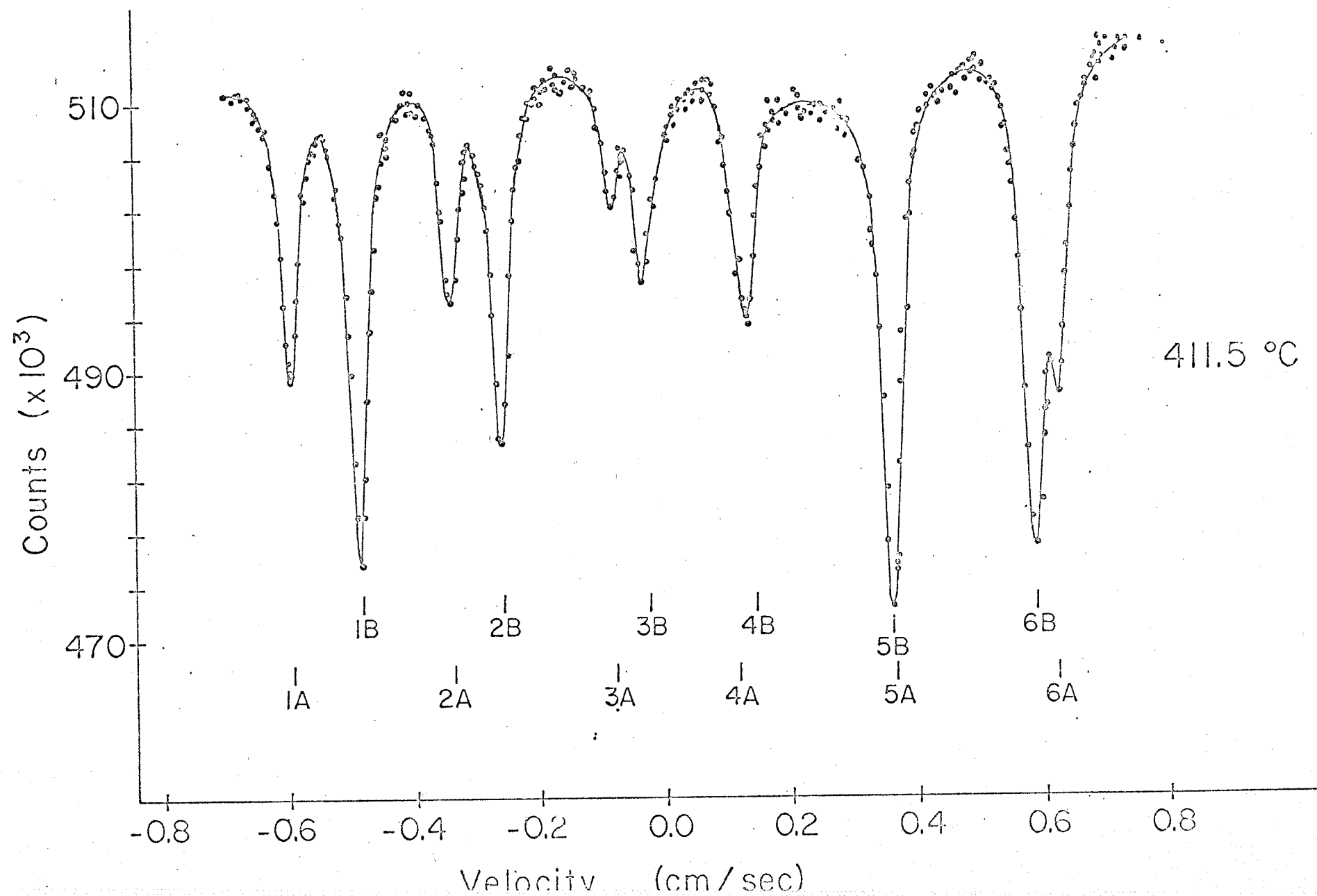


FIGURE 4-4

Mössbauer spectrum of Fe_3O_4 at 552°C . A and B
refers to Fe^{57} in A and B sites

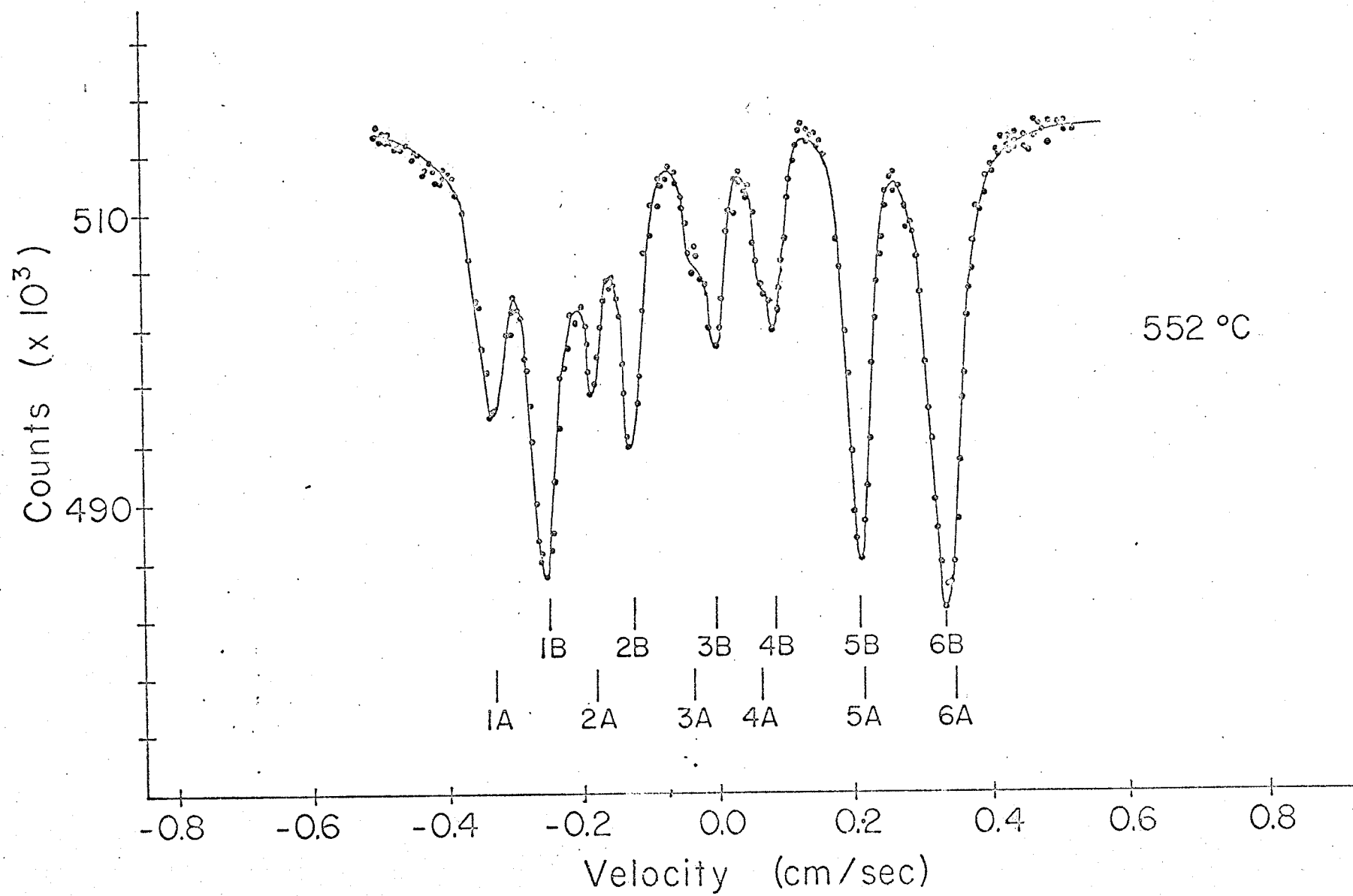


Figure 4-5

Mössbauer spectrum of Fe_3O_4 at 586°C . A and B refer to Fe^{57} in A and B sites.

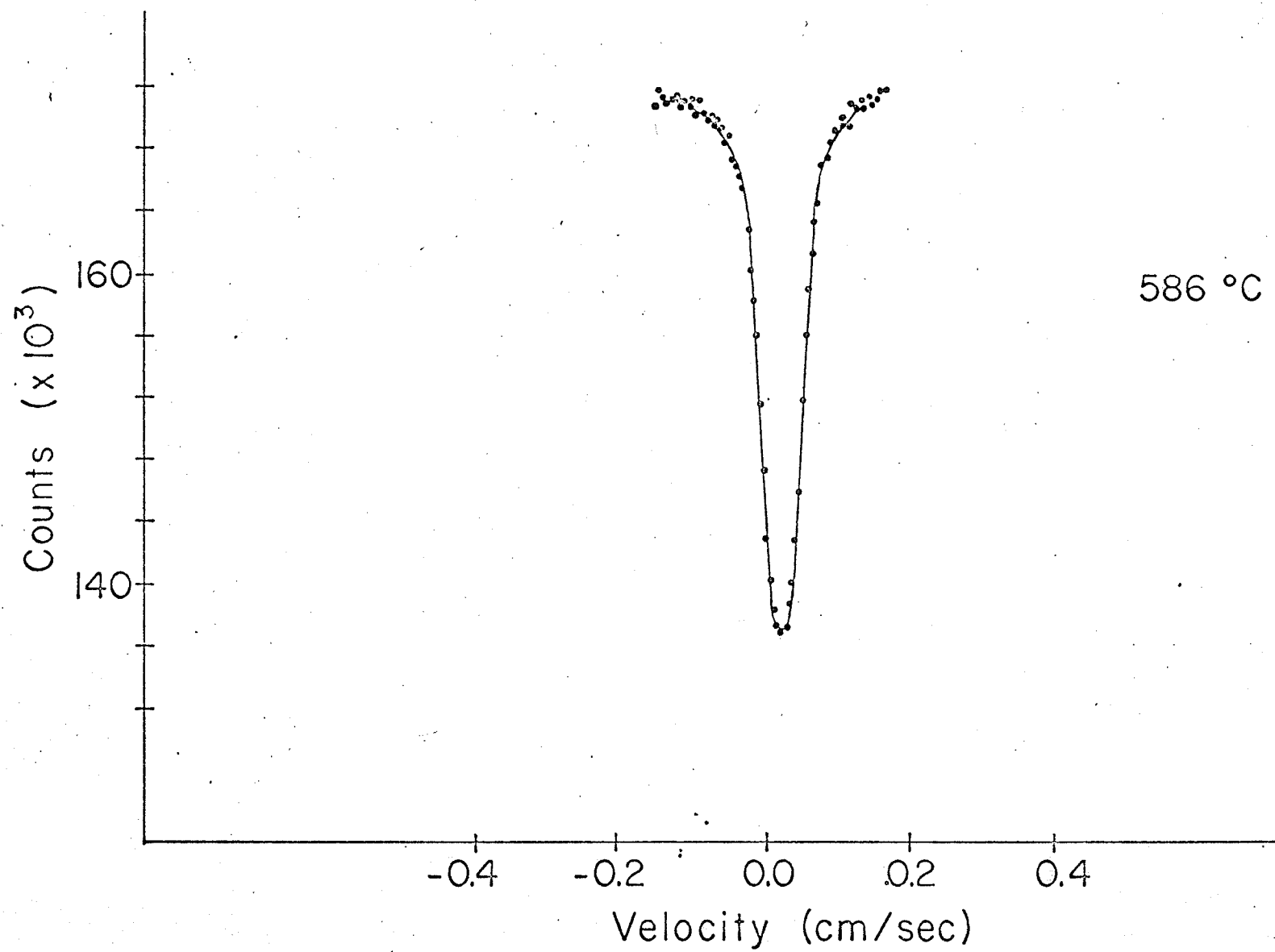
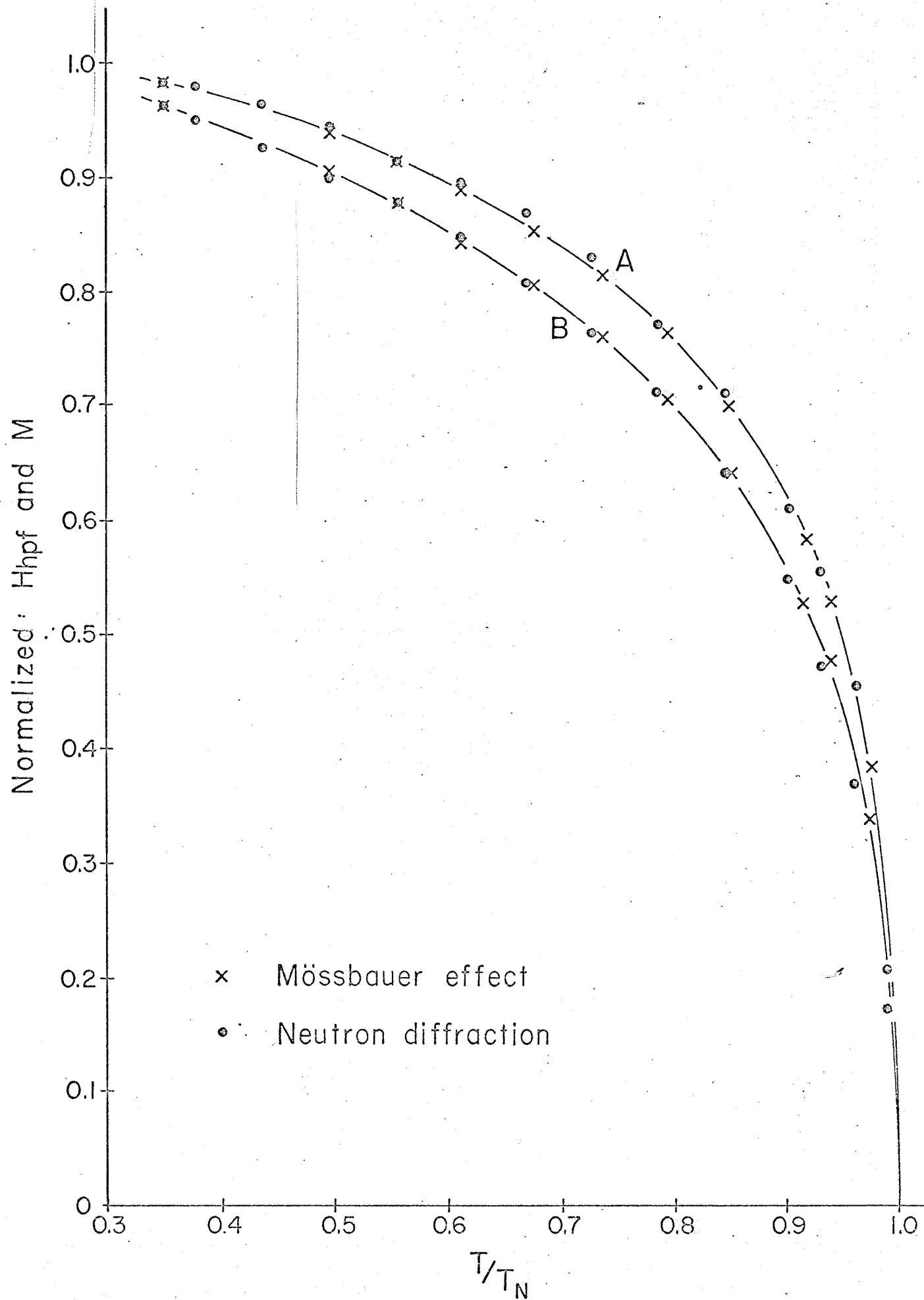


Figure 4-6

Normalized hyperfine magnetic fields at Fe^{57} nuclei and sublattice magnetizations of A and B sites in Fe_3O_4 as a function of the reduced temperature T/T_{FN} . The hyperfine magnetic fields have been determined from Mössbauer spectra and the sublattice magnetization have been taken from Ref. 71.



cannot be called significant. Therefore we conclude that within the experimental error of 1 percent the hyperfine magnetic field at Fe^{57} nuclei in A- and B-sites of Fe_3O_4 have the same temperature dependences as the respective sublattice magnetizations.

4.3 Discussion

In a recent survey article (61) Van Loef has tabulated, for ferrimagnets, the relative hyperfine magnetic field $H_{\text{hpf}}(T)/H_{\text{hpf}}(0)$ obtained from ME or NMR measurements and the relative sublattice magnetization $M(T)/M(0) = m_s(T)$ as deduced from neutron diffraction data. It turns out that for a number of ferrimagnetic spinels and a garnet these two quantities differ by about 5 percent at $0.5 T_{\text{FN}}$ and even more at $0.75 T_{\text{FN}}$. Van Loef suggests that time fluctuations of the ionic spin may be responsible for this difference. This influence can be discussed on the basis of the following relation between H_{hpf} and the magnetic quantum number of the ionic spin m_s ;

$$H_{\text{hpf}}(t, T) = A(T) m_s(t, T). \quad [1]$$

Here, t refers to time and T to temperature. $A(T)$ is the hyperfine coupling constant. The quantization direction has been chosen along the magnetization. Relaxation phenomena in the Mössbauer effect have been discussed by several authors (72-77). The discussion has mainly been directed towards paramagnetic materials. However, one conclusion will also hold for magnetically ordered materials : viz., if the fluctuation of the ionic spin is rapid compared to the Larmor precession

frequency ν_L of the nucleus, $\overline{H_{\text{eff}}(t)}$ will be proportional to $\overline{m_s(t)}$.

In Fe_3O_4 as well as in the spinels and the garnet tabulated in reference (61), this fluctuation frequency will be of the order of 10^{13} c/s, which is much larger than $\nu_L = 10^8$ c/s in a field of 500 kOe in the case of Fe^{57} . So, for these materials we may write [1] as

$$\overline{H_{\text{hpf}}(T)} = A(T) \overline{m_s(T)} \quad [2]$$

It may be noticed, that a similar expression is in common usage in NMR.

A second factor that may impede a close connection between H_{hpf} and M is the temperature dependence of the hyperfine constant A . Only for metallic iron (70) and $(\text{Mn}^{55})^{2+}$ in oxides (78, 79) and in halides (80, 81), has $A(T)$ been investigated experimentally and theoretically. Here the relation between A and the temperature can be represented empirically as

$$A(T) = A(0) [1 - cT^n] \quad [3]$$

where, $A(0)$ refers to A at 0°K , c and n are constants depending on the materials in question. In the above mentioned materials the difference between $A(0^\circ \text{K})$ and $A(1000^\circ \text{K})$ may vary from almost zero to ten percent. In the spinels and the garnet tabulated in reference (61) the different temperature behavior of H_{hpf} and M must be due to $A(T)$, assuming that the experimental results are suitable for such a comparison.

Since magnetite is a completely inverse spinel, only ferric ions occupy the A-sites. It is reasonable to expect that other inverse spinels of the type MFe_2O_4 would exhibit a similar behavior for A site ions. Of course, the temperature independence found for the hyperfine coupling constant may be a consequence of all the A site ions being in S-states.

Of the inverse spinels, magnetite is unusual in that the B sites are occupied by equal numbers of ferric and ferrous ions. Above room temperature however, the ferrous and ferric ions are indistinguishable because fast electron exchange occurs. Therefore, the temperature independence of the hyperfine coupling constant observed for the B site ions of magnetite may not be a general property for all spinels.

For the spinels and the garnet discussed by Van Loef (61), there appeared to be a decrease in the hyperfine coupling constant, $A(T)$, of at least 5 percent for the ions in both A- and B-sites. The difference in the temperature dependence of the hyperfine field and that of the sublattice magnetization is in many of the examples given by Van Loef not unexpected. With the Mössbauer effect one measures only the temperature dependence of H_{hpf} for Fe ions whereas neutron diffraction measures the temperature dependence of all the ions in a particular sublattice. That the temperature dependence of the magnetization of say a Ni ion in $NiFe_2O_4$ in the B site is different from that of an iron ion is expected, because the Ni(B) - Fe(A) superexchange interaction can be

different from the Fe(B) - Fe(A) interaction. Also Ni^{2+} has a spin of 1 while Fe^{3+} has a spin of $\frac{5}{2}$. It has for example been shown by us and this will be discussed in a latter section that even Fe ions in B sites with different A site ions as nearest neighbors in the same material have a different temperature dependence of the hyperfine field.

Another difficulty which arises in the comparison made by Van Loef relates to the quality of the samples used. RT used single crystals of NiFe_2O_4 obtained from Lynde Air. We also obtain a sample of NiFe_2O_4 from Lynde Air but this sample has a Mössbauer spectrum quite different from the powdered samples prepared by us and also those used by Morel (82).

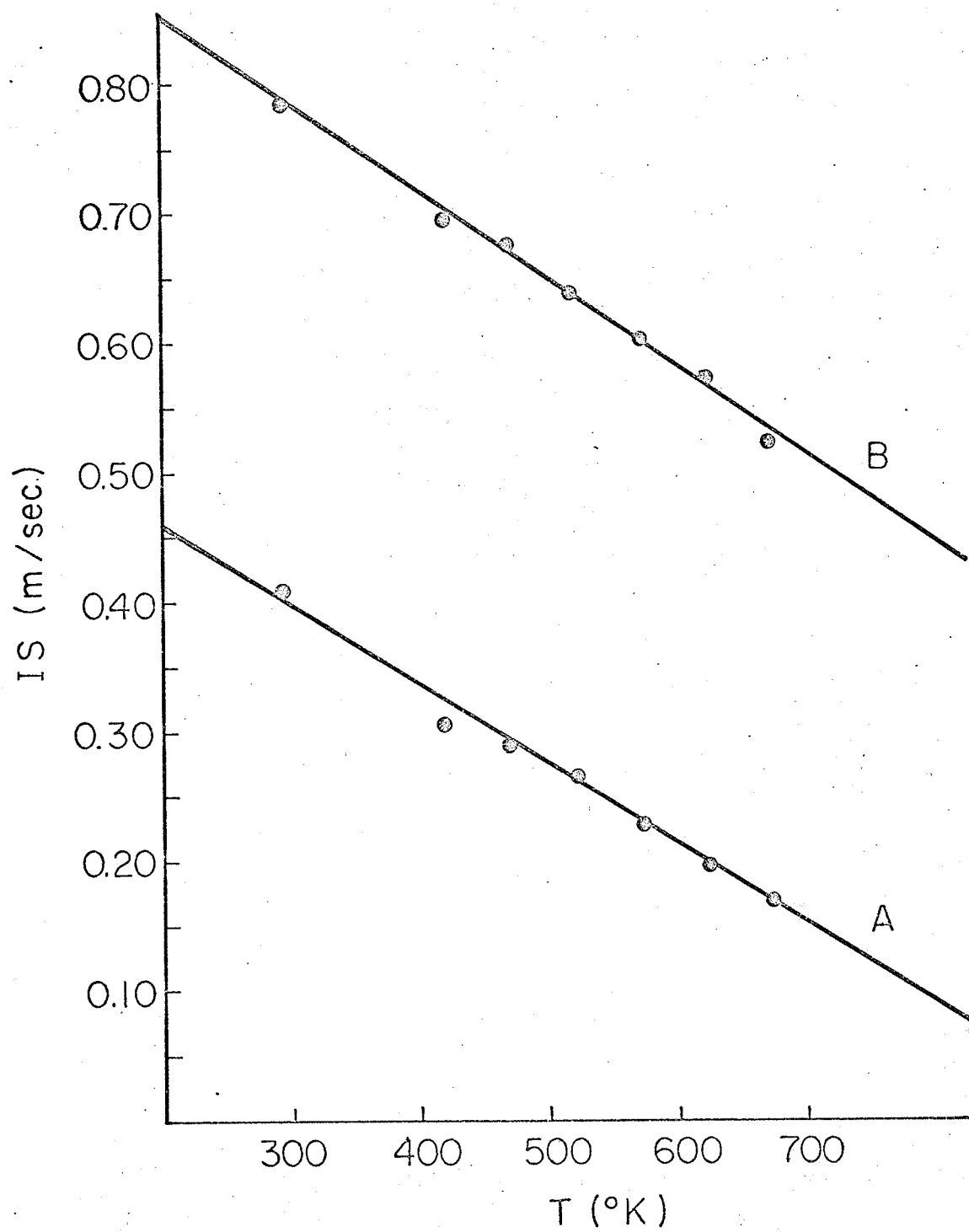
From the preceding we will assume that the hyperfine field in the other ferrites which we have studied is directly proportional to the sublattice magnetization.

Other interesting parameters which have been found from this study are the isomer shift temperature dependence and the quadrupole interaction $\frac{e^2qQ}{2}$. The latter was found to be less than 0.02 mm/sec. for both the A and B sites. The isomer shifts at room temperature differ by 0.44 mm/sec. Most of this difference can be attributed to the fact that the B site ions are part Fe^{2+} and part Fe^{3+} . It should be noted that the isomer shift data are quite inaccurate i.e. ± 0.03 mm/sec. especially at high temperatures. This is because of the difficulty in locating peak 6 accurately for the A and B sites. The hyperfine field of course is still accurate to within 0.5% or better even if peak 6 can only be located to within ± 0.03 mm/sec. In figure 4-7 is plotted the

FIGURE 4-7

Plot of the isomer shift versus temperature.

A and B refer to Fe^{57} in A and B sites



temperature dependence of the I.S. The data is only plotted up to 450° C because of the inaccuracy above this temperature. The slopes of the two lines drawn are 6.7×10^{-4} mm/sec/°K and 6.2×10^{-4} mm/sec/°K for the B and A sites respectively. The errors in the slopes are about ± 0.5 mm/sec/°K. These results indicate that the B site isomer shift decreases more rapidly with increasing temperature than that of the A site although the two values are within experimental error of each other. The values tabulated by Van Loef (61) usually show a difference in slopes of 1×10^{-4} mm/sec/°K, and also the slopes are considerably lower than the ones we found.

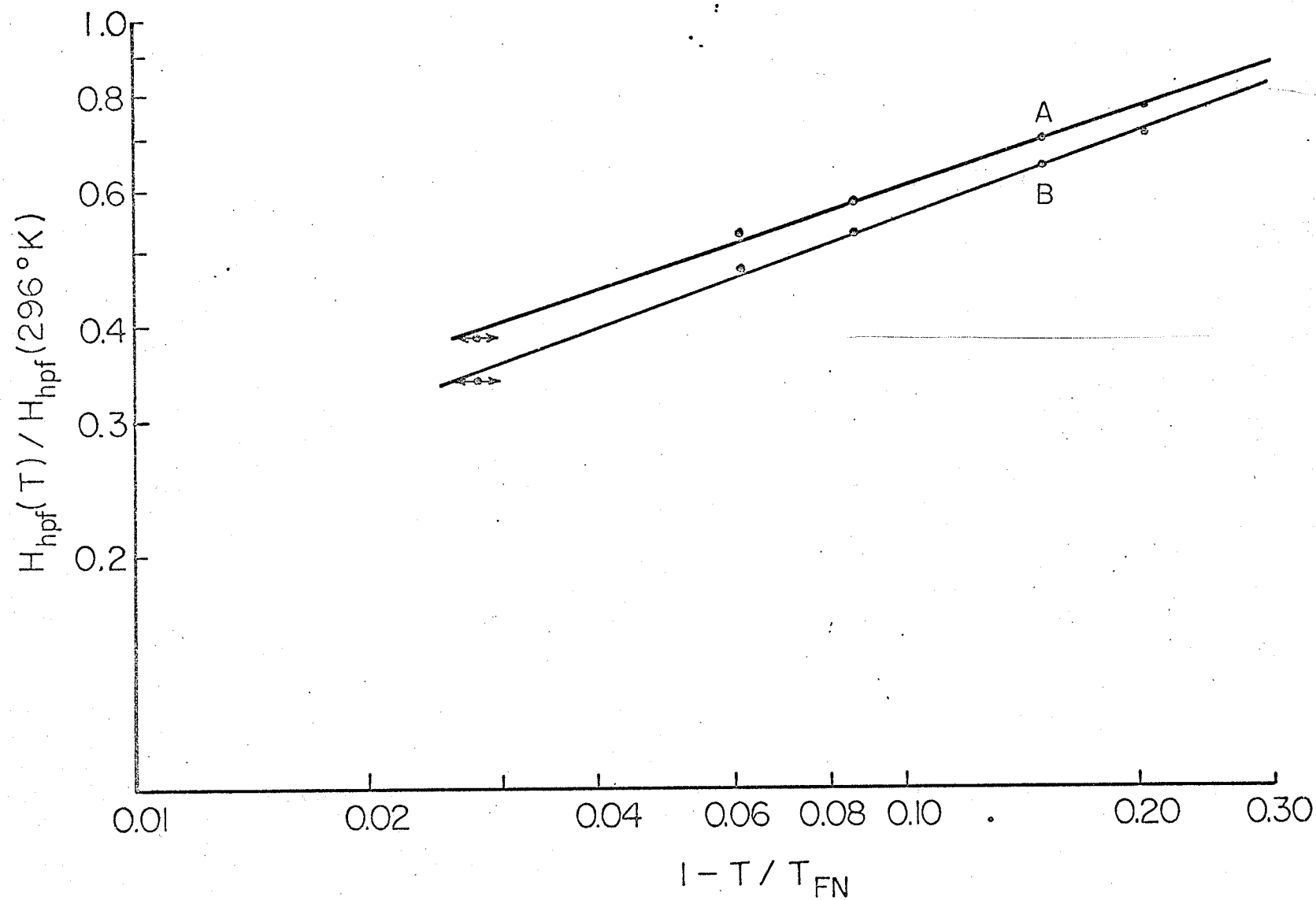
Another interesting point is the behaviour of the hyperfine fields close to the Néel temperature. It has been shown experimentally and indicated theoretically that the behavior is given by

$$\frac{H_{\text{hpf}}(T)}{H_{\text{hpf}}(0)} = C \left(1 - \frac{T}{T_{\text{FN}}} \right)^{\beta}$$

for a large number of materials (83-86). For the ferrites, however, it is known that the hyperfine fields at the two sites have a different temperature dependence at low temperatures. Thus, it is interesting to find the coefficients β for the two sites. In figure 4-8 is plotted the normalized hyperfine field versus $(1 - \frac{T}{T_{\text{FN}}})$ on a log-log plot. The coefficients β for the two sites are 0.33 ± 0.03 and 0.36 ± 0.03 for $0.792 < \frac{T}{T_{\text{FN}}} < 0.972$. It is seen that β is slightly different for the two sites although they are within experimental error of each other and also

FIGURE 4-8

Plot on a log-log scale of $H_{\text{hpf}}(T)/H_{\text{hpf}}(296^\circ \text{ K})$
versus $1 - T/T_{\text{FN}}$ for Fe^{57} in A and B sites



are within experimental error of the usually found value of 0.33. A more detailed study of this behaviour is being carried out and will be reported elsewhere.

CHAPTER 5NiFe₂O₄5.1 Introduction

The simplest of the ferrites which we have studied is NiFe₂O₄. The reason for studying this material is to compare these results with those of the more complicated compounds which will be discussed later. NiFe₂O₄ has usually been assumed to be a colinear Néel-type ferrimagnet with the cation distribution given by (Fe[NiFe]O₄). It has however been suggested (87), that NiFe₂O₄ has a Yafet-Kittel type of triangular spin arrangement. Chappert et al (88) have shown that this suggestion is unlikely by studying NiFe₂O₄ using the Mössbauer effect in an applied magnetic field. By applying a magnetic field parallel to the direction of propagation of the γ -rays the $\Delta m = 0$ transitions should disappear if one has a colinear ferrimagnet. If the $\Delta m = 0$ transitions do not disappear, one can obtain from the intensity of these transitions the angles involved in the triangular spin arrangement.

Morel (82) has studied the temperature dependence of the sublattice magnetization utilizing the Mössbauer effect. He also determined some of the relevant superexchange interactions in the molecular field approximation. I will therefore not discuss in detail our results on the temperature dependence of the hyperfine field.

5.2 Sample Preparation

NiFe_2O_4 can be prepared in several ways. The simplest being by mixing the separate oxides in the correct proportion and firing the sample at high temperatures. We prepared NiFe_2O_4 in two ways :

(1) By adding $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to a NaOH solution in the correct proportions. The precipitate of $\text{Fe}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ is thoroughly washed and heated at low temperatures to form Fe_2O_3 and NiO . These oxides will be very well mixed. This mixture is then prefired at 900°C for 24 hours, reground and fired at 1200°C for 24 hours in air.

(2) By adding $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ to a solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and oxalic acid. The precipitate of $\text{FeNi}(\text{C}_2\text{O}_4)_3$ is heated at low temperatures and subsequently heated as in case 1. No difference was found in these two cases as far as magnetic moment measurements and Mössbauer spectra were concerned.

5.3 Magnetic Moment

The magnetic moment of NiFe_2O_4 was measured as described in section 2-1. We measured a magnetic moment of $2.2 \mu_B$ at 4.2°K extrapolated to infinite internal field. If NiFe_2O_4 is completely inverse the magnetic moment is given by

$$M = M_{\text{Fe}}(\text{B}) - M_{\text{Fe}}(\text{A}) + M_{\text{Ni}}(\text{B}).$$

At 0°K $M_{\text{Fe}}(\text{A}) = M_{\text{Fe}}(\text{B}) = 5 \mu_B$ so that $M = M_{\text{Ni}}(\text{B})$. At 0°K then

$M_{Ni}(B) = 2.2 \mu_B$ which is $0.2 \mu_B$ higher than the spin only value. This is in agreement with g factor measurements (89) and indicates a small unquenched orbital angular momentum.

5.4 Mössbauer Effect

Figure 5-1 shows a Mössbauer spectrum of $NiFe_2O_4$ at room temperature. It is obvious from the doublets in the regions marked 1, 5 and 6 that there must be 2 six line hyperfine patterns. These two patterns are due to Fe in A and B sites. To identify the two spectra with Fe in the two sites we applied a magnetic field of 17 KOe. in a direction perpendicular to the direction of γ -ray propagation. The spectrum obtained in the applied field is shown in figure 5-2. The doublets which appeared without the applied field have now collapsed. Since the applied field will add to $H_{hpf}(A)$ and subtract from $H_{hpf}(B)$ we conclude that the spectra of Fe in A and B sites are identified as shown in figure 5-1.

The next problem is to check whether or not $NiFe_2O_4$ is a completely inverse spinel. The cation distribution can be found from the ratio of areas $\frac{I_B}{I_A}$ as discussed in section 3. This ratio was found from a least squares fit to the spectrum shown in figure 5-3 which was taken at $106^\circ K$ and in which the A and B site lines are well resolved. The area ratio $\frac{I_B}{I_A}$ is 1.02 ± 0.06 for line 1 of the spectrum and 0.84 ± 0.06 for line 6. In the fit to line six however the full widths at half height of the A site line was 30% greater than that of the B site

Figure 5-1

Mössbauer spectrum of NiFe_2O_4 at room temperature.

A and B refer to Fe^{57} in A and B sites

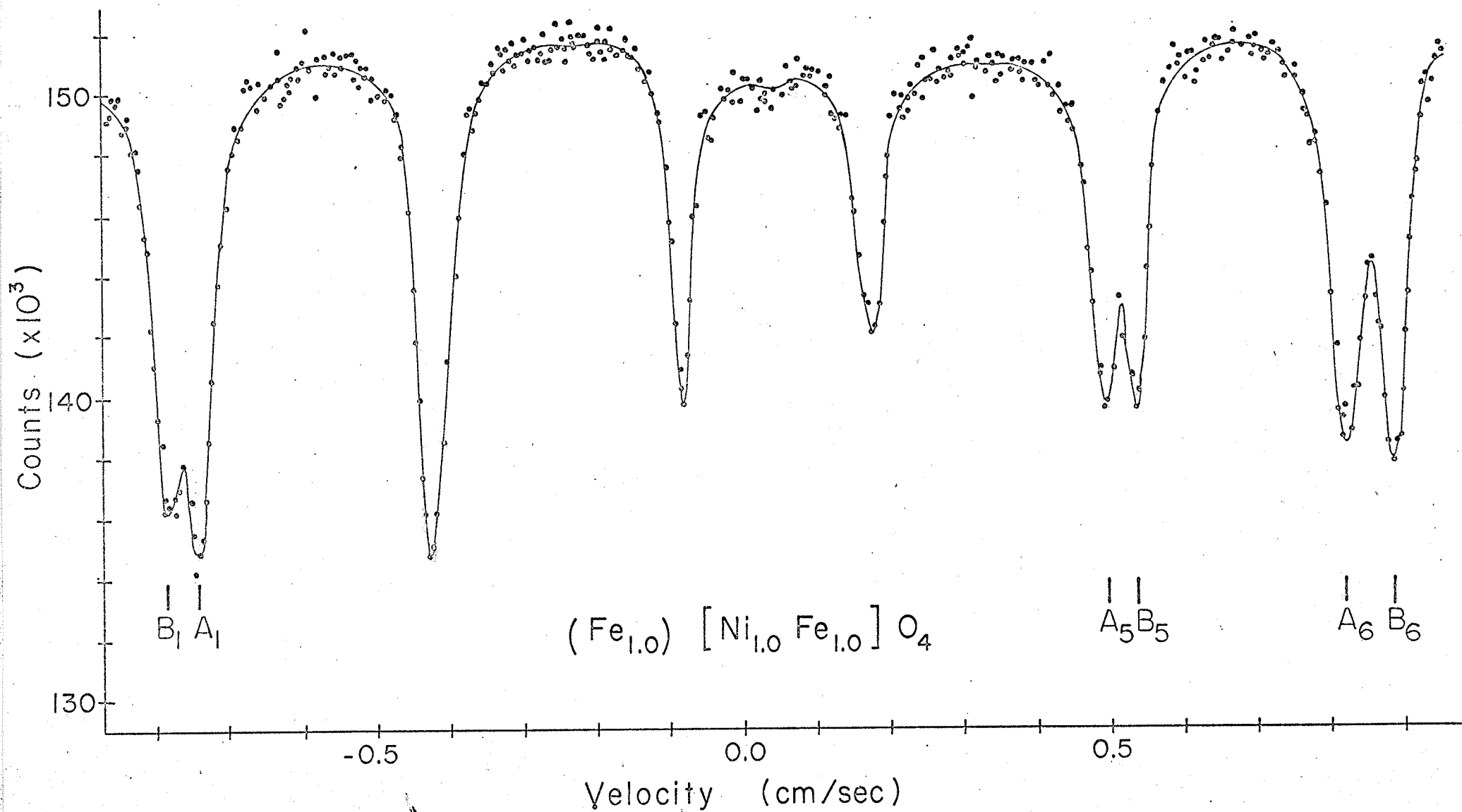


Figure 5-2

Mössbauer spectrum of NiFe_2O_4 in an applied field of 17 KOe. The field direction is perpendicular to the direction of propagation of the γ rays.

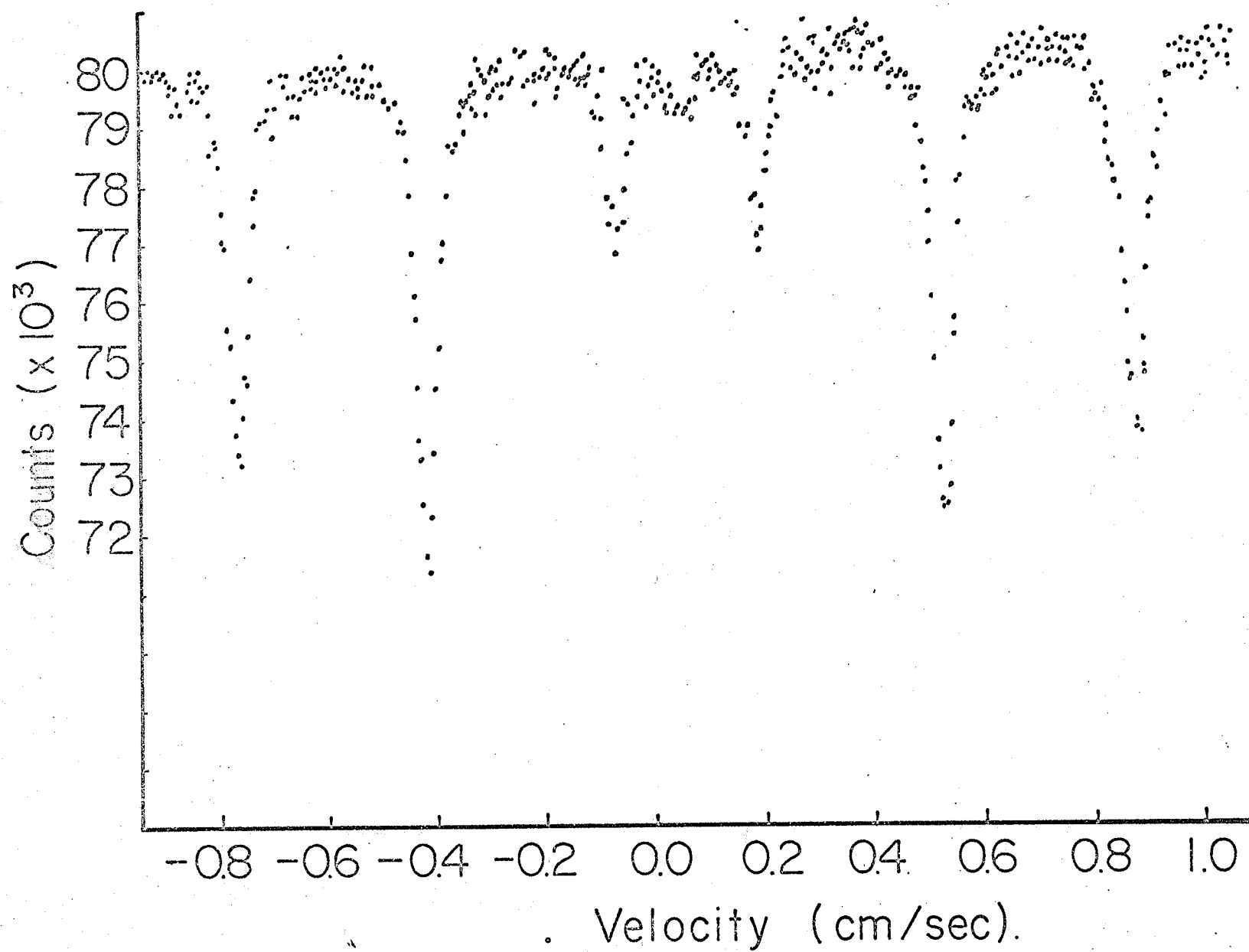
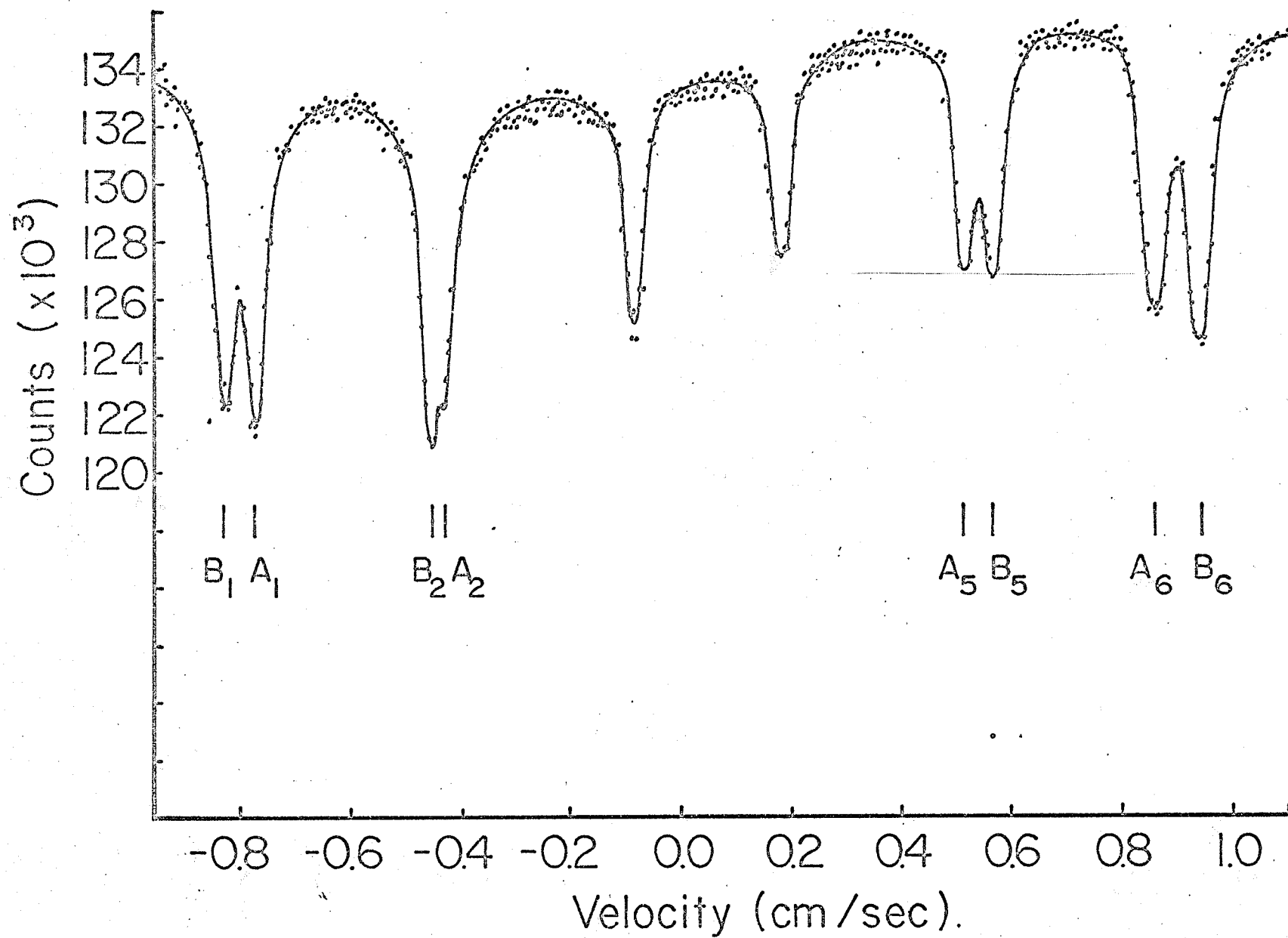


Figure 5-3

Mössbauer spectrum of NiFe_2O_4 at 106°K . A and B refer to Fe^{57} in A and B sites.



line. The low area ratio is caused mainly by this large A site line width. Since the line widths for line one differ by only 5% we feel that 1.02 for $\frac{I_B}{I_A}$ is the more reliable value. This indicates that NiFe_2O_4 is a completely inverse spinel.

Another way of finding out whether or not NiFe_2O_4 is completely inverse is to heat-treat the sample. If the B site preference of Ni is not too high one should be able to force some Ni into the A site by heating the material at high temperatures and quenching. In this way the Ni ions will be frozen into the A sites. Mössbauer spectra for a material quenched in water from 1200°C and a material slowly cooled from 1200°C at a rate of about $100^\circ\text{C}/\text{hour}$ are apparently identical. This shows that the B site preference of the Ni^{2+} is indeed very high in agreement with the calculations discussed in section 1.1.

Figures 5-4 and 5-5 show the spectra obtained at 365 and 623°K respectively. There is one unexpected complication in the spectra of figures 4 and 5, namely that the lines seem to broaden as the temperature increases. To see whether or not this broadening was reversible we heated the specimen at 600°C in our vacuum furnace and then cooled it to room temperature. Line 6 of the resulting spectrum is shown in figure 5-6, also shown is line 6 before the heat treatment. It is obvious that these spectra are considerably different in that the B site line seems to be broader and less intense after the heat treatment. The reason for this is not understood but we believe the material has probably reduced in the vacuum. This is indeed made more possible by the fact that

Figure 5-4

Mössbauer spectrum of NiFe_2O_4 at 365°K . A and B refer to Fe^{57} in A and B sites.

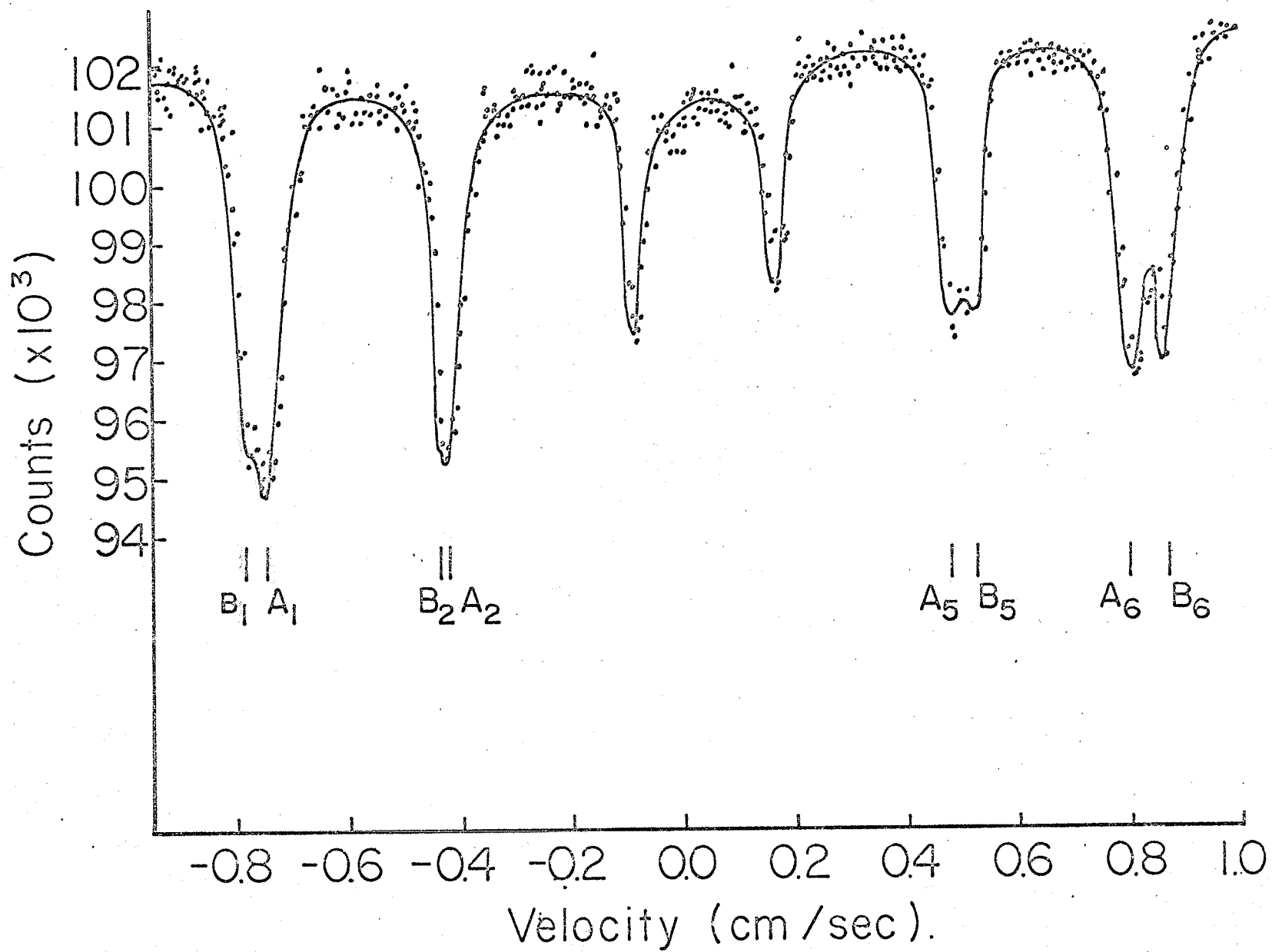


Figure 5-5

Mössbauer spectrum of NiFe_2O_4 at 623°K . A and B refer to Fe^{57} in A and B sites.

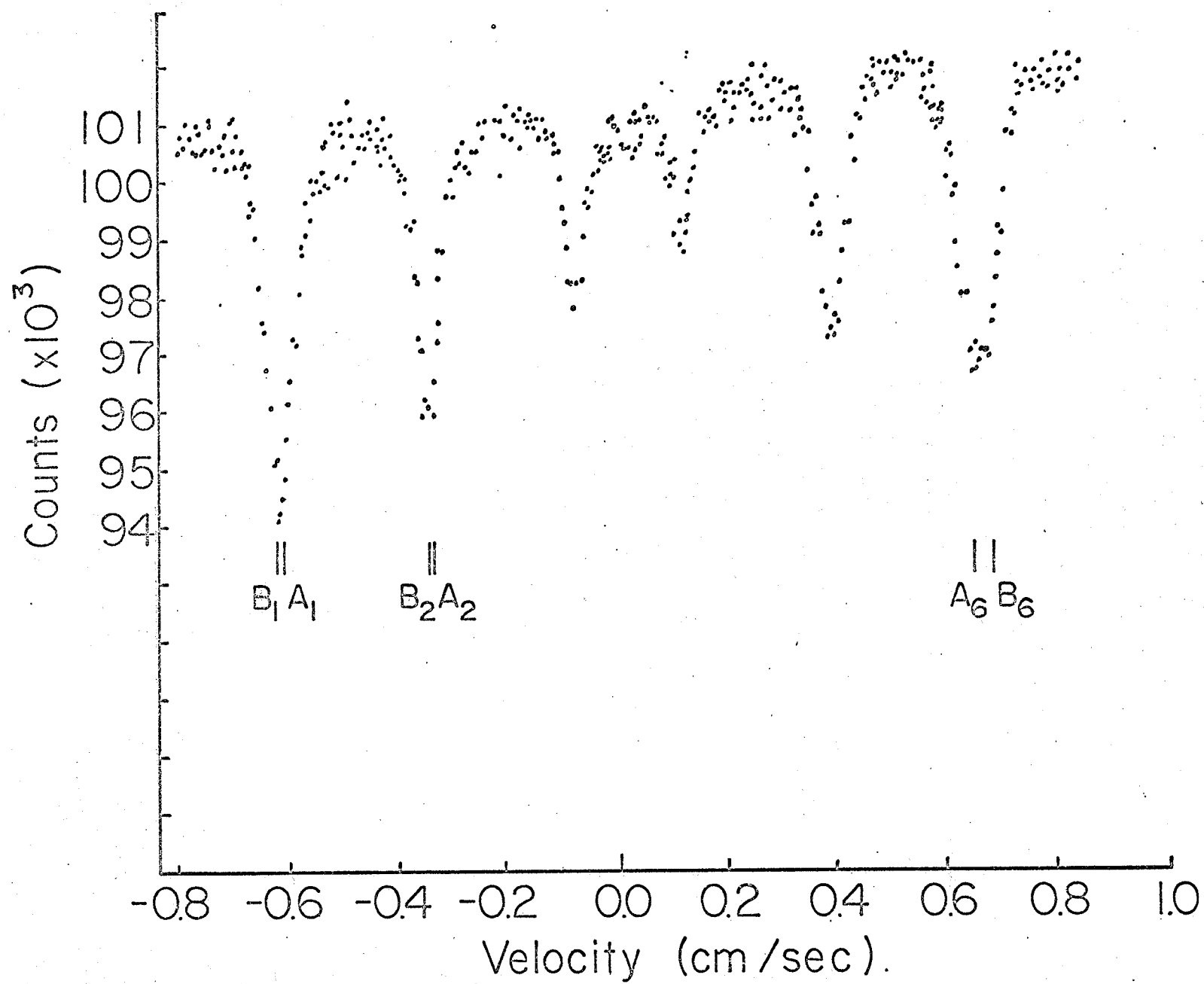
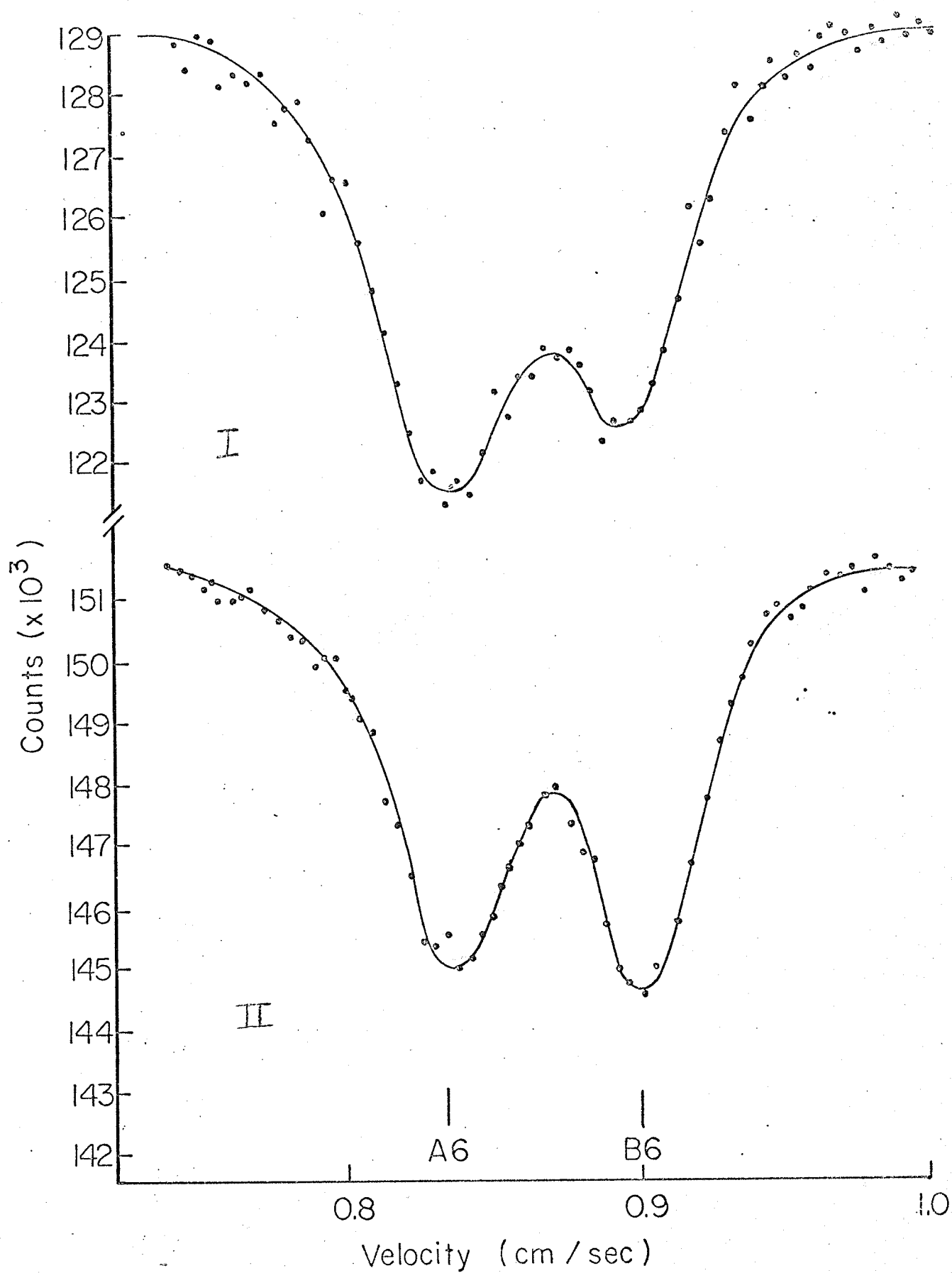


Figure 5-6

Line six of the Mössbauer spectrum of NiFe_2O_4 obtained at room temperature. I is the spectrum obtained after heating the material at 500°C for 24 hours in a vacuum and II is the spectrum obtained before the heat treatment.



the sample is a very fine powder and mixed with graphite. If this broadening were due to a change in the cation distribution then we should have observed the same effect by heating the sample at 600° C in air which we did not.

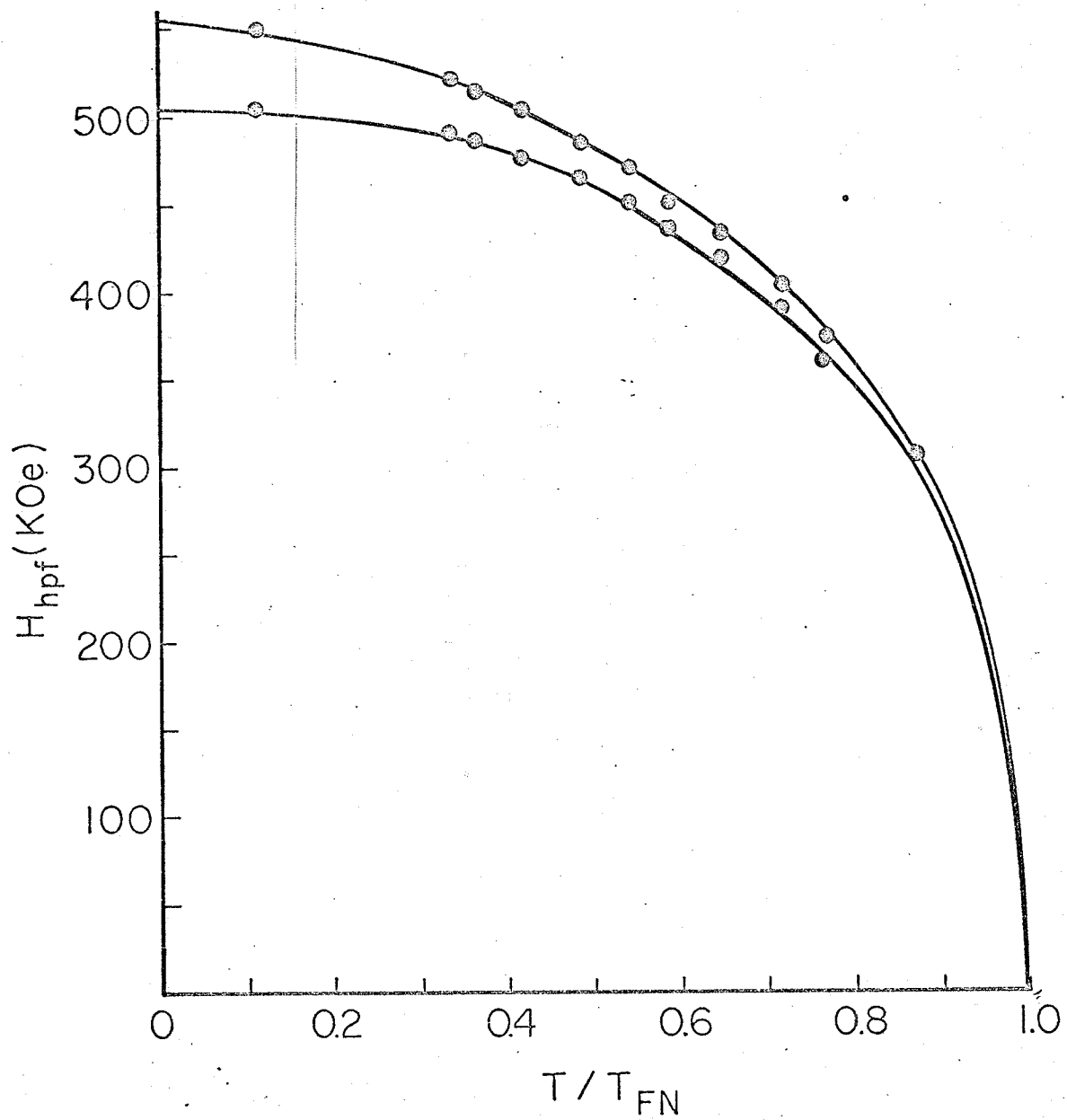
The ferrimagnetic Néel temperature was measured by the thermal scanning technique and was found to be 868° K in good agreement with values ranging from 858° K to 868° K found in the literature (90).

Figure 5-7 shows H_{hpf} plotted versus $\frac{T}{T_{\text{FN}}}$. This data is within experimental error the same as that obtained by Morel (82). The data shows that as previously mentioned the B site magnetization decreases more rapidly with increasing temperature than that of the A site.

The hyperfine fields extrapolated to 0° K are 555 KOe. and 515 KOe. for the B and A sites respectively. The isomer shifts at 106° K were found to be 0.60 mm/sec. and 0.47 mm/sec. relative to stainless steel for the B and A sites respectively. These data show the same behaviour as those found for YIG in section 3 in that $H_{\text{hpf}}(\text{A}) < H_{\text{hpf}}(\text{B})$ and $\text{IS}(\text{A}) < \text{IS}(\text{B})$. It should be pointed out however that both these differences are not as large for NiFe_2O_4 as for YIG.

Figure 5-7

Plot of the hyperfine fields versus T/T_{FN} . The lower curve is for Fe^{57} in A sites and the upper curve is for Fe^{57} in B sites. Curves are drawn through the data points and indicate possible extrapolations.



CoFe₂O₄6.1 Introduction

CoFe₂O₄ is different from most other spinels in that it has a large magnetic anisotropy. This anisotropy is generally assumed to be due to the Co²⁺ ion. Calculations by Tachiki (8) and Slonczewski (7) indicate that the anisotropy of the Co²⁺ ion is due to the crystal field splitting of the atomic orbital levels by a cubic and trigonal crystal fields together with the spin-orbit coupling. Theoretical calculations then agree reasonably well with the experimentally measured anisotropy constant. By assuming a model of ordering of the Co²⁺ and Fe³⁺ ions in the B sites it was also possible to explain the magnetically induced uniaxial anisotropy in both CoFe₂O₄ and Co doped Fe₃O₄. The above theoretical calculations also give values for the net magnetic moment. This according to Tachiki and Slonczewski should be about 3.5 μ_B per ion. The measured values of the magnetic moment of CoFe₂O₄ indicate that the moment of Co²⁺ is 3.3 to 3.94 μ_B per ion. This large discrepancy in the magnetic moments could be due to CoFe₂O₄ not being a completely inverse spinel.

The purpose of our experiments is to attempt to clear up this point together with the possibility of seeing in what way the cation distributions effect the Mössbauer spectra.

6.2 Sample Preparation

Samples of CoFe_2O_4 were prepared by the same methods as described for NiFe_2O_4 . In addition to this we also prepared samples by mixing together in the required proportions CoO and Fe_2O_3 . This mixture was prefired at 900°C for 24 hours and reground followed by another firing at 900°C for 24 hours. The material was then reground and fired at 1200°C and quenched in water. To obtain a slowly cooled material, we heated the quenched material to 1200°C and cooled it at a rate of 4°C per hour. These samples will be referred to as $\text{CoFe}_2\text{O}_4(\text{q})$ and $\text{CoFe}_2\text{O}_4(\text{s.c.})$ respectively.

6.3 Mössbauer Effect (cation distributions)

In figures 6-1 and 6-2 are shown Mössbauer spectra of $\text{CoFe}_2\text{O}_4(\text{q})$ and $\text{CoFe}_2\text{O}_4(\text{s.c.})$ taken at room temperature. Figure 6-2b shows an expanded view of line six of the spectra shown in figure 6-1 and 6-2. It is obvious that the two materials exhibit a different Mössbauer spectrum. If CoFe_2O_4 were completely inverse we would have expected spectra similar to those of NiFe_2O_4 as shown in figure 5-1. If, however, the spectra are different only because CoFe_2O_4 is not completely inverse we would expect the octahedral line to be more intense than the tetrahedral line. If we, however, identify the B site line in region 6 of figure 6-2 for $\text{CoFe}_2\text{O}_4(\text{s.c.})$ as being the line corresponding to the higher hyperfine field as for NiFe_2O_4 we see that this line would be less intense than the A site line. To find the cation distribution we collected spectra in an applied field of 55 KOe. at room temperature. These spectra are shown in figures 6-3 and 6-4. From these spectra it is easy to identify the A and B site lines

FIGURE 6-1

Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{q})$ at room temperature.

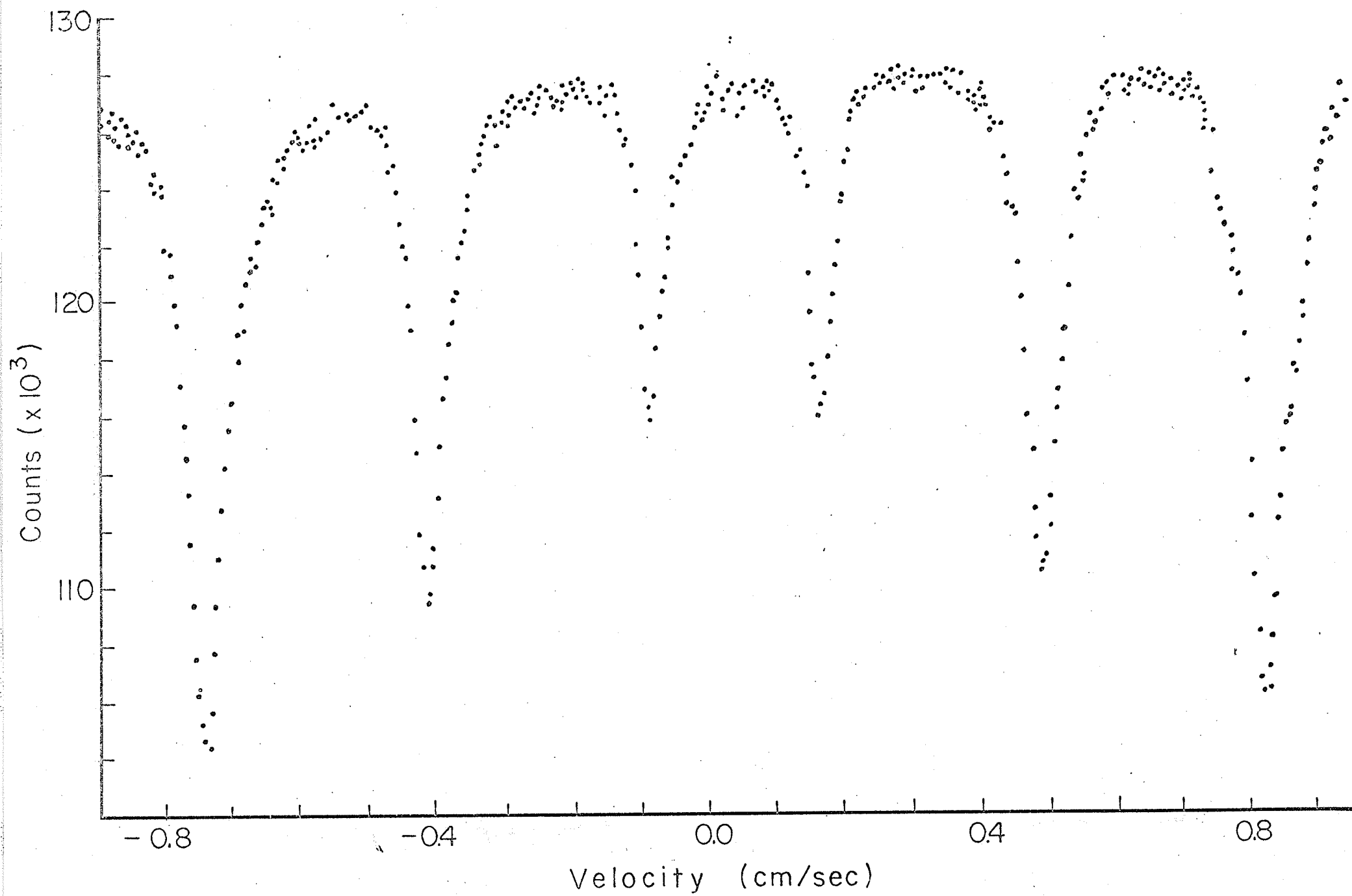


Figure 6-2

Mössbauer spectrum of CoFe_2O_4 (s.c.) at room temperature.

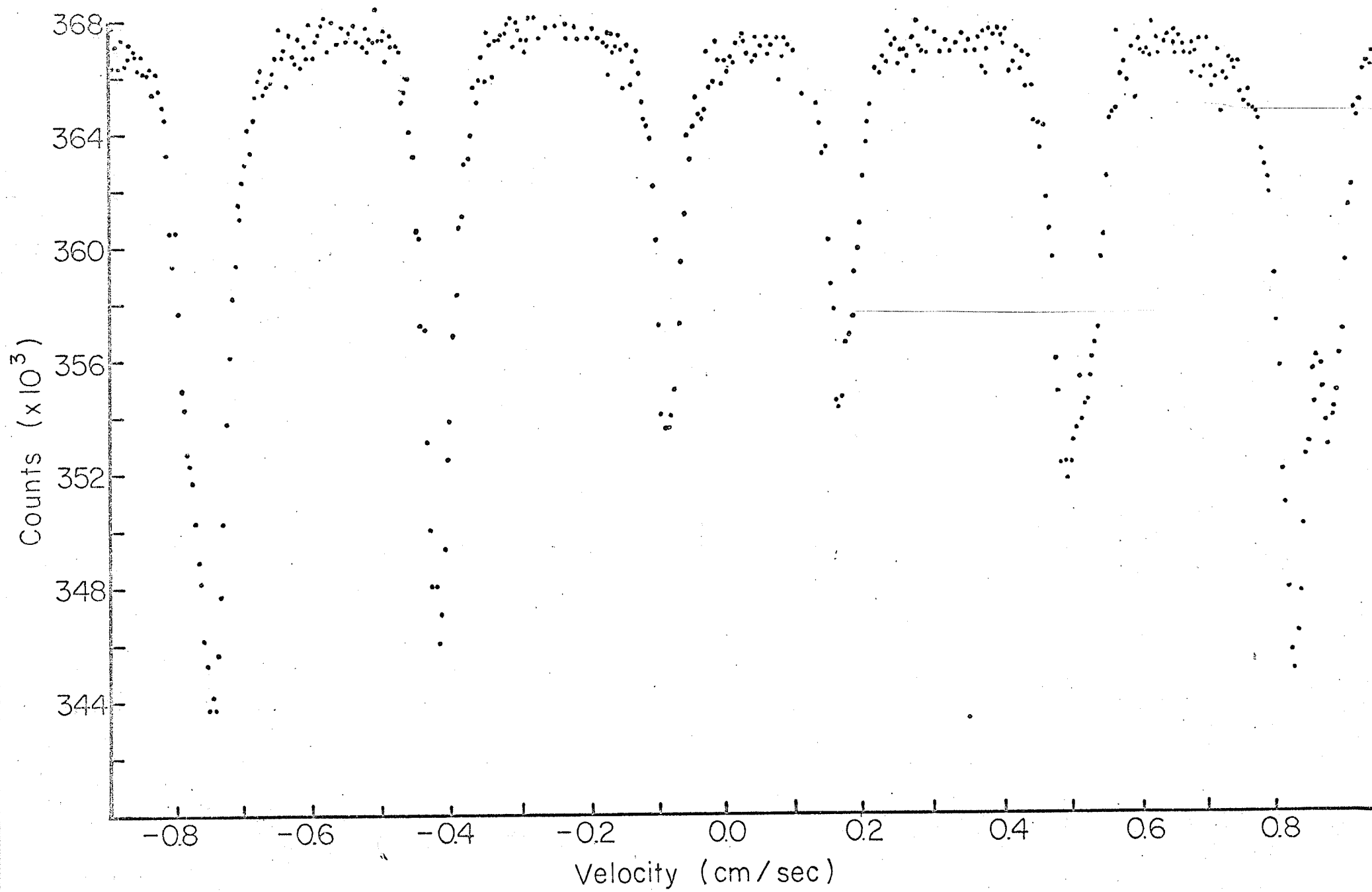


Figure 6-2b

Expanded view of line six of $\text{CoFe}_2\text{O}_4(\text{s.c.})$ (I) and $\text{CoFe}_2\text{O}_4(\text{q})$ (II). The vertical lines drawn are explained latter in the text.

Counts (x10⁴)

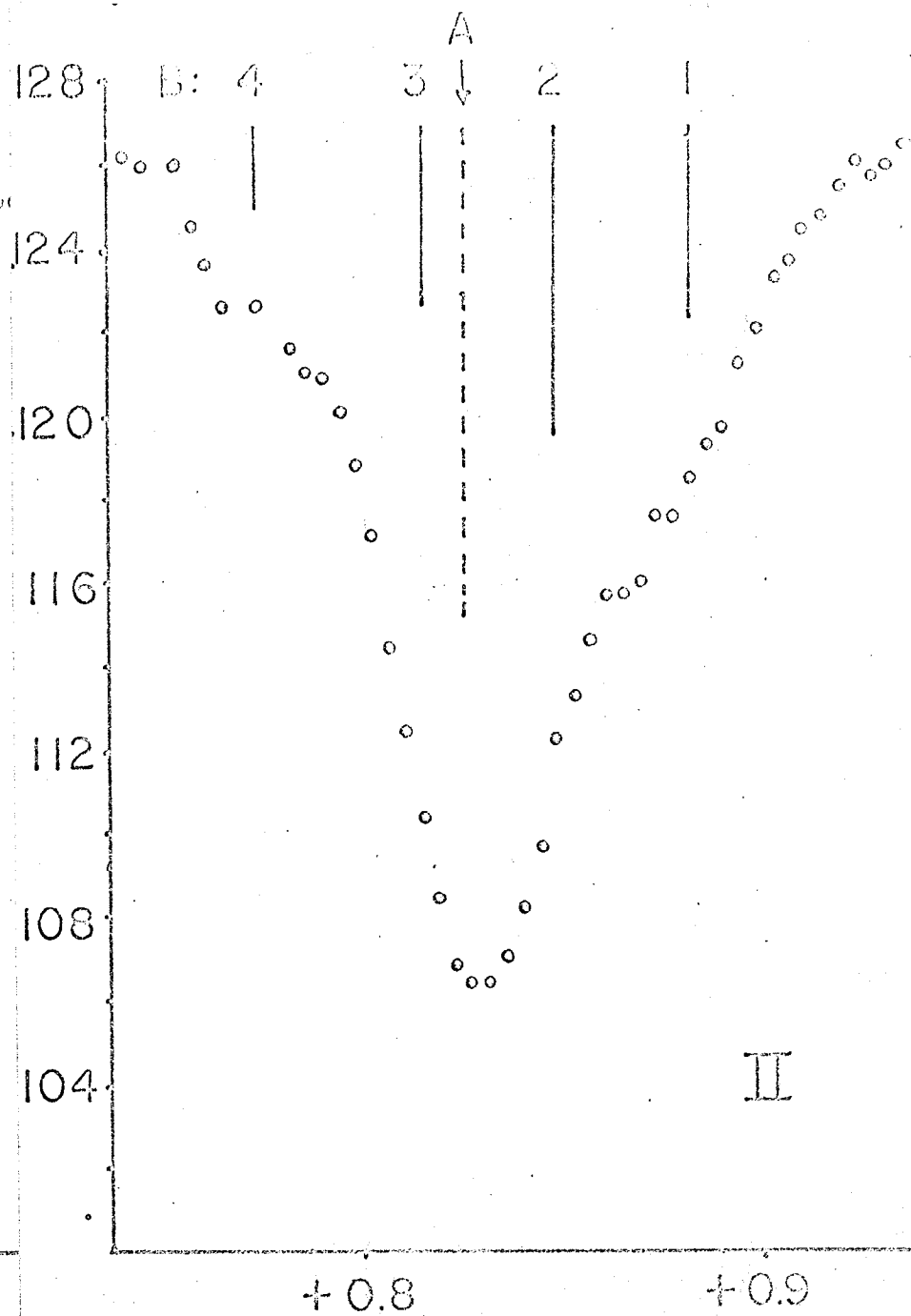
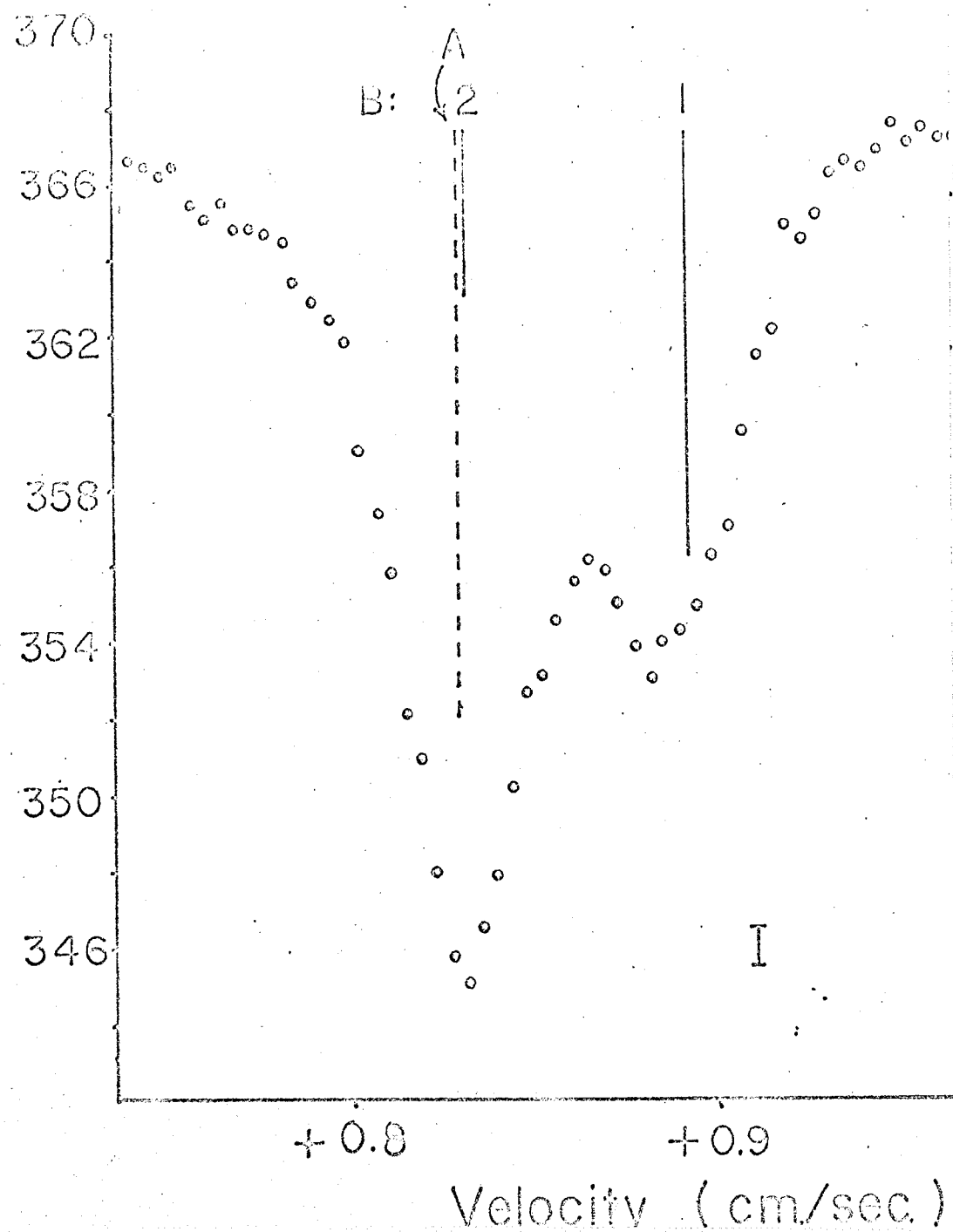


Figure 6-3

Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{q})$ in an applied field of 55 KOe. The field direction is parallel to the direction of propagation of the γ rays. A and B refer to Fe^{57} in A and B sites.

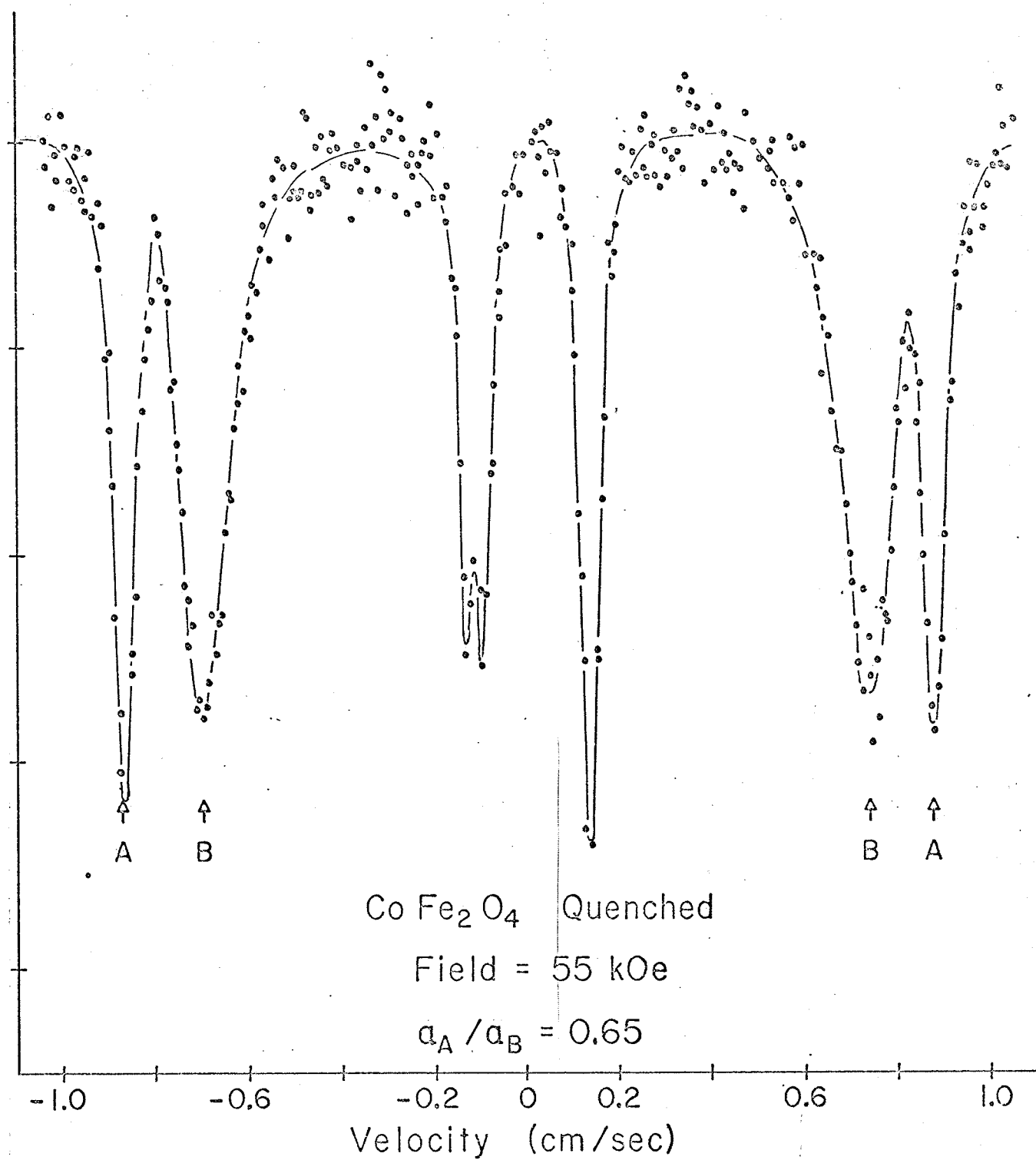
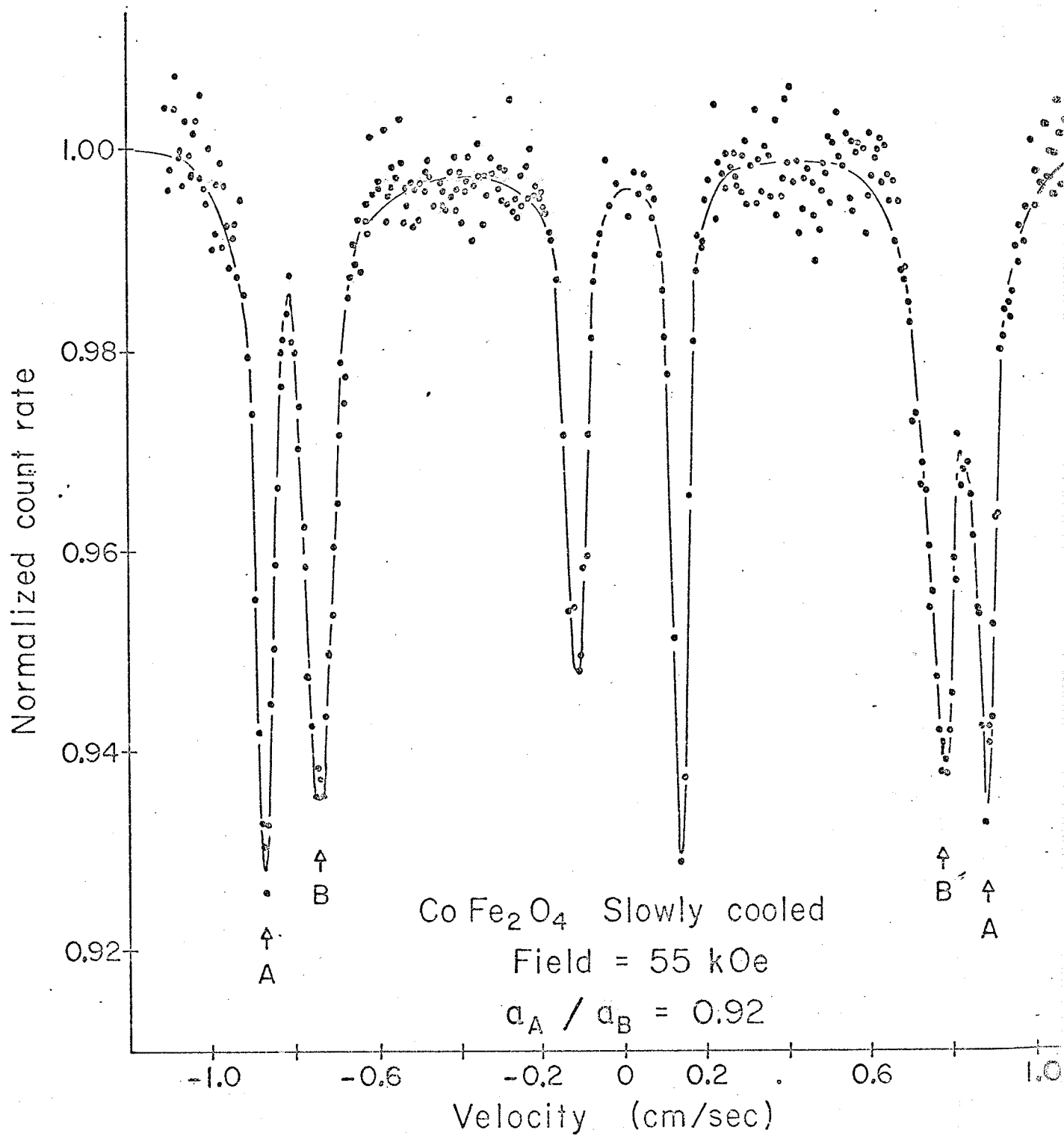
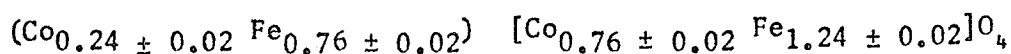


Figure 6-4

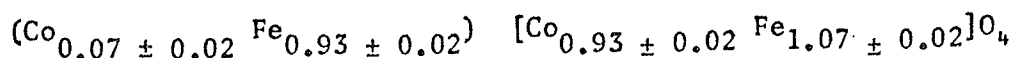
Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{s.c.})$ in an applied field of 55 KOe. The field direction is parallel to the direction of propagation of the γ rays. A and B refer to Fe^{57} in A and B sites.



as indicated in the figures. The absence of the lines corresponding to the $\Delta m = 0$ transitions is consistent with a colinear spin arrangement. Another point worth noting is that the B site line is very broad compared to the A site line and is broader for $\text{CoFe}_2\text{O}_4(\text{q})$ than for $\text{CoFe}_2\text{O}_4(\text{s.c.})$. This broadening of the B site line will be discussed later. To obtain the cation distribution we measured the area of absorption lines corresponding to Fe^{57} in A and B sites. The area measurements were done with a planimeter and the accuracy in the area ratio $\frac{I_A}{I_B}$ was about 5%. This was determined from the scattering in the results of several measurements. The area ratio was found to be 0.65 ± 0.03 for $\text{CoFe}_2\text{O}_4(\text{q})$ and 0.92 ± 0.04 for $\text{CoFe}_2\text{O}_4(\text{s.c.})$. By making the previously mentioned correction for the ratio of recoilless fractions at room temperature, the values of $\frac{n_A}{n_B}$ become 0.61 ± 0.03 and 0.88 ± 0.04 respectively. The cation distribution calculated from these values is given by



for CoFe_2O_4 quenched and



for $\text{CoFe}_2\text{O}_4(\text{s.c.})$ This shows that CoFe_2O_4 is not completely inverse and that the degree of inversion depends on the heat treatment. This result is consistent with the calculation that the B site preference of a Co^{2+} ion is less than that for a Ni^{2+} ion. These calculations have been discussed in section 1.3. A discussion of some other results and interpretations as far as the Mössbauer spectra are concerned is reserved for later.

6.4 Magnetic Moment

The magnetic moment of CoFe_2O_4 reported by several authors ranges from 3.3 to 3.9 μ_B per unit formula (90-93). The value of 3.3 μ_B (90) was however obtained at low applied fields, i.e. 5 KOe. and the sample is not completely saturated at this field. The large variations in the magnetic moments may however be due to variations in the cation distribution.

We have measured the magnetic moments of both the quenched and slowly cooled materials at room temperature, liquid nitrogen and liquid helium temperature. The apparatus used has been described in section 2.1. The results are given in table 6-1. Both the values as obtained by extrapolating $H = 0$ and $\frac{1}{Hi} \rightarrow 0$ show that the s.c. and q materials have considerably different magnetic moments which is qualitatively consistent with the difference in cation distributions. By using the cation distributions as found previously and assuming a magnetic moment of 5 μ_B for Fe^{3+} and 3 μ_B for Co^{2+} in A sites we calculate a magnetic moment of 3.1 $\leftrightarrow$ 3.2 μ_B for the Co^{2+} ion in the B sites. This is considerably less than the value calculated by Tachiki (8) and Slonczewski (7) $\approx 3.5 \mu_B$. The low magnetic moment could be due to several factors. The contributions from the spin may be considerably less than 3.0 μ_B or the effective orbital angular momentum may be considerably less than the assumed value of 1. By fitting the anisotropy data Slonczewski (7) obtained a value for $\alpha\lambda = 132 \text{ cm}^{-1}$ where λ is the spin-orbit coupling parameter, and α determines the effective orbital

TABLE 6-1

Tabulated values of the magnetic moment of $\text{CoFe}_2\text{O}_4(\text{s.c.})$ and $\text{CoFe}_2\text{O}_4(\text{q})$ at 296, 77 and 4.2° K . Both the values obtained by extrapolating to zero applied field and infinite internal field core given.

<u>Temp (°K)</u>	<u>CoFe₂O₄ (q)</u>		
	<u>H → 0</u>	<u>H = 18 KOe.</u>	<u>H_i → ∞</u>
293° K	3.47	3.64	3.72
77° K	3.68	3.98	4.02
4.2° K	3.66	3.91	4.00

<u>Temp (°K)</u>	<u>CoFe₂O₄ (s.c.)</u>		
	<u>H → 0</u>	<u>H = 18 KOe.</u>	<u>H_i → ∞</u>
293° K	2.95	3.30	3.47
77° K	3.14	3.38	3.50
4.2° K	3.14	3.37	3.45

angular momentum. In a recent paper Shafer (94) obtained a value of $\lambda = 190 \text{ cm}^{-1}$ for Co^{2+} in RbCoF_3 . If this value can be used for Co^{2+} in CoFe_2O_4 , then α would be 0.7 which would give an orbital contribution to the magnetic moment of about $0.35 \mu_B$. Taking a value of $2.95 \mu_B$ for the spin contribution (8) one gets a total of $3.3 \mu_B$ which is in reasonable agreement with our results. It is however not clear whether it is α being less than 1 or λ being less than 190 which causes the low value of $\alpha\lambda$ in CoFe_2O_4 . Since the covalency in oxides is usually larger than in fluorides one would perhaps expect the spin orbit coupling in the oxides to be less than that in the fluorides.

It should also be pointed out that the value obtained for the exchange field splitting ($2g\mu_B H_e = 640 \text{ cm}^{-1}$) by Slonczewski (7) may be somewhat high. From molecular field theory we obtain an exchange field of

$$\frac{2\mu_B H_e}{k} = 659^\circ \text{ K}$$

acting on B site Fe ions in Li ferrite, taking the ferrimagnetic Néel temperature to be 943° K . The calculation was done assuming the A-A and B-B exchange interactions to be negligible. By comparing the ferrimagnetic Néel temperature of CoFe_2O_4 ($\approx 800^\circ \text{ K}$) to that of LiFe_2O_4 we obtain an exchange field splitting of the Co^{2+} ion of

$$\frac{2\mu_B H_e}{k} = 284^\circ \text{ K}.$$

This value probably has to be corrected upwards because of the inadequacy of the molecular field theory. By comparing the results of molecular field

theory with those obtained by Pushbrooke and Wood (95) for an antiferromagnet with $S = \frac{5}{2}$ and six nearest neighbors we should perhaps correct the value to $\approx 400^\circ \text{ K}$ or 330 cm^{-1} . By using then the formula given by Slonczewski (7) to calculate the spin contribution to the magnetic moment, i.e.

$$M_s = 3 - \frac{(\alpha\lambda)^2}{(2\mu_B H_e)}$$

we get $2.84 \mu_B$. The total magnetic moment of the Co^{2+} ion would then be $3.10 \mu_B$. The above discussion merely shows that a value of 3.1 or $3.2 \mu_B$ for a Co^{2+} ion in CoFe_2O_4 can be justified and is not totally unexpected.

Since the degree of inversion of CoFe_2O_4 depends on the heat treatment of the sample it is of interest to determine the minimum temperature at which cation diffusion takes place. In table 6-2 are listed the magnetic moment of $\text{CoFe}_2\text{O}_4(q)$ after heating for 20 hours at various temperatures. These measurements were done at room temperature and all values are obtained at 17 KOe. It is seen that cation diffusion takes place at temperatures as low as 500° C .

The low temperatures required for cation diffusion in the spinels is probably due to the previously mentioned highly vacant structure of the spinels.

Using the Boltzman distribution the cation distribution after the sample has been heated at a temperature T for a long enough period of time to reach equilibrium will be given by

TABLE 6-2

Tabulated values of the magnetic moment measured at room temperature in an applied field of 17 KOe. after various heat treatments. Also listed is the weight of the sample after each heat treatment.

<u>Heat Treated at (T°C)</u>	<u>for (hrs)</u>	<u>Weight (grams)</u>	<u>Mag. Moment (arbitrary units)</u>
650	24	0.3480	0.4311
540	12	0.3480	0.4140
510	24	0.3480	0.4103
480	24	0.3480	0.4035
460	24	0.3479	0.3955
430	48	0.3481	0.3965

$$\frac{x(1+x)}{(1-x)^2} = \exp \frac{-E}{kT}$$

where x is the concentration of Co ions in the A site, k is the Boltzman constant and E is the activation energy, that is the octahedral site stabalization energy. x can be found from the magnetization measurements. In figure 6-5 we have plotted

$$\frac{x(1+x)}{(1-x)^2} \text{ versus } \frac{1}{T}$$

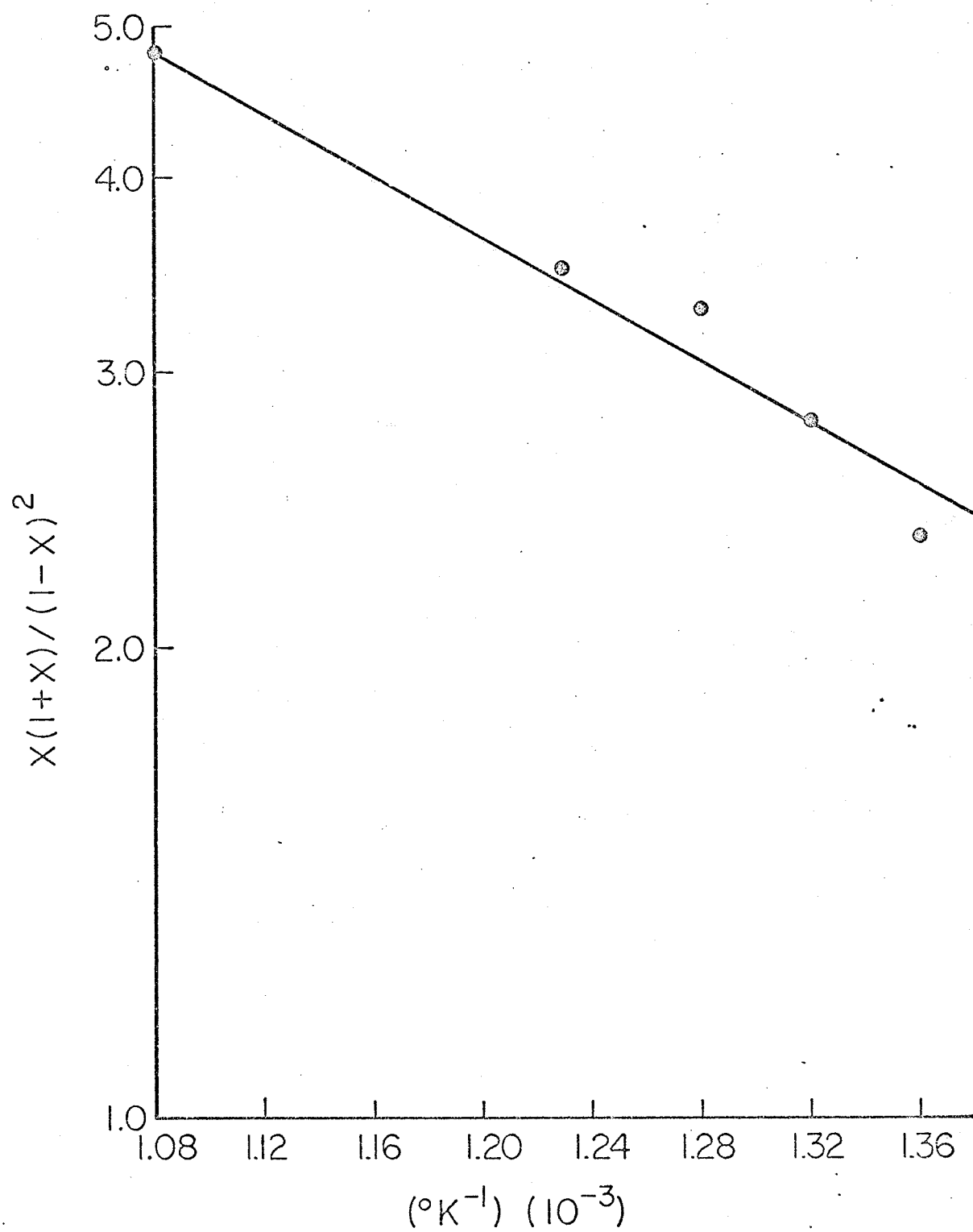
on a semi-log scale. The activation energy found is 0.18 ev which is slightly higher than the values of 0.14 found for MgFe_2O_4 and CuFe_2O_4 (96, 97, 98). This calculation shows that the octahedral site preference of a Co^{2+} ion is only slightly larger than that of a Mg or Cu ion.

Also listed in table 6-2 is the weight of the sample after each heat treatment. It is seen that the weight of the sample does not change which is an indication that oxygen content remains constant.

Figure 6-5

Plot on a semi-log scale of $\frac{x(1+x)}{(1-x)^2}$ versus $\frac{1}{T}$ where

T is the temperature at which the material was heated, x is the concentration of Co^{2+} ions in the A sites calculated from the magnetic moment of the material.



6.5 Details of Mössbauer Spectra

As can be seen from the spectrum in an applied field of 55 KOe. i.e. figures 6-3 and 6-4, the B site lines are extremely broad and asymmetrical especially in the case of $\text{CoFe}_2\text{O}_4(\text{q})$. From the spectrum in the applied field we can also determine that the lower intensity peaks in region 6 of the $\text{CoFe}_2\text{O}_4(\text{s.c.})$ i.e. figure 6-2, belongs to Fe^{57} in B sites. We, however, also determined that the total B site area was larger than that corresponding to Fe^{57} in A sites. This indicates that the high intensity line in region 6 of figure 6-2 contains some absorption due to Fe^{57} in B sites and some due to Fe^{57} in A sites. Also it can be seen from the spectra in the applied field (figures 6-3, 6-4) that the A site lines are relatively narrow. We now attempt to explain the line broadening for Fe^{57} in B sites and the apparent dependence of the broadening on heat treatment.

As a starting point we note that the B site lines in the case of NiFe_2O_4 were quite narrow, i.e. see figure 5-1. This indicates that the line broadening in the case of CoFe_2O_4 could be due to the presence of more than one kind of ion in the A site. We then assume that this is the reason and we assume that only nearest neighbor A site ions effect the internal fields at B site ions. We can now calculate the probability of a B site ion having I nearest neighbor Co^{2+} A site ions and $6-I$ nearest neighbor Fe^{3+} A site ions. This probability is given by

$$P(I) = \frac{6!}{(6-I)!I!} x^I (1-x)^{6-I}$$

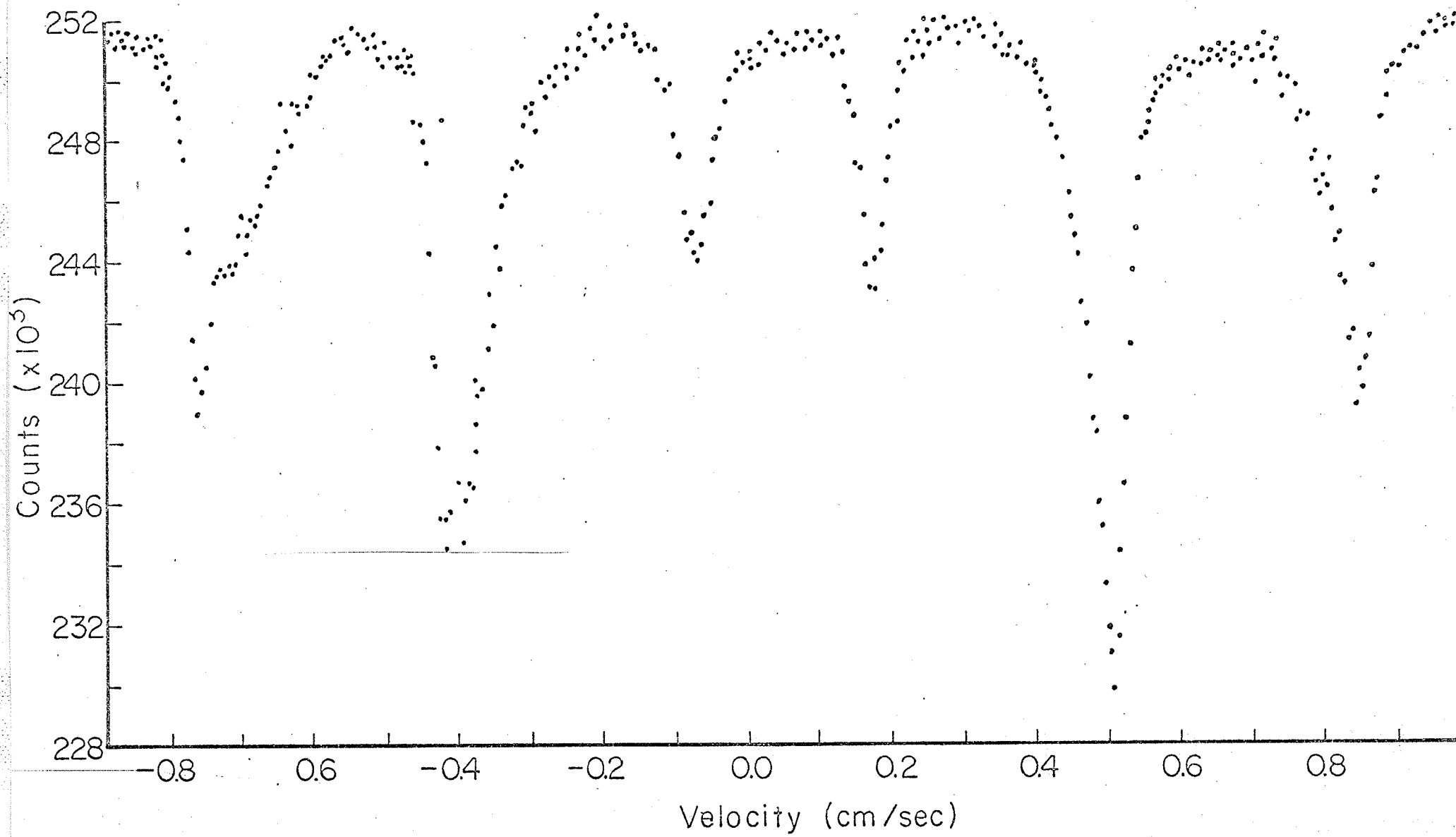
if we assume a random distribution of Co^{2+} and Fe^{3+} ions in the A site, x is the fractional occupation of A sites by Co^{2+} ions. In Appendix A we list $P(I)$ for various values of x .

From the above discussions we would expect the B site line of CoFe_2O_4 to be composed of the sum of several Lorentzians with intensities proportional to the probabilities as given in Appendix A. Since the A site line in the applied field of 55 KOe. was relatively narrow we treat this as one Lorentzian. In order to attempt to show the structure expected in the B site line we collected a spectrum with an applied field of 17 KOe. with an experimental arrangement as discussed in section 2.4.

The spectrum was run with better resolutions than that obtained in the 55 KOe. field. The spectrum obtained for $\text{CoFe}_2\text{O}_4(q)$ is shown in figure 6-6 and for $\text{CoFe}_2\text{O}_4(s.c.)$ in figure 6-7. In figure 6-8 we show the first line of the spectrum of $\text{CoFe}_2\text{O}_4(q)$ in an expanded scale. The Lorentzians drawn are a least squares fit to the data done as follows. The data was fit to the sum of five Lorentzians one corresponding to Fe^{57} in A sites and four for Fe^{57} in B sites. The four Lorentzians corresponding to Fe^{57} in B sites were constrained to have equal full widths at $\frac{1}{2}$ height (Γ) and their intensities were constrained to agree with the probabilities given in Appendix A. Only four lines were used because as can be seen from Appendix A the others have negligibly small probabilities. The fit was done using three different values of x , i.e. 0.20, 0.22, 0.24. From these fits we can obtain the area ratio $\frac{I_A}{\sum I_B}$ which should be consistent with the value of x used. For the ratio of recoilless fractions at room temperature

Figure 6-6

Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{q})$ in an applied field of 17 KOe. The field direction is perpendicular to the direction of propagation of the γ rays.



Mössbauer spectrum of CoFe_2O_4 (s.c.) in an applied field of 17 Koe. The field direction is perpendicular to the direction of propagation of the γ rays.

Figure 6-7

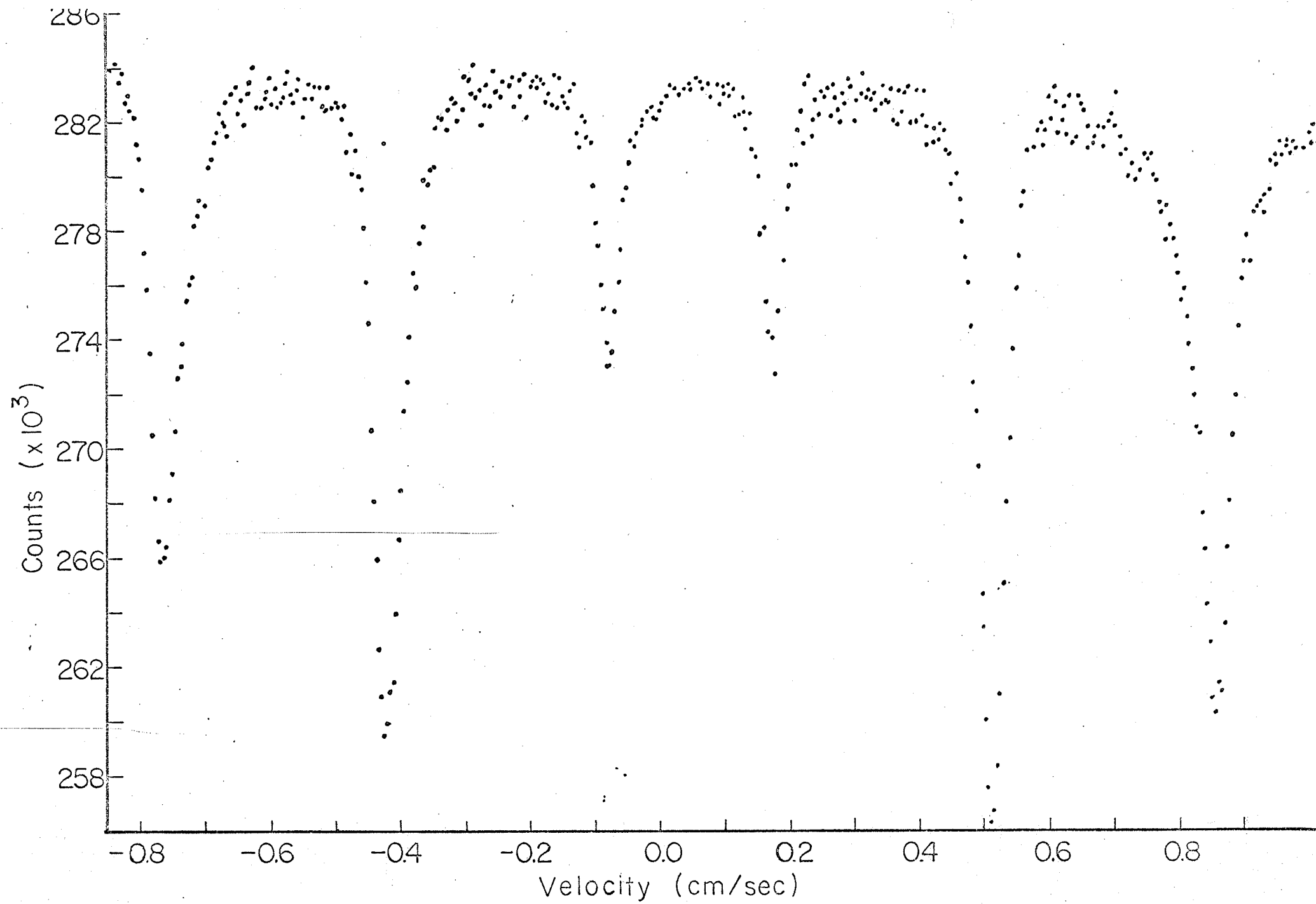
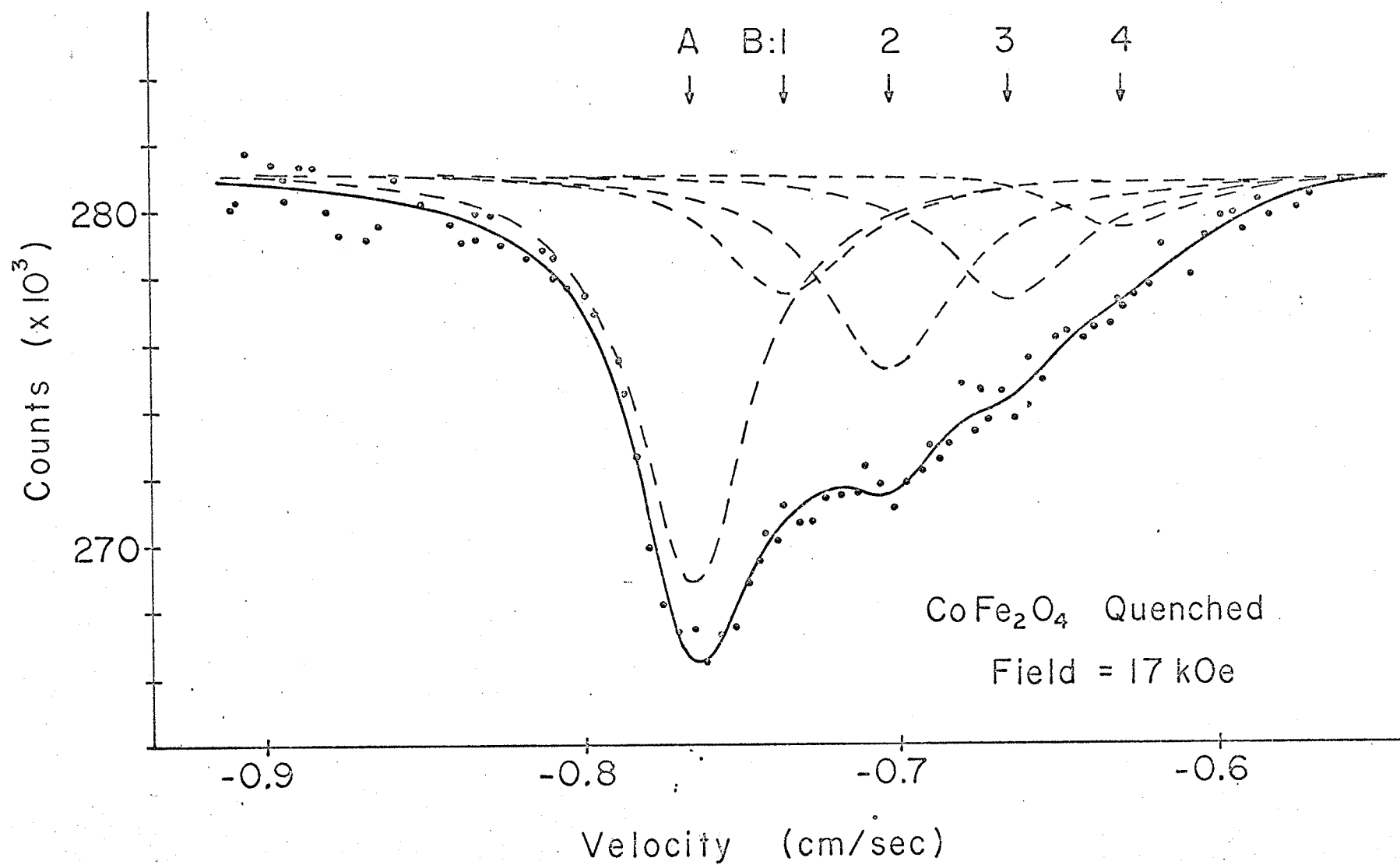


Figure 6-8

Line 1 of the Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{q})$ in an applied field of 17 KOe. A and B refer to Fe^{57} in A and B sites. B:1, 2, 3, 4 refer to Fe^{57} in B sites with 0, 1, 2, 3 nearest neighbor Co A site ions respectively.



we take 0.94 as determined for Fe_3O_4 and YIG. x will then be given by

$$\frac{(1 - x)}{(1 + x)} = \frac{I_A}{\Sigma I_B} \quad (0.94)$$

From the fits to the data it was found that the fits were acceptable for a large range of values of $\frac{I_A}{\Sigma I_B}$. This value could range from 0.5 to 0.6 without an appreciable change in the goodness of fit. This was true for all values of x from 0.20 to 0.24. The main reason for this was a fairly large range of acceptable values of the full width at half height especially for the octahedral lines. The full width at half height was found to be 0.46 mm/sec. for the components of the octahedral line. The fact that the B site lines are wider than that of the A site could be due to next nearest neighbor effects which have not been taken into account. Line 6 was analyzed in the same way as line 1 and showed the same behaviour.

The CoFe_2O_4 (s.c.) spectrum shown in figure 6-7 was analyzed in the same way as CoFe_2O_4 (q) except that x was taken to be 0.06.

From the above discussion it is concluded that the model suggested can explain in good detail the spectra obtained for both CoFe_2O_4 (q) and CoFe_2O_4 (s.c.). The hyperfine fields and isomer shifts corresponding to the various lines are given in table 6-3. From these we conclude that the substitution of Fe^{3+} ions in the A site by a Co^{2+} ions effects mainly the hyperfine field. It is seen from table 6-3 that the more A site Co^{2+} nearest neighbors an Fe^{3+} B site ion has the lower is the hyperfine field acting at the Fe^{3+} nucleus.

Table 6-3

Hyperfine fields and isomer shifts of the A and B site lines at room temperature. $I = 0, 1, 2, 3$ refer to the number of nearest neighbor Co A site ions.

	<u>A</u>	<u>I=0</u>	<u>I=1</u>	<u>I=2</u>	<u>I=3</u>
H_{hpf} (KOe.)	490	515	499	475	445
IS* (mm/sec)	0.53	0.56	0.64	0.64	0.67

* relative to Fe^{57} in a Cr matrix

Error in H_{hpf} = ± 5 KOe.

Error in IS. = ± 0.04 mm/sec

We now give a possible explanation for the dependence of the hyperfine field acting on the B site Fe^{3+} ion on the kind of A site nearest neighbor.

Actually there are two possibilities. If we write $H_{\text{hpf}} = A\langle S_z \rangle$ where A the hyperfine coupling constant includes supertransferred effects, dipolar effects, contact term, and the orbital term and $\langle S_z \rangle$ simply describes the z component of the spin, then H_{hpf} can be dependent on the kind of nearest neighbors ions an iron ion has in that A and/or $\langle S_z \rangle$ can have such a dependence. The dependence of A on the kind of nearest neighbors could come from supertransferred hyperfine fields or from dipolar fields. The dependence of $\langle S_z \rangle$ on the kind of nearest neighbors could be due to a temperature dependence which depends on the superexchange interaction which in turn is nearest neighbor dependent.

The presence of the latter case is quite easy to show in that all one need show is that the different hyperfine fields acting on the B site Fe^{3+} ions have different temperature dependences.

In figures 6-9 to 6-15 are shown spectra obtained at various temperatures from 300° K to 550° K. Also shown are the positions of the various octahedral lines. It is obvious that the spread in the hyperfine fields increases as the temperature increases indicating that the $\langle S_z \rangle$ has a temperature dependence which depends on the kind of A site nearest neighbors. For $\text{CoFe}_2\text{O}_4(\text{q})$ the least squares fits to the spectra were not very decisive. This was due to the large amount of overlap of the tetrahedral line with the octahedral lines. The test for the goodness of

Figure 6-9

Mössbauer spectrum of CoFe_2O_4 (s.c.) at 105° K .

The vertical lines drawn indicate the peak positions and intensities of the various lines. A refers to Fe^{57} in A sites and B1 and B2 refer to Fe^{57} in B sites with 0 and 1 nearest neighbor Co A site ions respectively.

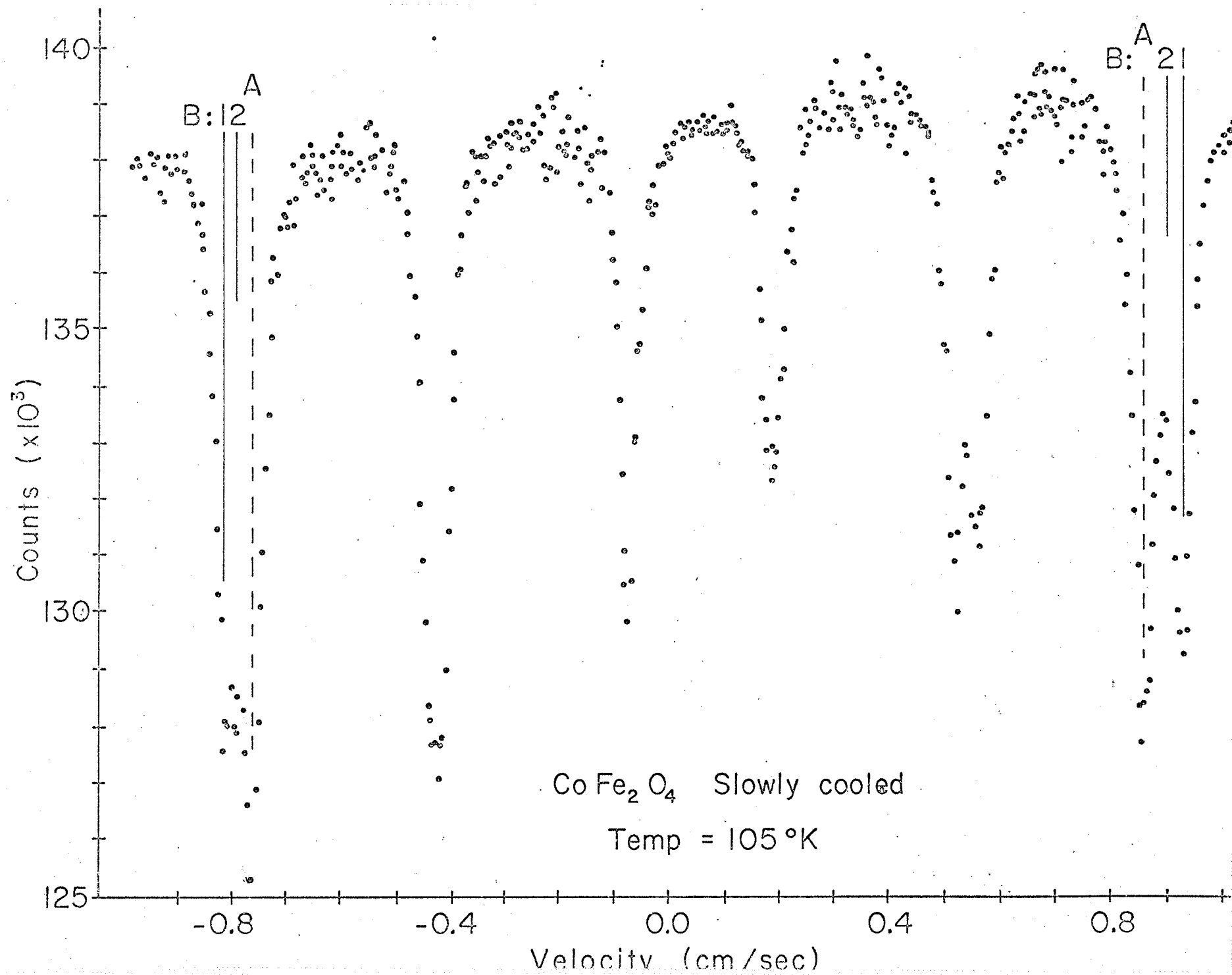


Figure 6-10

Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{s.c.})$ at 296°K .

The vertical lines drawn indicate the peak positions and intensities of the various lines. A refers to Fe^{57} in A sites and B1 and B2 refer to Fe^{57} in B sites with 0 and 1 nearest neighbor Co A site ions respectively.

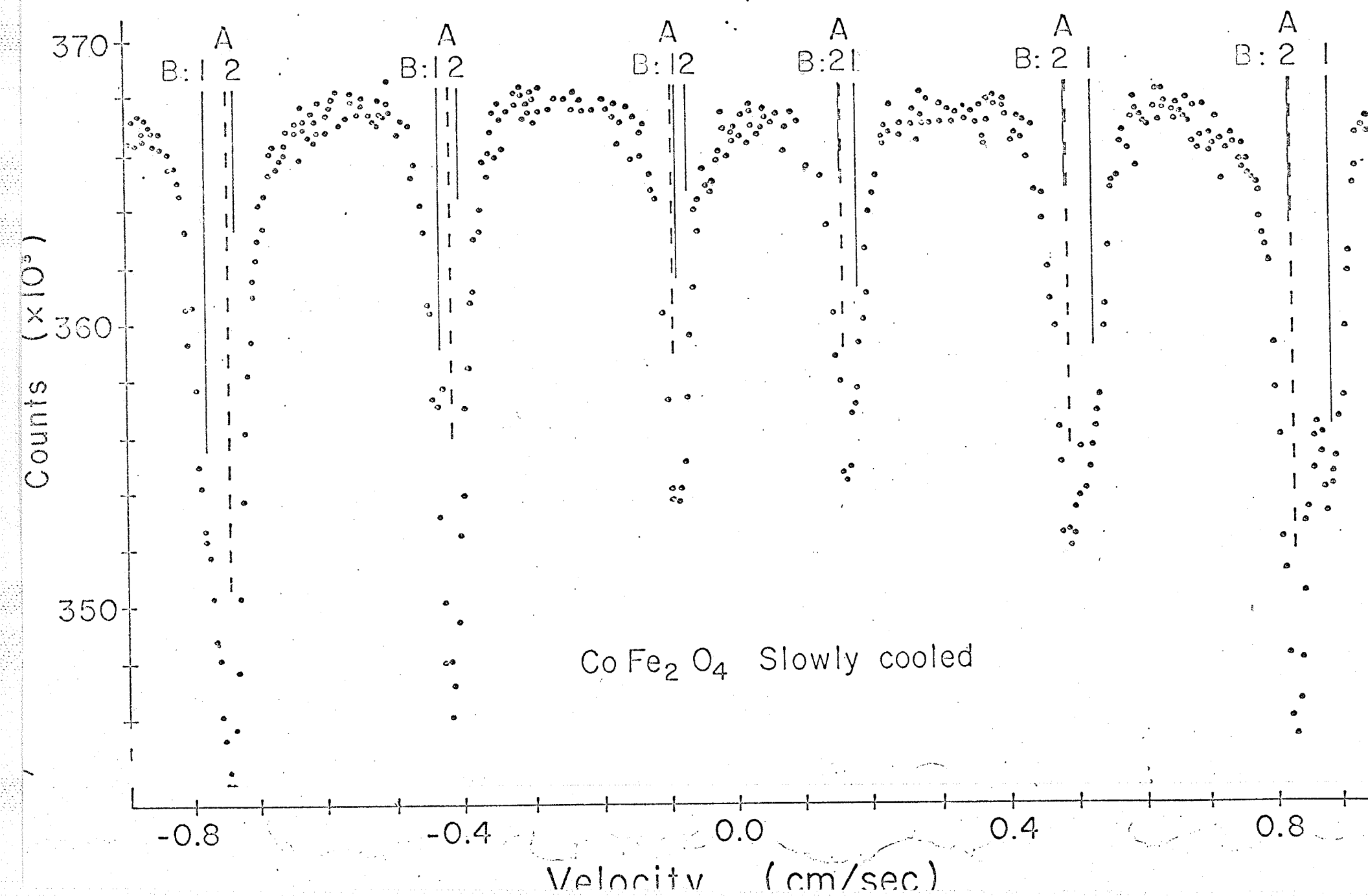


Figure 6-11

Mössbauer spectrum of CoFe_2O_4 (s.c.) at 567°K .

The vertical lines drawn indicate the peak positions and intensities of the various lines. A refers to Fe^{57} in A sites and B1 and B2 refer to Fe^{57} in B sites with 0 and 1 nearest neighbor Co A site ions respectively.

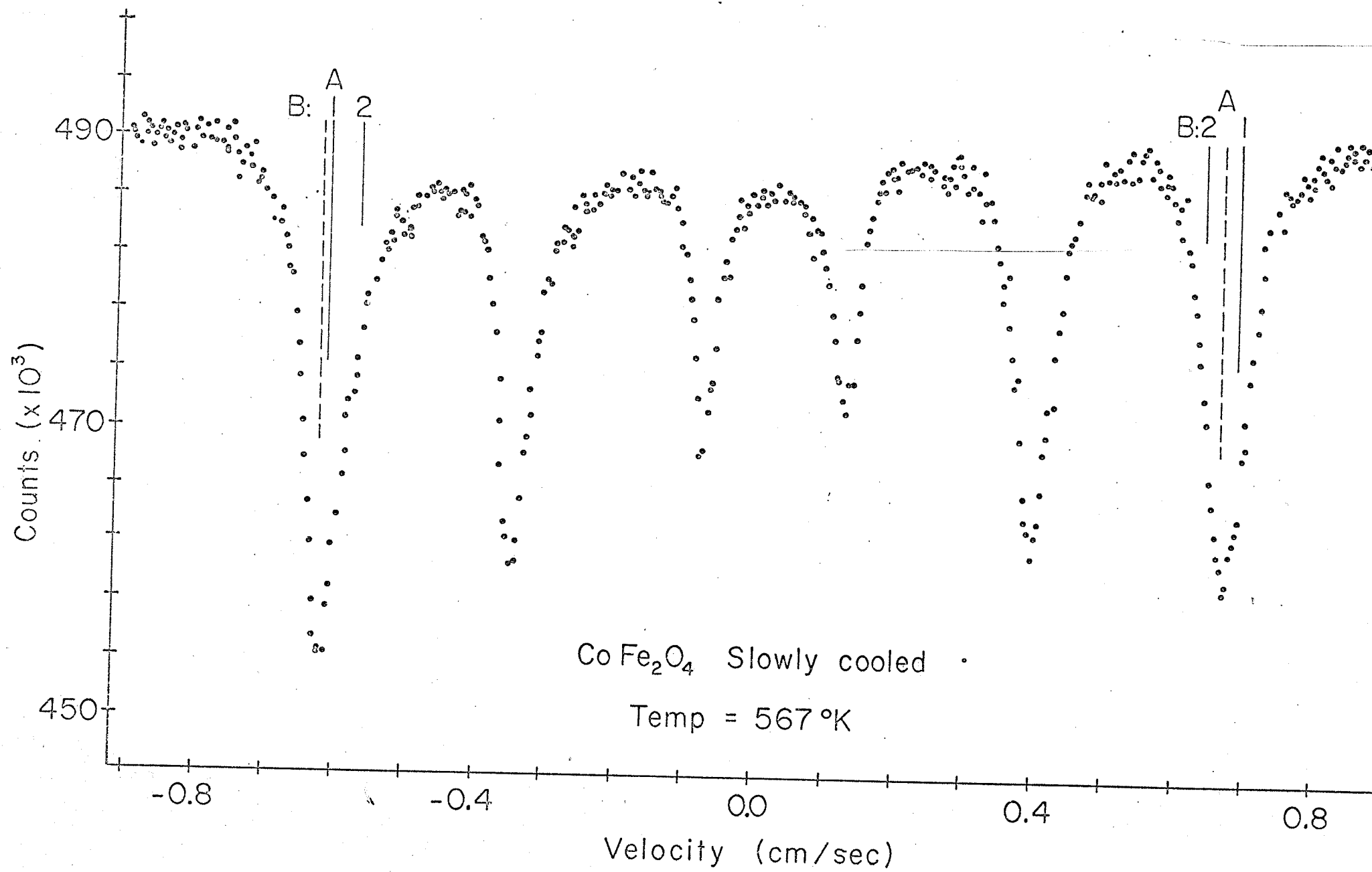


Figure 6-12

Mössbauer spectrum of CoFe_2O_4 (q) at 105° K .

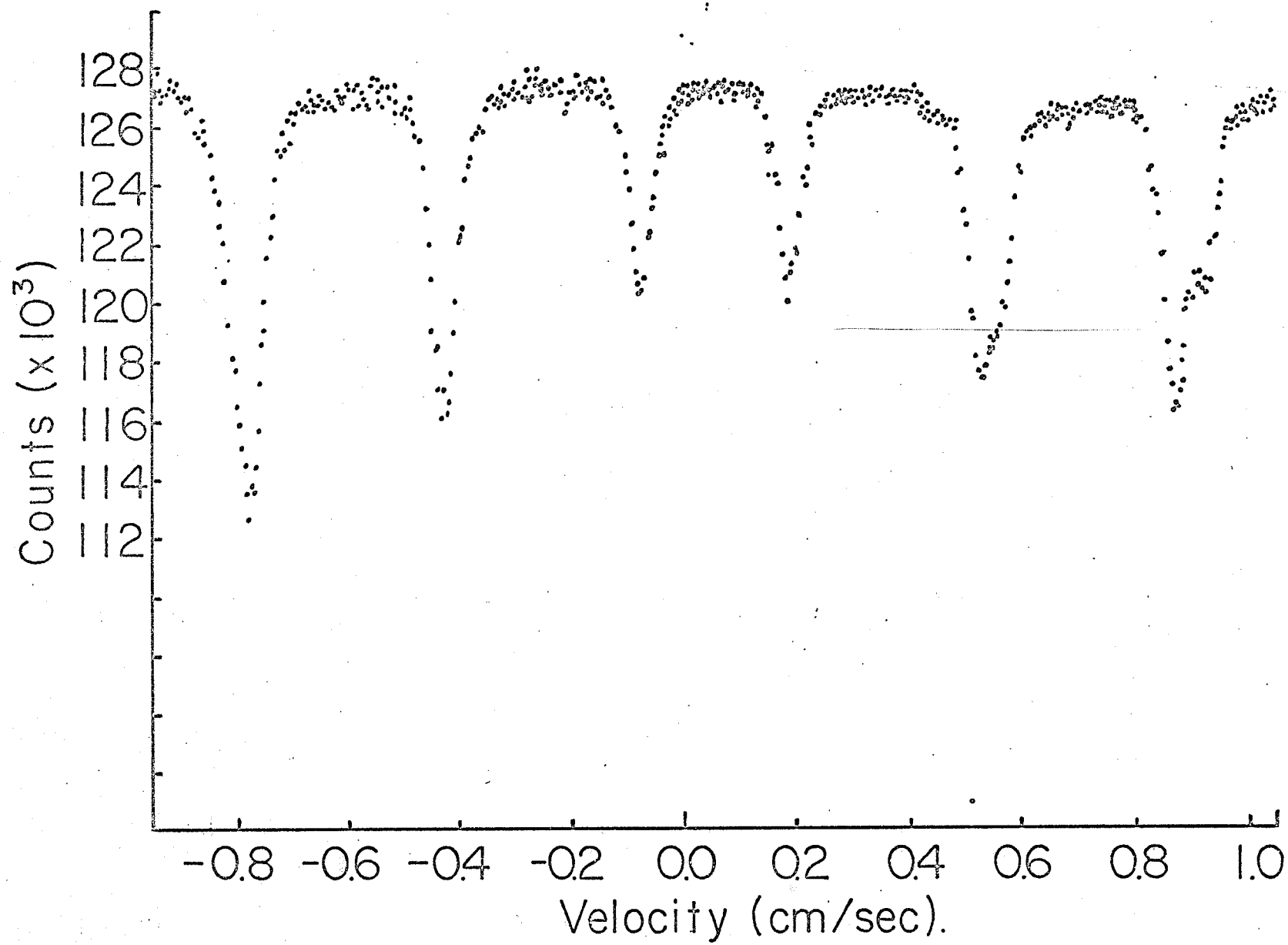


Figure 6-13

Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{q})$ at 296°K . The vertical lines drawn indicate the peak positions and intensities of the various lines. A refers to Fe^{57} in A sites and B:1, 2, 3, 4 refer to Fe^{57} in B sites with 0, 1, 2, 3 nearest neighbors Co A site ions respectively.

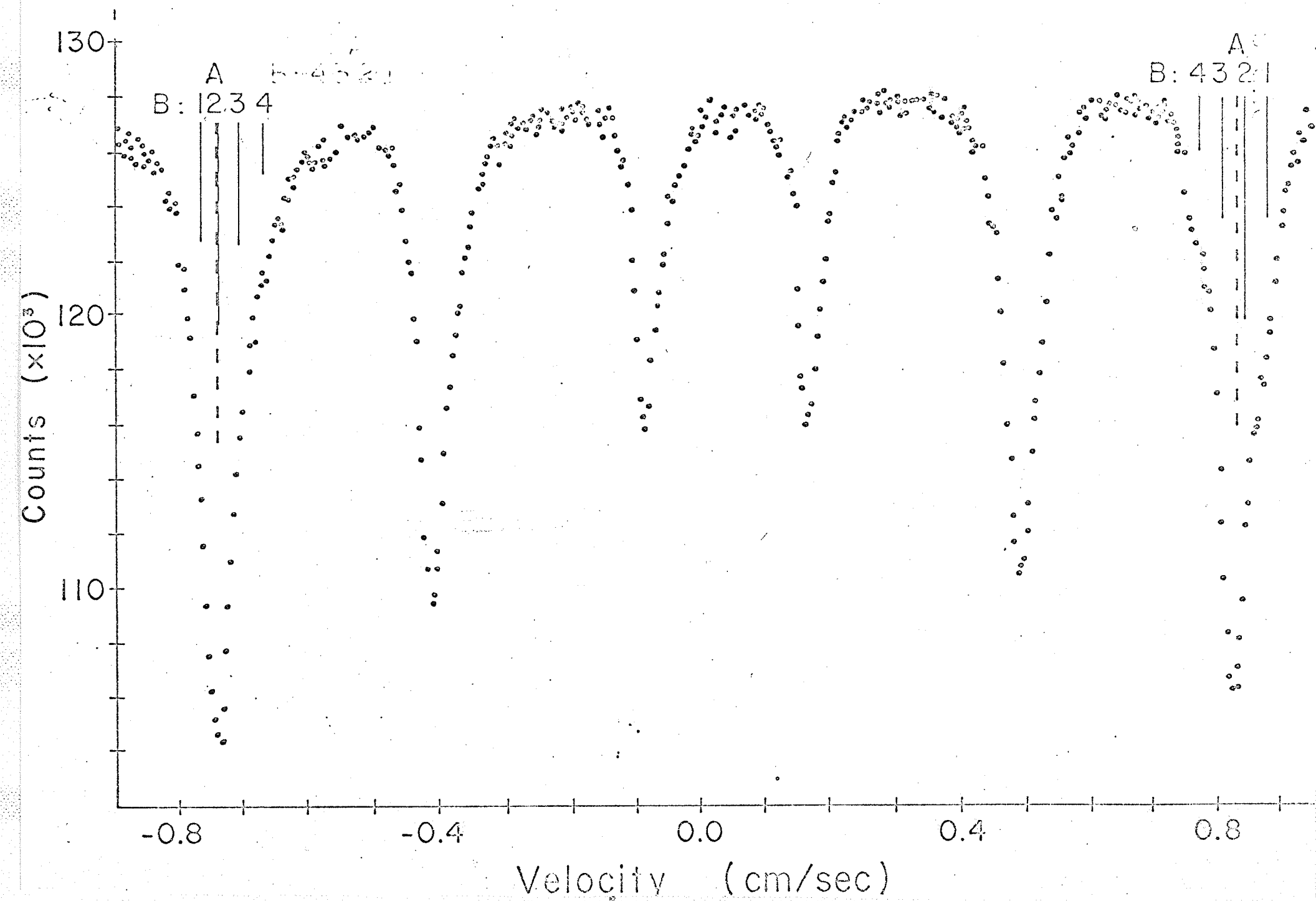


Figure 6-14

Mössbauer spectrum of $\text{CoFe}_2\text{O}_4(\text{q})$ at 416°K . The vertical lines drawn indicate the peak positions and intensities of the various lines. A refers to Fe^{57} in A sites and B:1, 2, 3, 4 refer to Fe^{57} in B sites with 0, 1, 2, 3 nearest neighbors Co A site ions respectively.

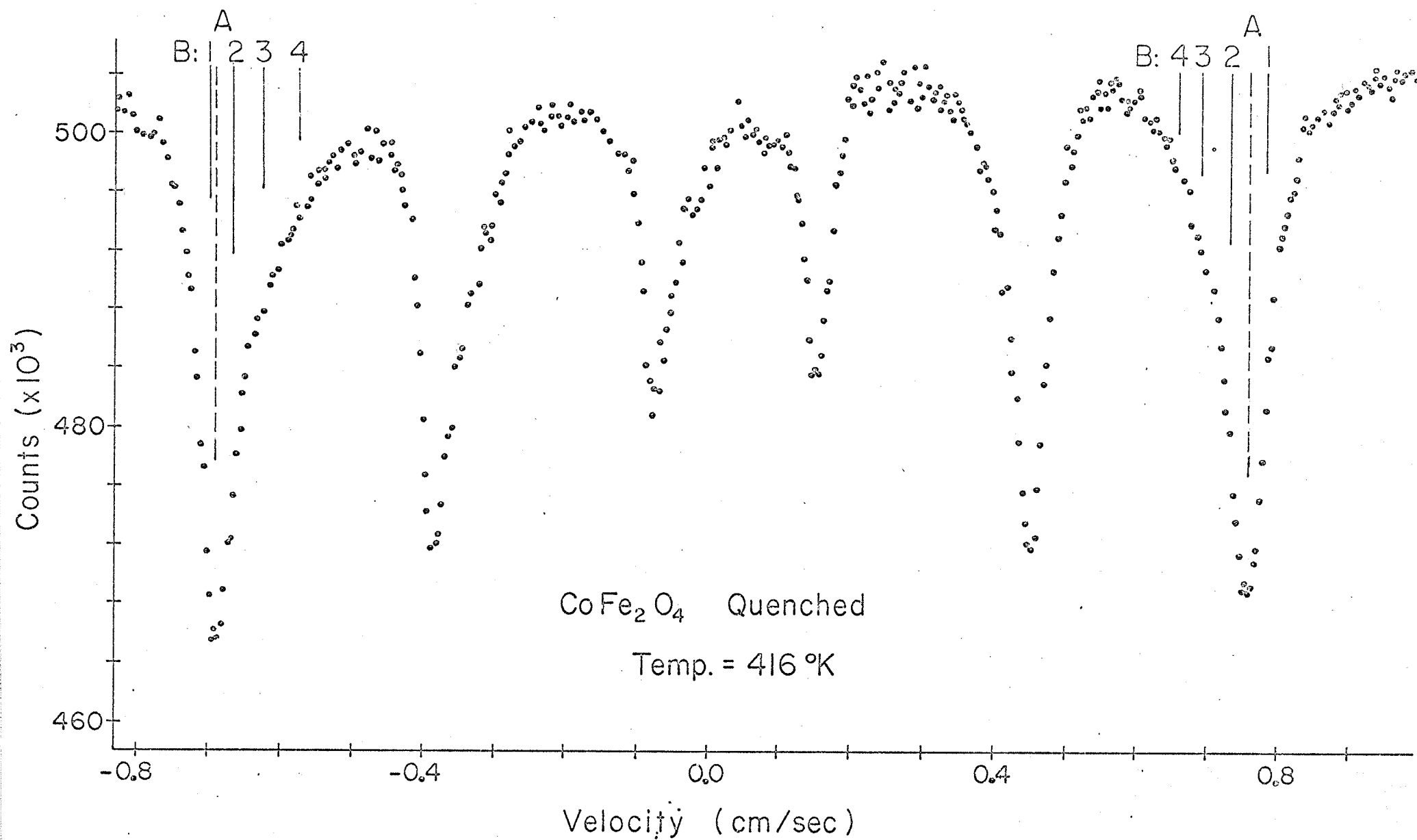
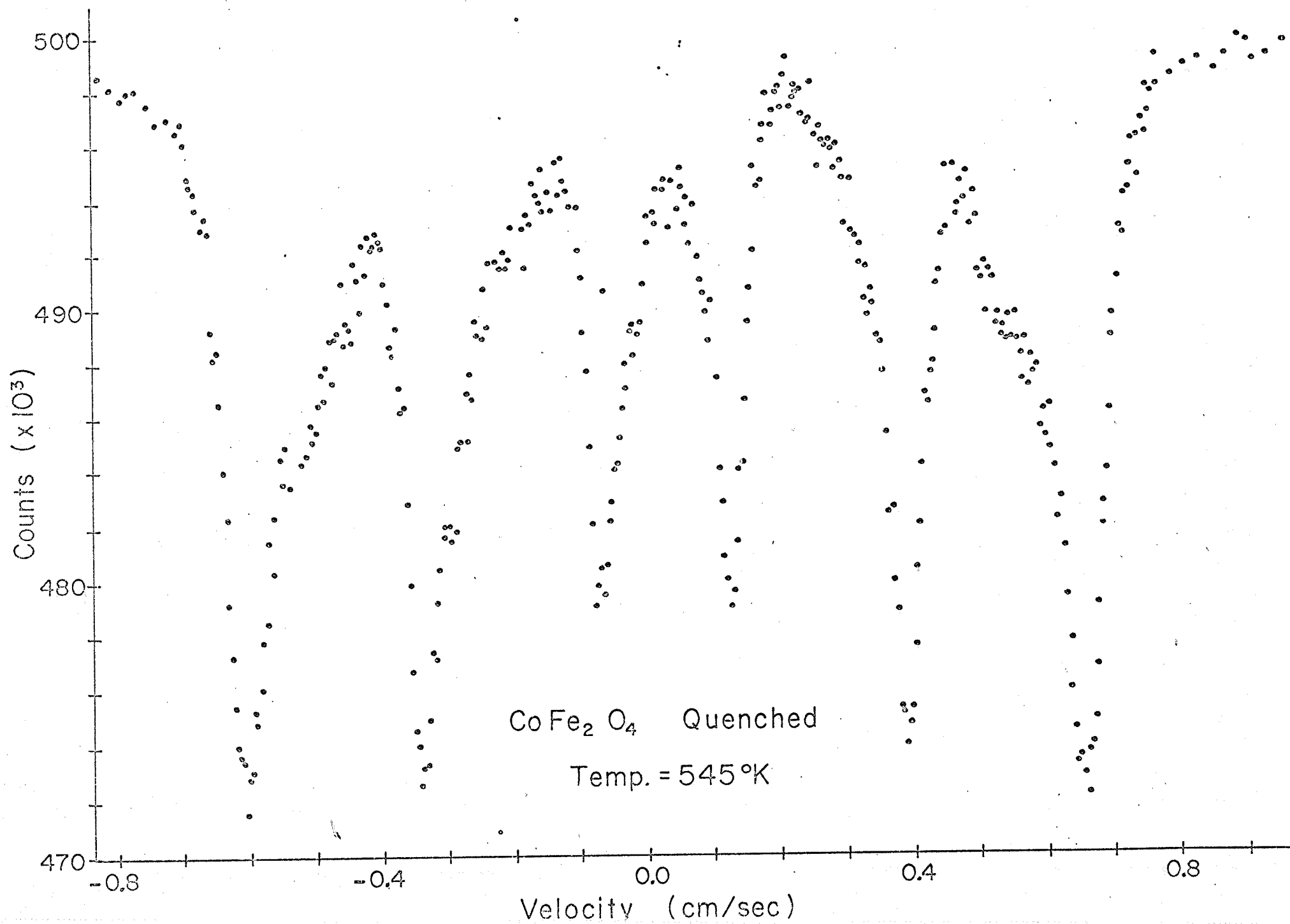


Figure 6-15

Mössbauer spectrum of CoFe_2O_4 (q) at 545° K .



fit had quite acceptable values for a numerous number of different parameters even if the previously mentioned constraints on the full width at half height and intensity were imposed. We chose the fit which gave the most acceptable value of the area ratio $\frac{I_A}{\Sigma I_B}$ as determined by $x = 0.2 \leftrightarrow 0.24$ for $\text{CoFe}_2\text{O}_4(\text{q})$ and $x = 0.04 \leftrightarrow 0.08$ for $\text{CoFe}_2\text{O}_4(\text{s.c.})$. We also neglected fits which had obviously too small values for the full widths at half height. The hyperfine fields and especially the isomer shifts would then have considerable errors. We estimate the error in the hyperfine fields to be about 1% and in the isomer shifts to be about ± 0.03 mm/sec.

In figures 6-16 and 6-17 are shown a plot of the various hyperfine fields versus $\frac{T}{T_{\text{FN}}}$ where T_{FN} is the ferrimagnetic Néel temperature.

Measurement of T_{FN} presents a problem because as was pointed out previously cation diffusion takes place at 500°C while T_{FN} is around 800°K . We measured T_{FN} by the thermal scanning technique described in 4.1 and obtained values of 792 and 798°K for $\text{CoFe}_2\text{O}_4(\text{q})$ and $\text{CoFe}_2\text{O}_4(\text{s.c.})$. Since as shown in section 8 we expect the Co(A) - Fe(B) superexchange interaction to be about 0.68 of the Fe-Fe superexchange interaction we conclude that T_{FN} for $\text{CoFe}_2\text{O}_4(\text{q})$ should be about 50°K lower than that for $\text{CoFe}_2\text{O}_4(\text{s.c.})$. A Mössbauer spectrum taken at room temperature of $\text{CoFe}_2\text{O}_4(\text{q})$ after it had been heated at 520°C for 2 hours (about the time taken to measure T_{FN}) showed that this material was about half-way between the s.c. and q materials. Although an error of 25°K in T_{FN} will not make much difference as far as the plots in figures 6-16 and

Figure 6-16

Plot of the hyperfine fields versus T/T_{FN} for $\text{CoFe}_2\text{O}_4(\text{s.c.})$. A refers to Fe^{57} in A sites. B1 and B2 refer to Fe^{57} in B sites with 0 and 1 nearest neighbor Co A site ions respectively.

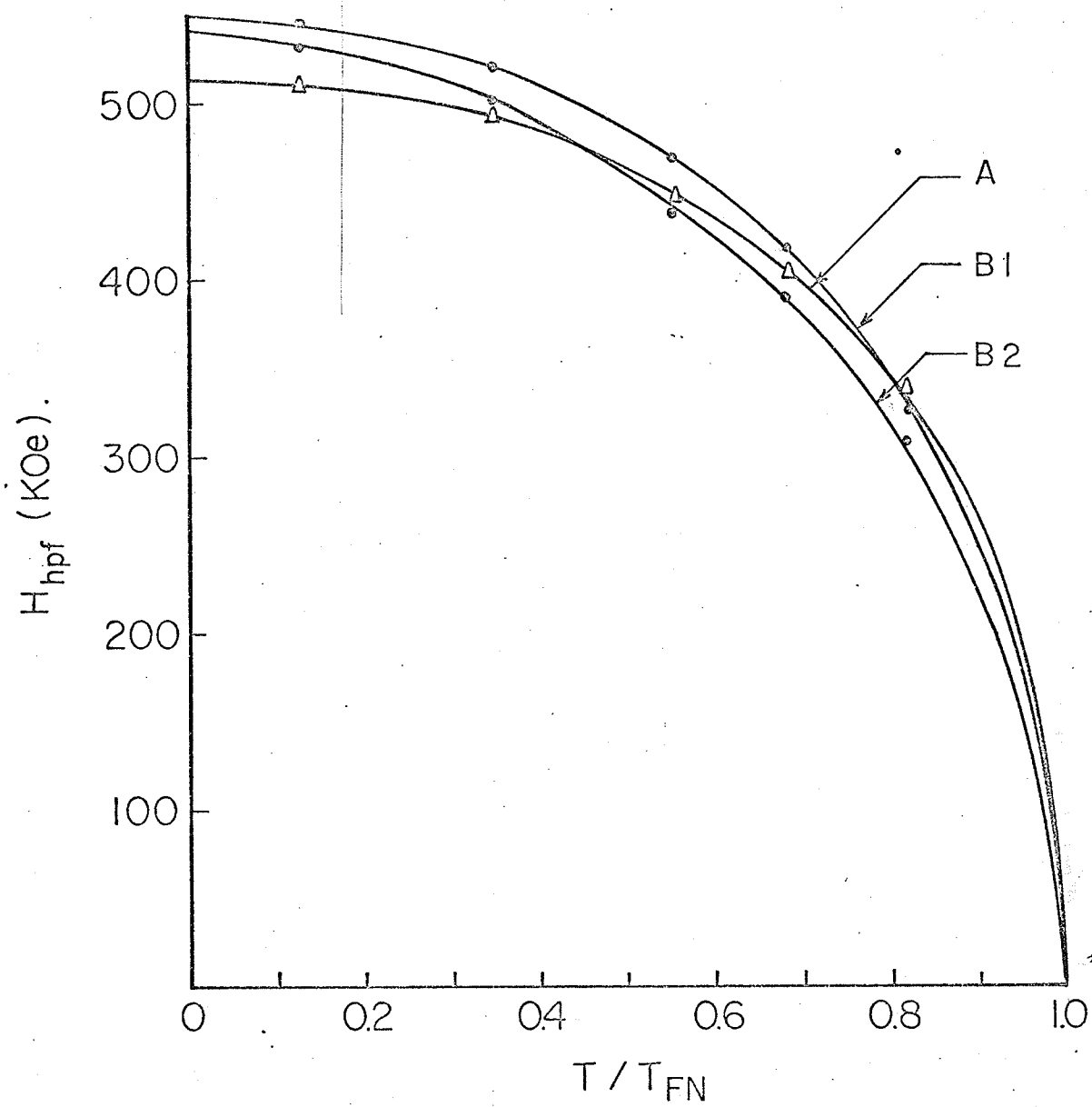
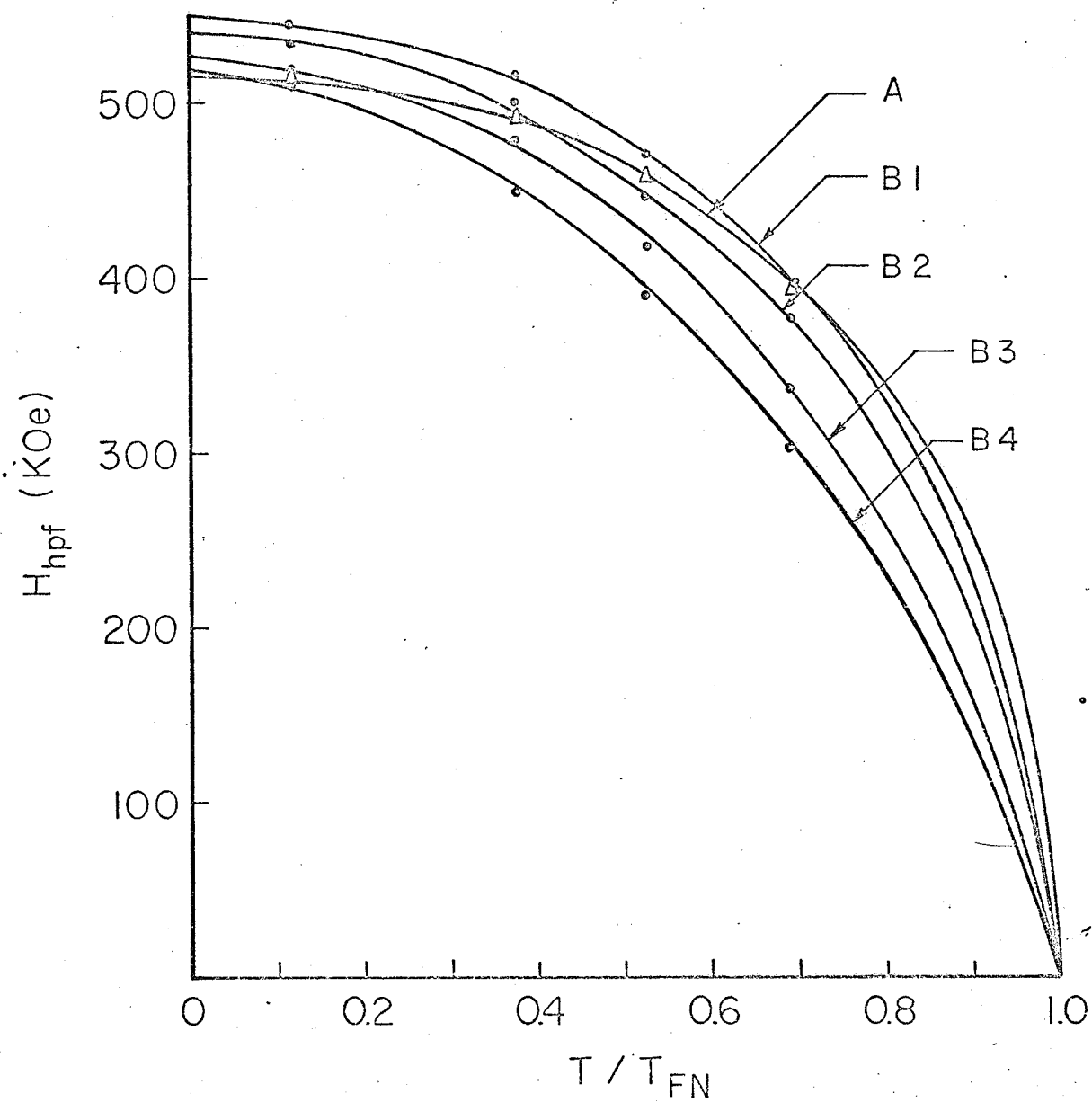


Figure 6-17

Plot of the hyperfine fields versus T/T_{FN} for $\text{CoFe}_2\text{O}_4(q)$. A refers to Fe^{57} in A sites. B:1, 2, 3, 4 refer to Fe^{57} in B sites with 0, 1, 2, 3 nearest neighbor Co A site ions respectively.



6-17 are concerned it is of interest to measure T_{FN} for the two materials to see if the difference agrees with the molecular field theory prediction.

Since the temperature dependence of the A site hyperfine field is not expected to be much different for the two materials we can use this as a method for finding the ratios of the two transition temperatures. This was done by plotting $H_{hpf}(A)$ versus $\frac{T}{T_{FN}}$ for $CoFe_2O_4(q)$ in the same plot as for $CoFe_2O_4(s.c.)$ $\frac{T_{FN}(s.c.)}{T_{FN}(q)}$ was then adjusted until the two curves coincided. This plot is shown in figure 6-18. From this we determine that

$$\frac{T_{FN}(s.c.)}{T_{FN}(q)} \text{ was } 1.07$$

which gives

$$T_{FN}(s.c.) \approx 820^\circ \text{ K taking } T_{FN}(q) = 770^\circ \text{ K.}$$

These values are in agreement with the predicted difference of 50° K .

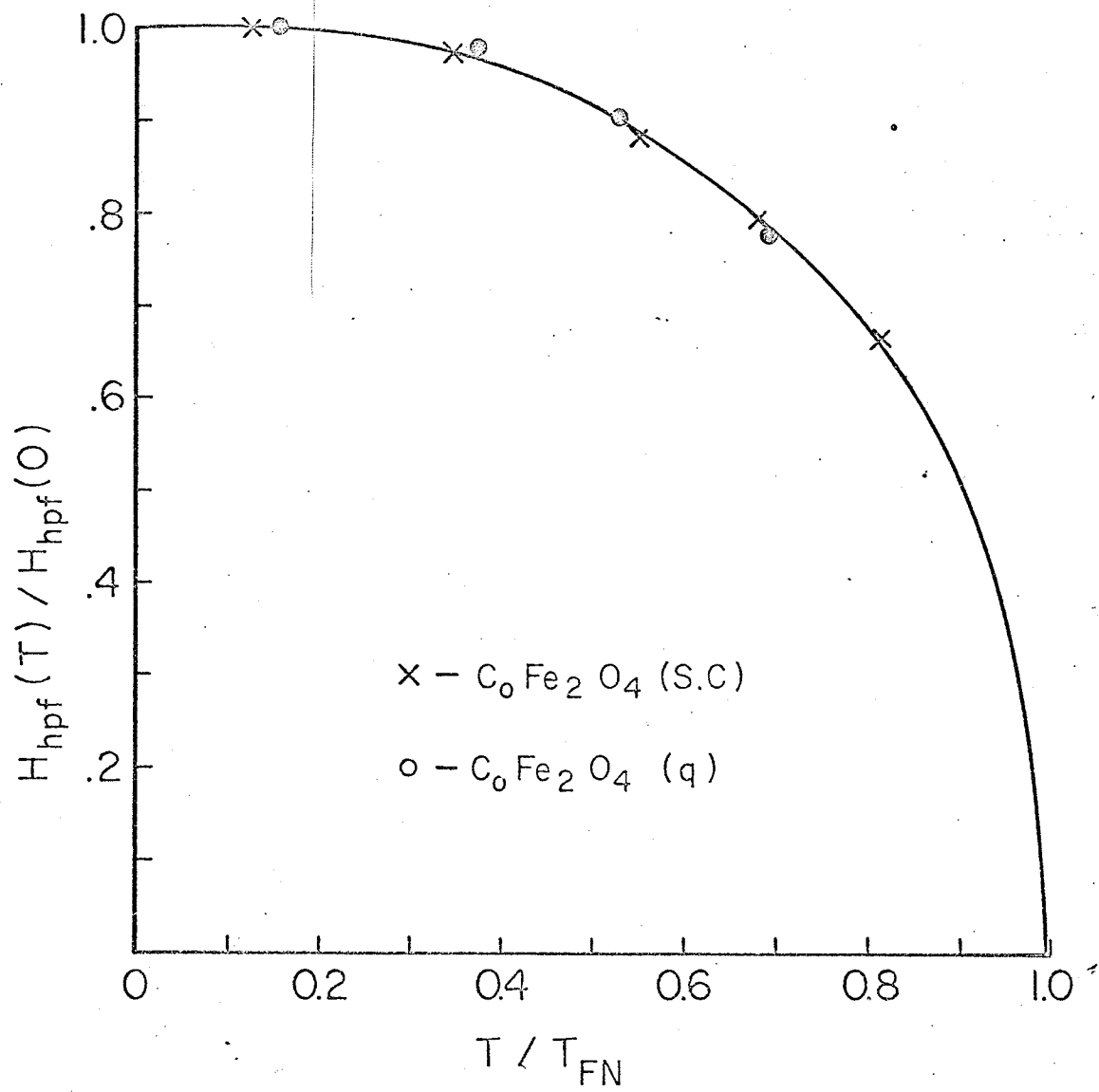
Although a more detailed discussion of the hyperfine fields will be reserved for later it should be pointed out that :

- (1) The hyperfine field at an Fe^{3+} B site ion seems to decrease at 0° K with an increase in the number of Co^{2+} A site nearest neighbors.
- (2) The temperature dependence of the hyperfine field at an Fe^{3+} B site ion increases as the number of Co^{2+} A site nearest neighbors decreases.

Figure 6-18

Plot of the A site hyperfine field for $\text{CoFe}_2\text{O}_4(\text{s.c.})$
and $\text{CoFe}_2\text{O}_4(\text{q})$ versus T/T_{FN} where

$$\frac{T_{\text{FN}}(\text{s.c.})}{T_{\text{FN}}(\text{q})} = 1.07$$



- (3) The hyperfine fields and isomer shifts for A site Fe^{3+} ions are considerably less than those for the B site ions.

CHAPTER 7MnFe₂O₄7.1 Introduction

It has been shown from neutron diffraction measurements (99) that MnFe₂O₄ has the cation distribution given by $(\text{Mn}_{0.8}\text{Fe}_{0.2}) \text{Mn}_{0.2}\text{Fe}_{1.8}\text{O}_4$. This makes this material suitable for a Mössbauer study of the kind just described for CoFe₂O₄ since the A sites are occupied by two different kinds of ions. There are several unexplained properties of MnFe₂O₄, some of which we hope to explain at least in part. The magnetic moment for the case where all the Mn ions are divalent is expected to be $5\mu_B$ at 0° K. The measured magnetic moments, however, are $4.5 \leftrightarrow 4.8\mu_B$ (99:-101). These low values could be due to several things : that is some of the Mn ions could be trivalent and some of the Fe ions could be divalent. This has been proposed by several authors (135, 136) although calculations by Lotgering (105) have shown that this is unlikely. Since with the Mössbauer effect technique one can usually distinguish between Fe²⁺ and Fe³⁺ spectra the Mössbauer effect could provide a means for determining whether or not there is any Fe²⁺ present. Another possible explanation for the low-magnetic moment could be that the spin arrangement is not collinear. As discussed in the section on NiFe₂O₄, this property of some ferrites can also be determined by the Mössbauer effect. In this section I will first of all discuss these unexplained properties and then go on to discuss the details of the Mössbauer spectra.

The samples of MnFe_2O_4 were prepared by prefiring a mixture of MnO and Fe_2O_3 in the required proportions at 900°C . This material was then reground and fired at 1400°C in air and water quenched. The material must be cooled quickly because if it is heated at low temperatures in air it decomposes to form MnO and Fe_2O_3 . As to whether or not the oxides have reacted completely was checked by x-ray diffraction. Another way to see if the oxides have reacted completely is from the Mössbauer spectrum. In figure 7-1 we show the first line of a Mössbauer spectrum of MnFe_2O_4 after it was heated at 500°C . This line is identical in position and width to the corresponding line in a spectrum of $\alpha\text{-Fe}_2\text{O}_3$. This shows that the material has decomposed into the separate oxides.

7.3

Cation Distribution

Although the cation distribution of MnFe_2O_4 has been found by neutron diffraction techniques, it has been suggested (103) using the Mössbauer effect that the cation distribution is given by $(\text{Mn}_{0.54}\text{Fe}_{0.46})[\text{Mn}_{0.46}\text{Fe}_{1.54}]\text{O}_4$. The spectrum however was fit to the sum of two Lorentzians one for Fe in A sites and the other for Fe in B sites. From the area ratio of these two lines the cation distribution was calculated. In figure 7-2 is shown a Mössbauer spectrum obtained at room temperature. This spectrum is qualitatively the same as that obtained by Wieser et al (103). The shoulders on the left hand side of line 1 and the right hand side of line 6 are mainly due to the A site lines. In figure 7-3 (I and II) is shown line 1 with and without an applied field of 17 KOe. The spectrum in the applied field shows that the B site line is very broad and contains some structure. It is easy to see that a fit done to the spectrum without an applied field to the sum of only two Lorentzians can lead to a large error in

Figure 7-1

Line 1 of the Mössbauer spectrum of MnFe_2O_4 after heating the material in air at 500°C .

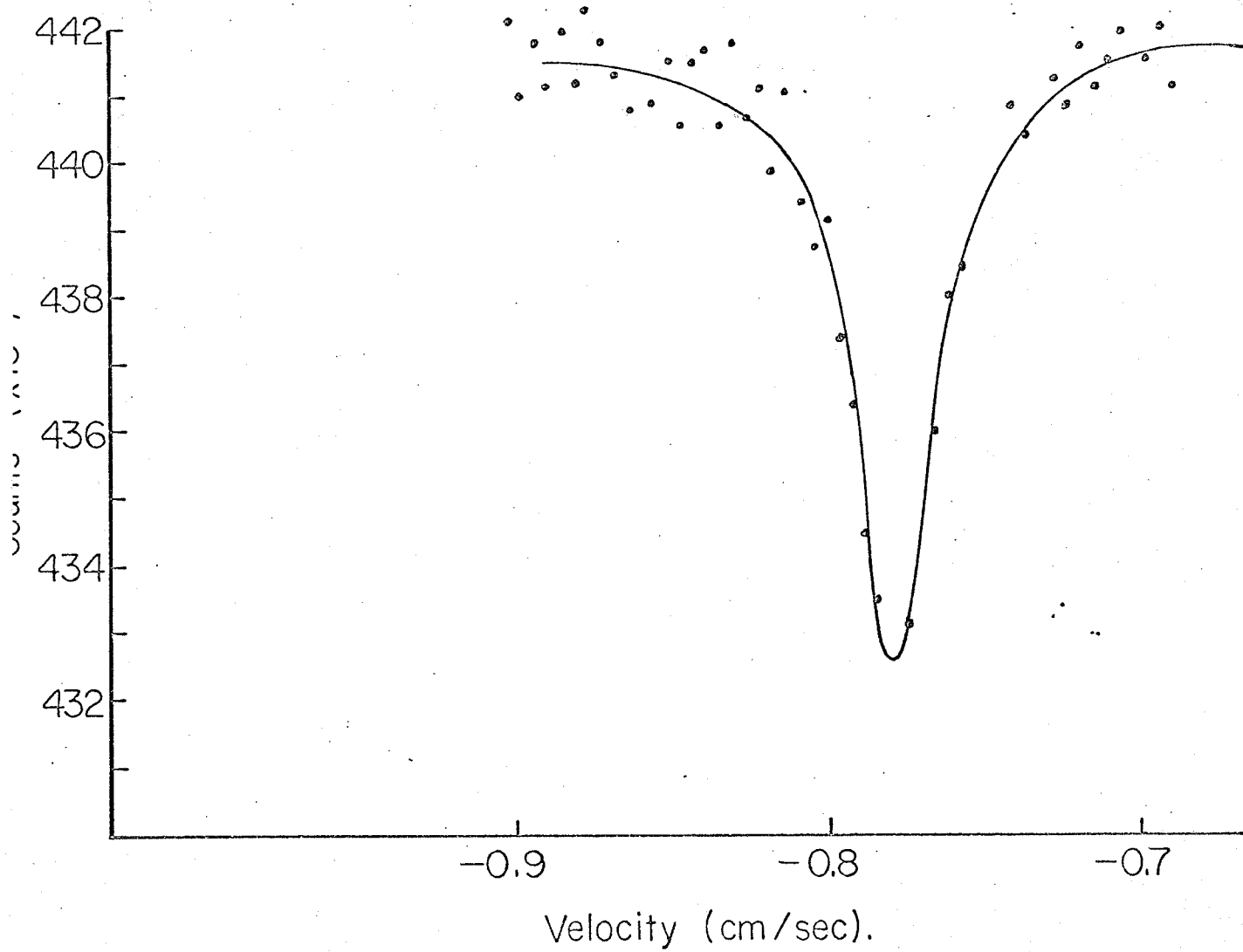


Figure 7-2

Mössbauer spectrum of MnFe_2O_4 at room temperature.

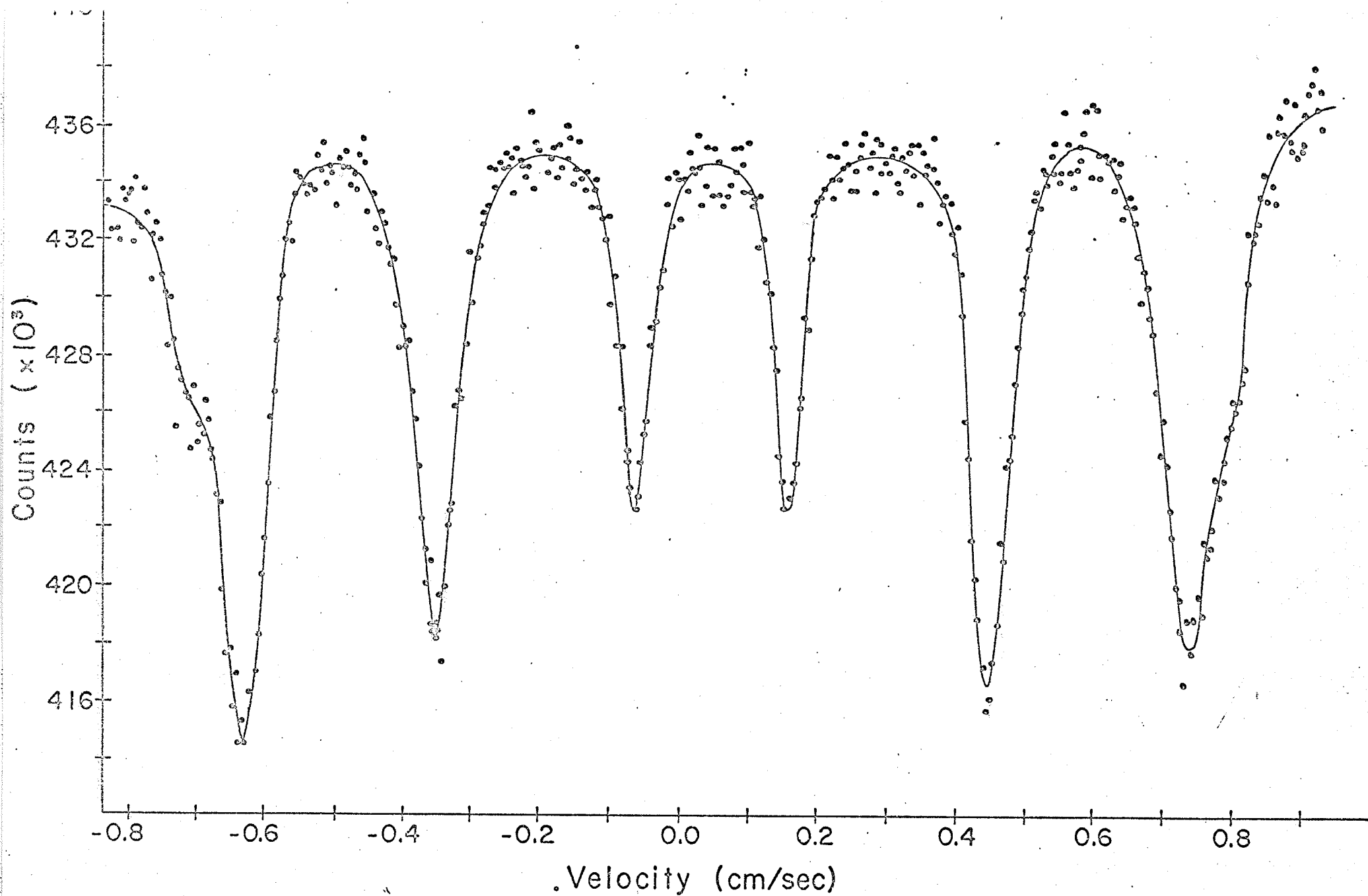
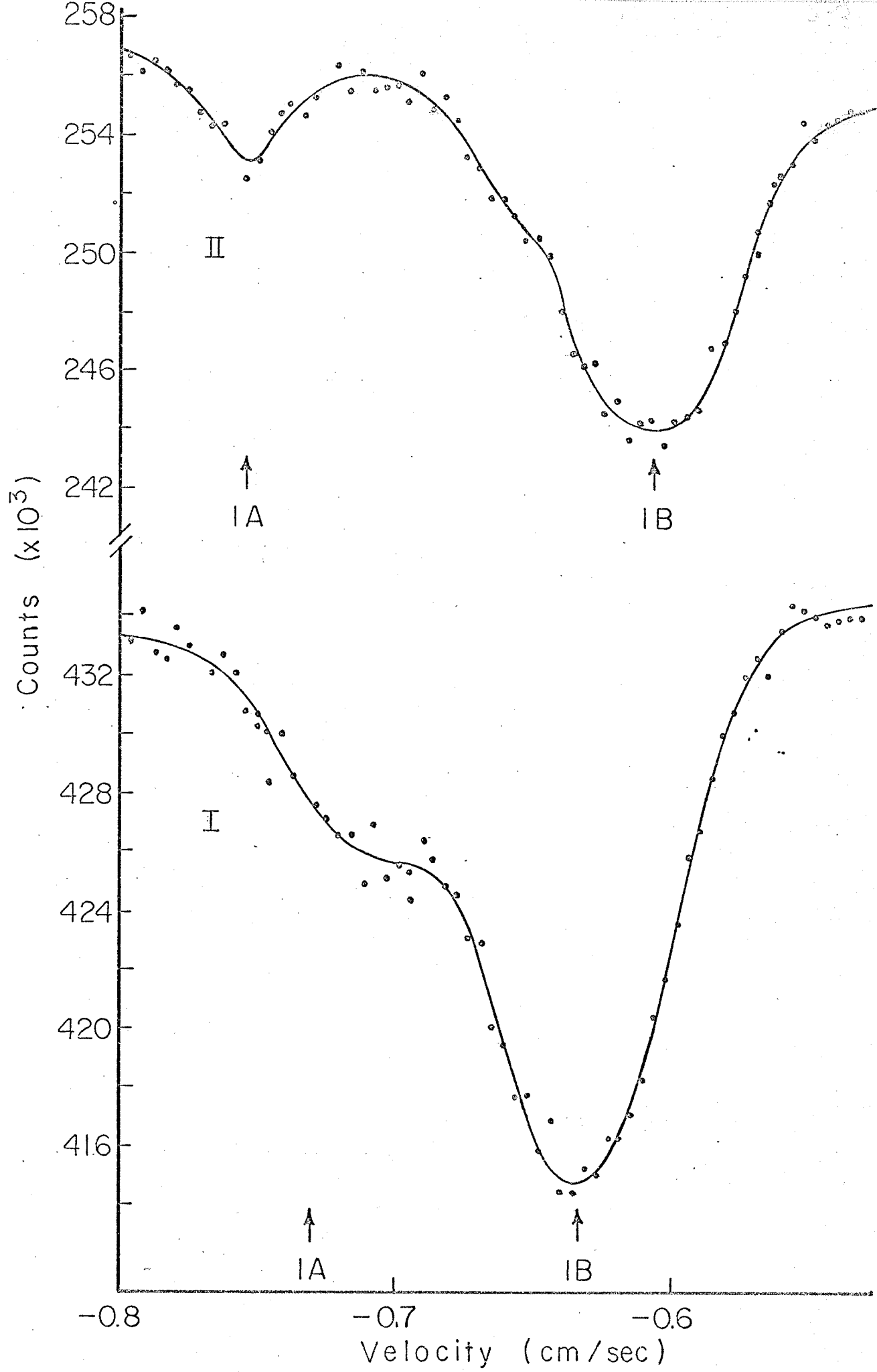


Fig. 2.
Velocity (cm/sec) vs. Counts ($\times 10^3$)

Figure 7-3

Line 1 of the Mössbauer spectrum of MnFe_2O_4 . I without an applied field. II with an applied field of 17 KOe. A and B refer to Fe^{57} in A and B sites.



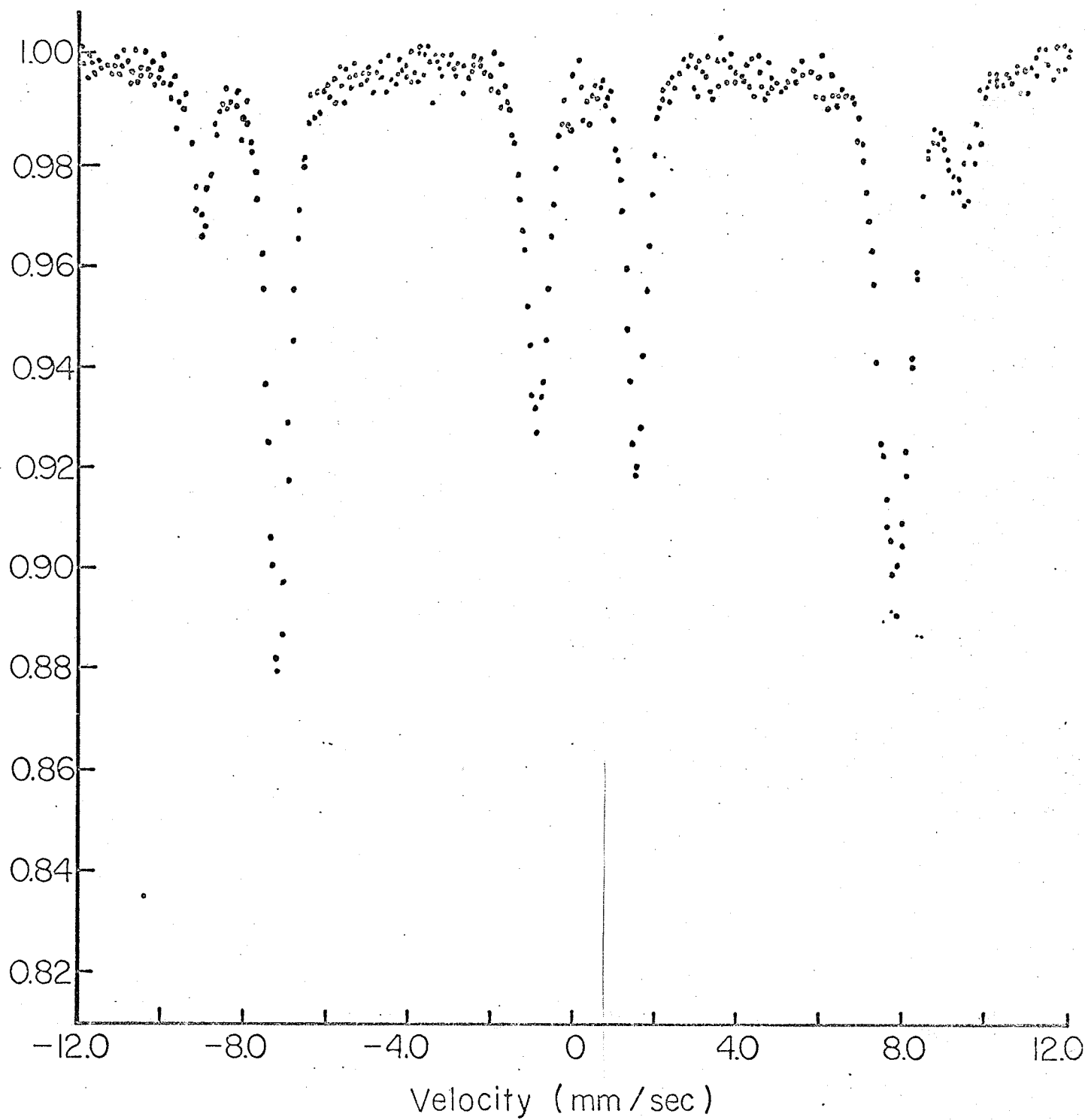
the calculated cation distributions. For the spectrum in the applied field the A and B site lines are well resolved. We measured the area ratio of these two lines using a planimeter and obtained a value of $\frac{I_A}{I_B} = 0.12 \pm 0.02$. Correcting this value for the ratio of recoilless fractions at room temperature we get that $\frac{n_A}{n_B} = (0.94) \frac{I_A}{I_B} = 0.11 \pm 0.02$ which yields a cation distribution given by $(\text{Mn}_{0.8}\text{Fe}_{0.2}) [\text{Mn}_{0.2}\text{Fe}_{1.8}] \text{O}_4$. This is in agreement with the cation distribution found by Hastings and Corliss (99).

7.4 Valency State and Spin Arrangements

In order to attempt to find evidence as to whether or not any divalent ion is present in MnFe_2O_4 we collected a Mössbauer spectrum at 7° K in an applied field of 55 KOe. with the field direction parallel to the direction of propagation of the γ rays. This is shown in figure 7-4. Although in Fe_3O_4 for temperatures below the Verwey transition, the Fe^{2+} spectrum is not well resolved from the Fe^{3+} B and A site spectra, it has been shown by B. J. Evans et al (104) that in an applied field the Fe^{2+} spectrum is at least partially resolved. It has also been pointed out (49) that Fe_3O_4 may be a specially complicated example because of the presence of 2 Fe^{2+} spectra which are probably due to the twinning below the transition temperature. The reason for taking the MnFe_2O_4 spectrum at such a low temperature is to make sure that any electron hopping has ceased so that we should be able to resolve the Fe^{2+} spectrum from that of Fe^{3+} if it is present. The spectrum shown in figure 7-4 shows no evidence of any component in addition to the Fe^{3+} A and B site spectra. This suggests that there is little if any Fe^{2+} in the B sites of MnFe_2O_4 . This is contrary to the suggestion made that MnFe_2O_4 has the cation distribution $(\text{Mn}_{0.8}^{2+} \text{Fe}_{0.2}^{3+}) [\text{Mn}_{0.2}^{3+} \text{Fe}_{0.2}^{2+} \text{Fe}_{1.6}^{3+}] \text{O}_4$. This cation distribution can explain the low magnetic moment and also the relatively high electrical conductivity. Since however we see no indication of Fe^{2+} in the Mössbauer

Figure 7-4

Mössbauer spectrum of MnFe_2O_4 in an applied field
of 55 KOe. and at 7° K.



spectra of MnFe_2O_4 , we are led to believe that the low magnetic moment cannot be explained in this way. This is the same conclusion as that reached by Lotgering (105) by considering the energy involved in electron transfer from Mn^{2+} to Fe^{3+} .

Another possible explanation for the low magnetic moment could be that the spin arrangement is not colinear. If however we assume that the Fe(B) spins are canted as in the Yafet-Kittel (12) triangular spin arrangement or even if we have a random angle as suggested by Geller (106) we would require an average angle between the spin and the magnetization direction of about $\theta = \cos^{-1}(0.95)$. In the Mössbauer spectrum in the 55 KOe. field we should see a $\Delta m = 0$ transition with intensity about 0.06 of the $\Delta m = 1, \frac{3}{2} \rightarrow \frac{1}{2}$ B site line, i.e. the intensity would be about 0.6 of the A site line. From the spectrum in the 55 KOe. field we can see that the upper limit of the intensity in the $\Delta m = 0$ region is 0.02 of the $\Delta m \pm 1, \frac{3}{2} \rightarrow \frac{1}{2}$ transitions. This shows that if there is a non-colinear spin arrangement the Fe ions are not involved to a large enough extent to explain the low magnetic moment.

In the case of MnFe_2O_4 there is however another possibility. We expect the Mn(A) - Mn(B) superexchange interaction to be quite small because of the low Néel temperature of Mn_3O_4 , also as will be shown later, the Mn(A) - Fe(B) interaction is about 0.66 of the Fe(A) - Fe(B) interaction and we expect the Mn(B) - Mn(A) interaction to be even smaller. Since however the B site neighbors of an Mn ion

in the B sites are mostly Fe neighbors one could have that the Mn(B) - Fe(B) superexchange interaction could be comparable to the Mn(B) - Mn(A) interaction. The spin arrangement one would get in this situation would be something like that shown in figure 7-5. That is the Mn(B) magnetic moments $M_{Mn}(B)$ could make a fairly large angle θ with $M_{Mn}(A)$ while the angle ϕ between $M_{Fe}(B)$ and $M_{Mn}(A)$ could be very small.

By making a few assumptions and approximations we can show that such a spin arrangement is energetically possible. The main assumptions are :

1. The Fe(B) - Fe(B) interaction can be neglected in comparison with the Fe(B) - Mn(A) interaction. This means that all the Fe(B) moments will be parallel.
2. The Mn(B) - Mn(B) interaction can be neglected in comparison with the Mn(A) - Mn(B) interaction. This means that the Mn(B) moments will all make the same angle θ with the magnetic moment of the A site ions.
3. For simplicity we assume all the A site ions to be identical. The calculations can easily be extended to the more general case.

The molecular field acting on the various spins will be given by :

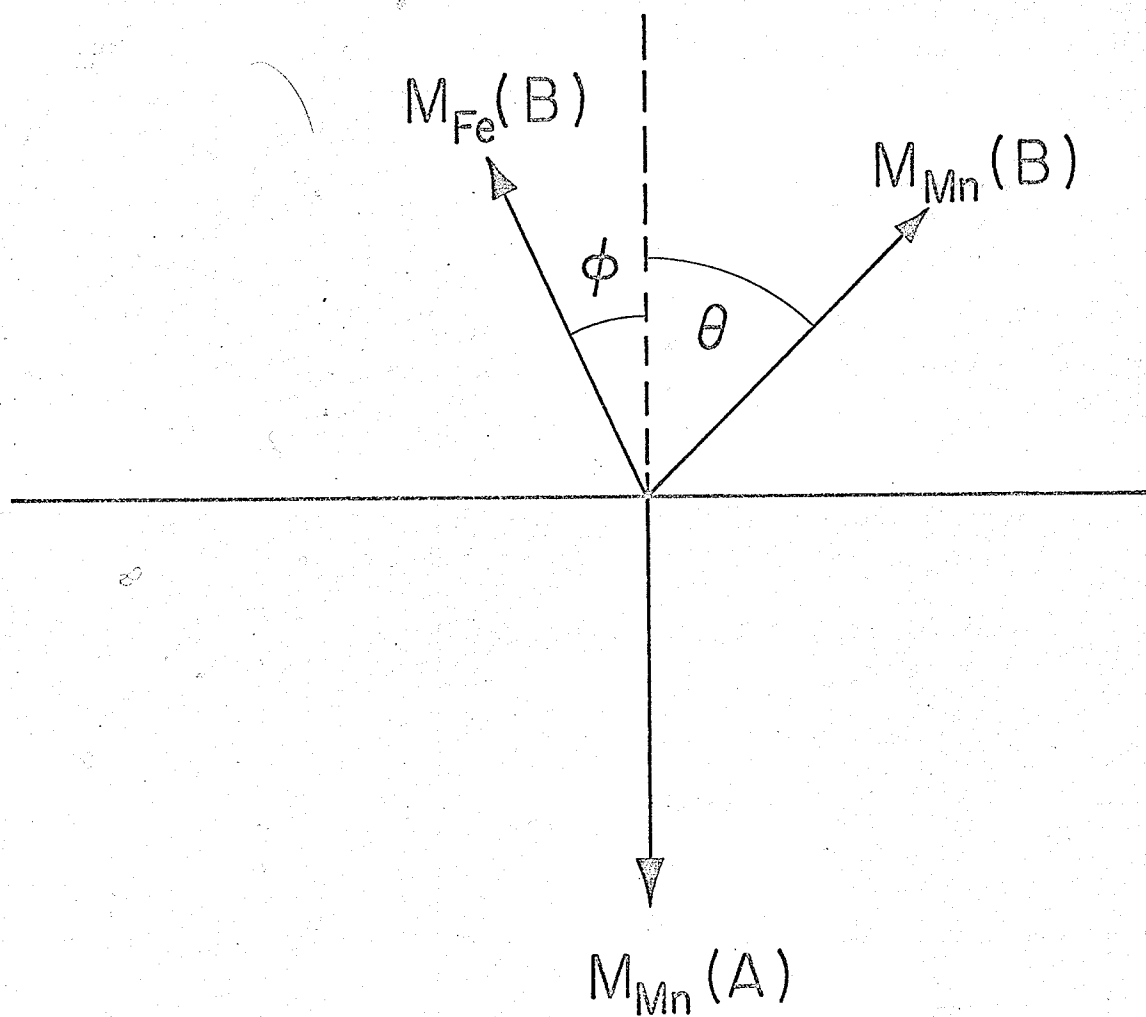
$$H(Mn(B)) = N_{AB}M_A + N_{BB}M_B$$

$$H(Fe(B)) = N_{AB}M_A + N_{BB}M_B$$

$$H(Mn(A)) = N'_{AB}M'_B + N_{AB}M_B$$

Figure 7-5

Possible spin arrangement in MnFe_2O_4 . $M_{\text{Fe}}(\text{B})$, $M_{\text{Mn}}(\text{B})$ and $M_{\text{Mn}}(\text{A})$ refer to the magnetic moments of Fe and Mn in B and A sites.



where N'_{AB} is the Mn(A) - Mn(B) molecular field coefficient, N_{AB} is the Fe(B) - Mn(A) molecular field coefficient, N_{BB} is the Mn(B) - Fe(B) molecular field coefficient, all molecular field coefficients are taken to be positive.

M_A is the magnetic moment of Mn(A)

M_B is the magnetic moment of Fe(B)

M'_B is the magnetic moment of Mn(B)

The free energy is written as

$$\begin{aligned} E &= \sum_i H_i \cdot M_i \\ &= 2N'_{AB} |M_A| |M'_B| \cos \theta - 2N_{BB} |M_B| |M'_B| \cos (\theta + \phi) \\ &\quad + 2N_{AB} |M_A| |M_B| \cos \phi \end{aligned}$$

On minimizing this energy with respect to θ and ϕ we get

$$+ N_{AB} |M_A| |M'_B| \sin \theta - N_{BB} |M_B| |M'_B| \sin(\theta + \phi) = 0 \text{ and} \quad [1]$$

$$-N_{BB} |M_B| |M'_B| \sin(\theta + \phi) + N_{AB} |M_A| |M_B| \sin \phi = 0 \quad [2]$$

From these two equations we find

$$\frac{\sin \theta}{\sin \phi} = \frac{N_{AB} |M_A| |M_B|}{N'_{AB} |M_A| |M'_B|}$$

$$= \frac{N_{AB}}{N'_{AB}} \cdot \frac{1.8}{0.2} = \frac{9N_{AB}}{N'_{AB}} \quad [3]$$

This is the case because

$$M_A = g\mu_B S_z N$$

$$M_B = 1.8 g\mu_B S_z N$$

and $M_B' = 0.29\mu_B g S_z N$

where g is the gyromagnetic ratio, μ_B is the Bohr magneton, S_z is the z component of the spin and N is the number of formula units per mole.

Rewriting equation [1] we get

$$\begin{aligned} N_{AB}' |M_A| |M_B'| \sin \theta - N_{BB} |M_B| |M_B'| \sin \theta \cos \phi \\ + N_{BB} |M_B| |M_B'| \cos \theta \sin \phi = 0 \end{aligned} \quad [4]$$

Then by substituting equation [3] into equation [4] we get :

$$\begin{aligned} N_{AB}' |M_A| |M_B'| + N_{BB} |M_B| |M_B'| \cos \phi \\ + N_{BB} |M_B| |M_B'| \frac{N_{AB}'}{9N_{AB}} \cos \theta = 0 \end{aligned}$$

Since $N_{AB}' < N_{AB}$

$$\sin \phi \ll \sin \theta$$

or $\cos \phi \approx 1$

Then we get

$$\cos \theta \approx - \frac{N_{BB} |M_B| |M_B'| + N_{AB}' |M_A| |M_B|}{N_{BB} |M_B| |M_B'| \frac{N_{AB}'}{9N_{AB}}}$$

or substituting for M_A , M_B and M_B^1 we get :

$$\cos \approx 9 \frac{N_{AB}}{1.8 N_{BB}} - \frac{N_{AB}}{N_{AB}^1}$$

For the total magnetic moment to be $4.5 \mu_B$ and taking $\cos \phi \approx 1$ we get $\cos \theta \approx 0.5$ which requires that

$$0.1 = \frac{N_{AB}}{N_{BB}} - \frac{1.8 N_{AB}}{N_{AB}^1}$$

Although we do not know $\frac{N_{AB}^1}{N_{AB}}$ i.e. the ratio of the Mn(A) - Mn(B) super-

exchange interaction to the Mn(A) - Fe(B) superexchange interaction a reasonable range of values would be from 0.2 to 0.5. In this range then we would get $\frac{N_{BB}}{N_{AB}}$ 0.1 to 0.27 which is perhaps not unreasonable for the

ratio of the Mn(B) - Fe(B) superexchange interaction to the Mn(A) - Fe(B) interaction. The above discussion shows that the previously assumed spin arrangement can be justified although whether or not this is the case depends largely on the various superexchange interactions.

7.5 Details of Mössbauer Spectra

The Mössbauer spectrum in an applied field of 17 KOe., shown in part in figure 7-3 shows that the B site line is very broad and shows some structure. This is the same kind of situation which arose for CoFe_2O_4 . In the case of MnFe_2O_4 , however the spectra are easier to analyze because the A and B site lines are resolved to a greater extent and also the A site line is much less intense so it does not mask the features of the B site line as much as for CoFe_2O_4 .

In figure 7-6 we show again line 1 of the spectrum obtained in a field of 17 KOe. and at room temperature. Also shown is the computer fit to this spectrum comprising the sum of five Lorentzians. The solid line drawn through the data points is the envelope as obtained from the fit. The fit was done in the same way as that for CoFe_2O_4 . That is, the intensities of the four Lorentzians composing the B site line were constrained to be proportional to the probability that an Fe B site ion has 3, 4, 5 or 6 nearest neighbor M_n A site ions. These probabilities have been given in Appendix A. We used the probabilities as calculated for $x = 0.20$. As can be seen from figure 7-6 the fit is very good and as for CoFe_2O_4 this shows that the model proposed (i.e. the B site hyperfine fields depend on the kind of A site nearest neighbor ions) describes in detail the Mössbauer spectra. Line 6 of the spectrum shows the same features as line 1. In table 7-1 are listed the hyperfine fields and isomer shifts for the various lines. It is seen that as I increases which means an increase in the number of Mn nearest neighbors, the hyperfine field decreases whereas the isomer shift remains constant to within the experimental error. This is what happened for CoFe_2O_4 .

We now proceed in much the same way as we did for CoFe_2O_4 . In figures 7-7 to 7-11 are shown line 1 of the Mössbauer spectrum together with the computer fit at various temperatures. Again line 6 behaves in much the same way. From these spectra it is seen that the separation of the peak positions of the components of the B site line increases as the temperature increases. This indicates that the Mn(A) - Fe(B) superexchange interaction is less than the Fe(A) - Fe(B) interaction. It should be

Figure 7-6

Line 1 of a Mössbauer spectrum of MnFe_2O_4 in an applied field of 17 KOe. A refers to Fe^{57} in A sites. B:1, 2, 3, 4 refer to Fe^{57} in B sites with 3, 4, 5, 6 nearest neighbor Mn A site ions. The Lorentzians shown are those obtained from a least squares fit to the spectrum. Also shown is the envelope of the separate Lorentzians.

Counts ($\times 10^3$)

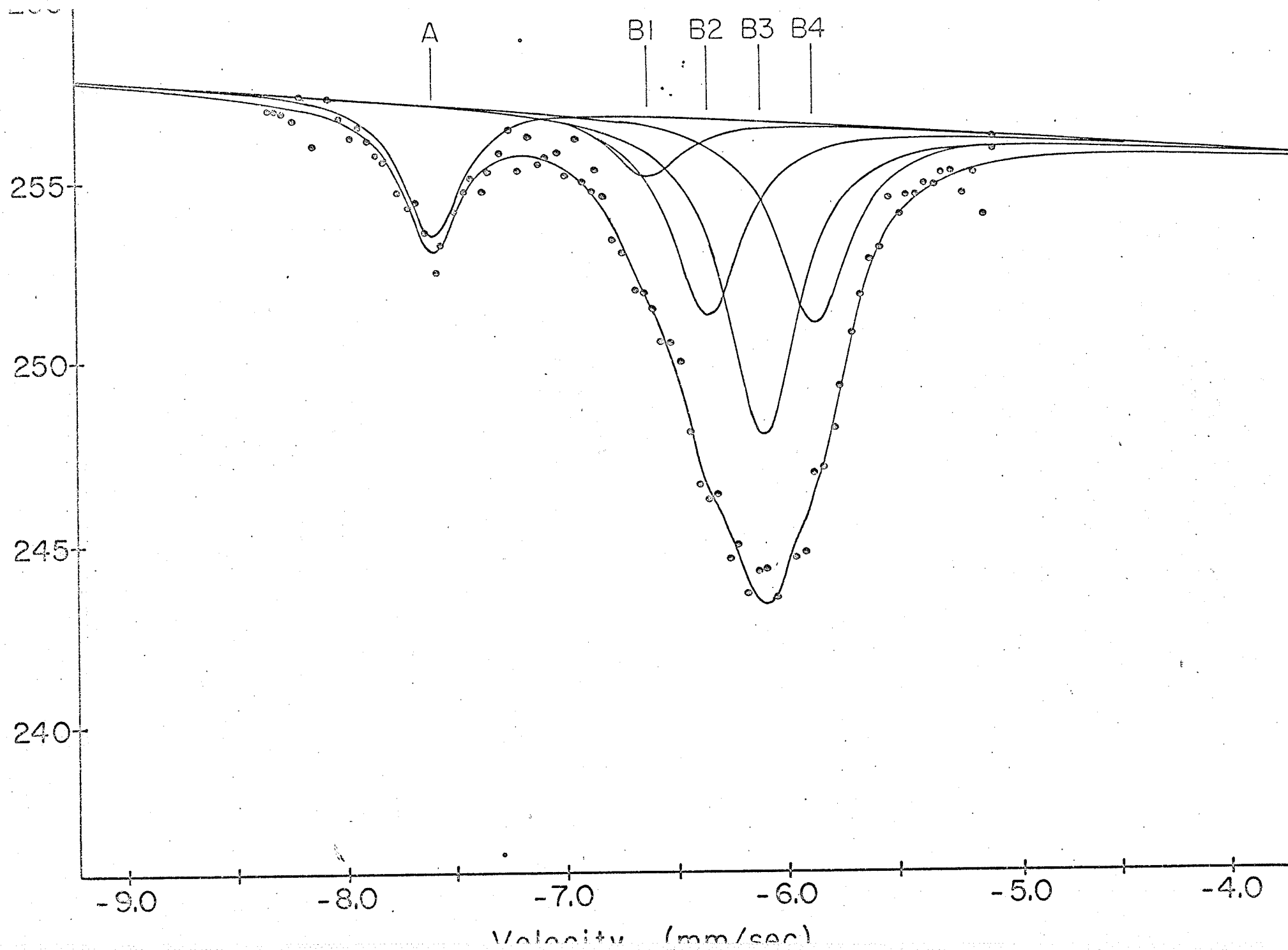


Table 7-1

Tabulated values of the hyperfine fields and isomer shift for Fe^{57} in A and B sites. I = 3, 4, 5, 6 refer to the number of Mn A site nearest neighbors of an iron ion in a B site.

	<u>A</u>	<u>I=3</u>	<u>I=4</u>	<u>I=5</u>	<u>I=6</u>
H_{hpf} (KOe.)	483	461	448	428	413
IS* (mm/sec)	.52	.60	.66	.61	.59

* relative to Fe^{57} in Cr matrix

Error in H_{hpf} = ± 5 KOe.

Error in IS = ± 0.04 mm/sec

Figure 7-7

Line 1 of the Mössbauer spectrum of MnFe_2O_4 at 106°K .

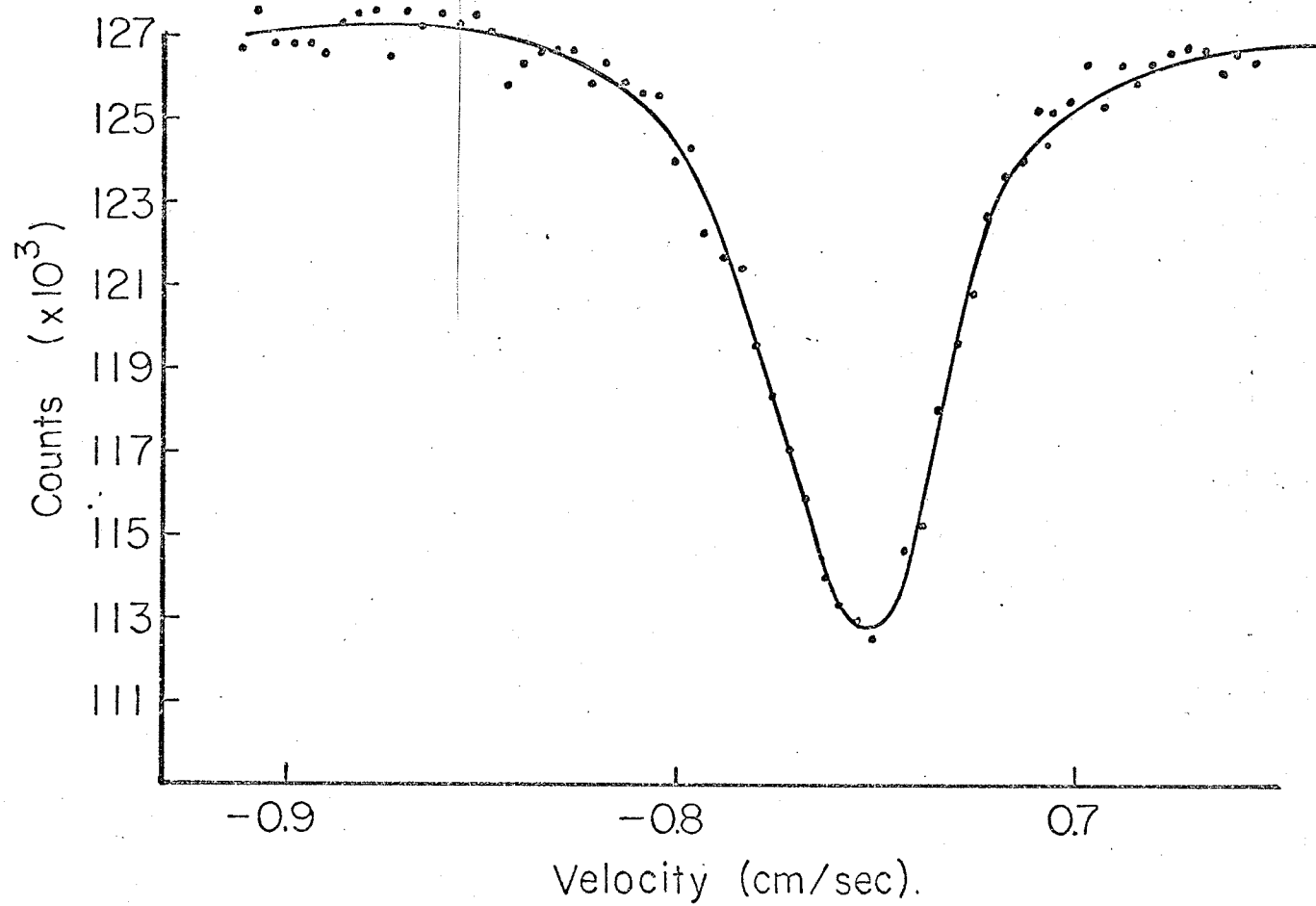


Figure 7-8

Line 1 of the Mössbauer spectrum of MnFe_2O_4 at 298°K .
A refers to Fe^{57} in A sites. B:1, 2, 3, 4 refer to
 Fe^{57} in B sites with 3, 4, 5, 6 nearest neighbor Mn
A site ions. The Lorentzians shown are those obtained
from a least squares fit to the spectrum. Also shown
is the envelope of the separate Lorentzians.

Counts ($\times 10^3$)

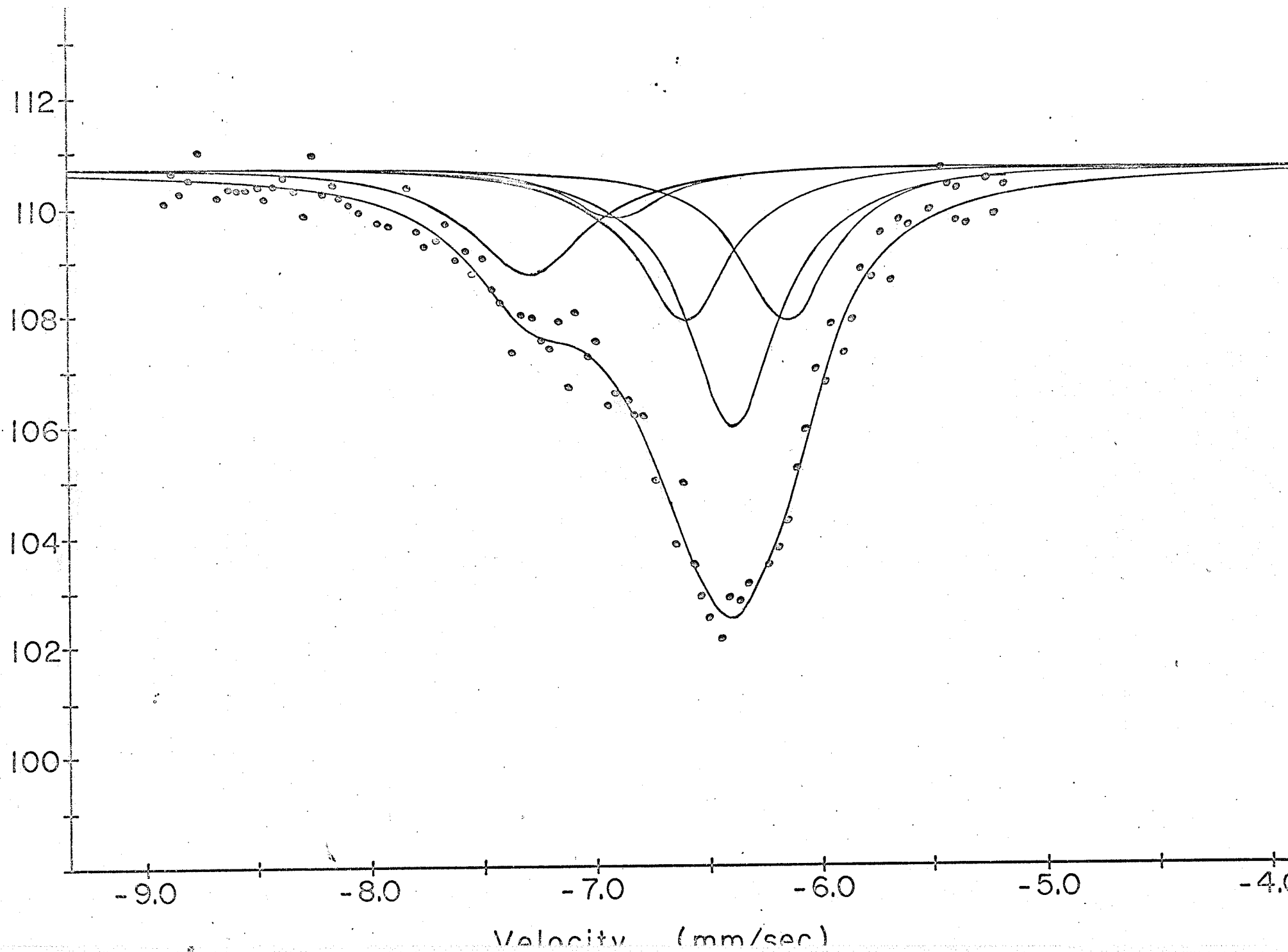


Figure 7-9

Line 1 of the Mössbauer spectrum of MnFe_2O_4 at 367°K . A refers to Fe^{57} in A sites. B:1, 2, 3, 4 refer to Fe^{57} in B sites with 3, 4, 5, 6 nearest neighbor Mn A site ions. The Lorentzians shown are those obtained from a least squares fit to the spectrum. Also shown is the envelope of the separate Lorentzians.

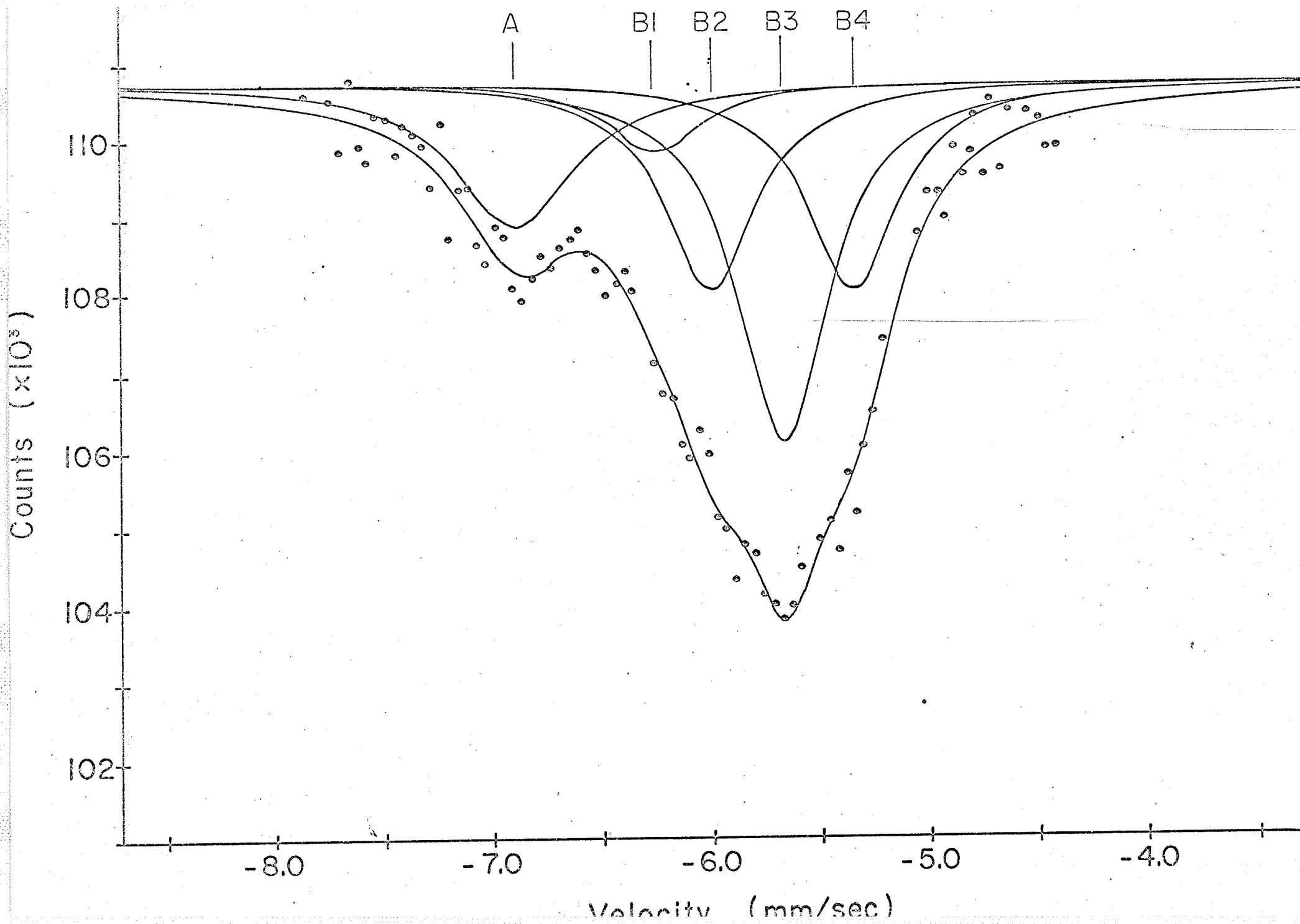


Figure 7-10

Line 1 of the Mössbauer spectrum of MnFe_2O_4 at 429°K . A refers to Fe^{57} in A sites. B:1, 2, 3, 4 refer to Fe^{57} in B sites with 3, 4, 5, 6 nearest neighbor Mn A site ions. The Lorentzians shown are those obtained from a least squares fit to the spectrum. Also shown is the envelope of the separate Lorentzians.

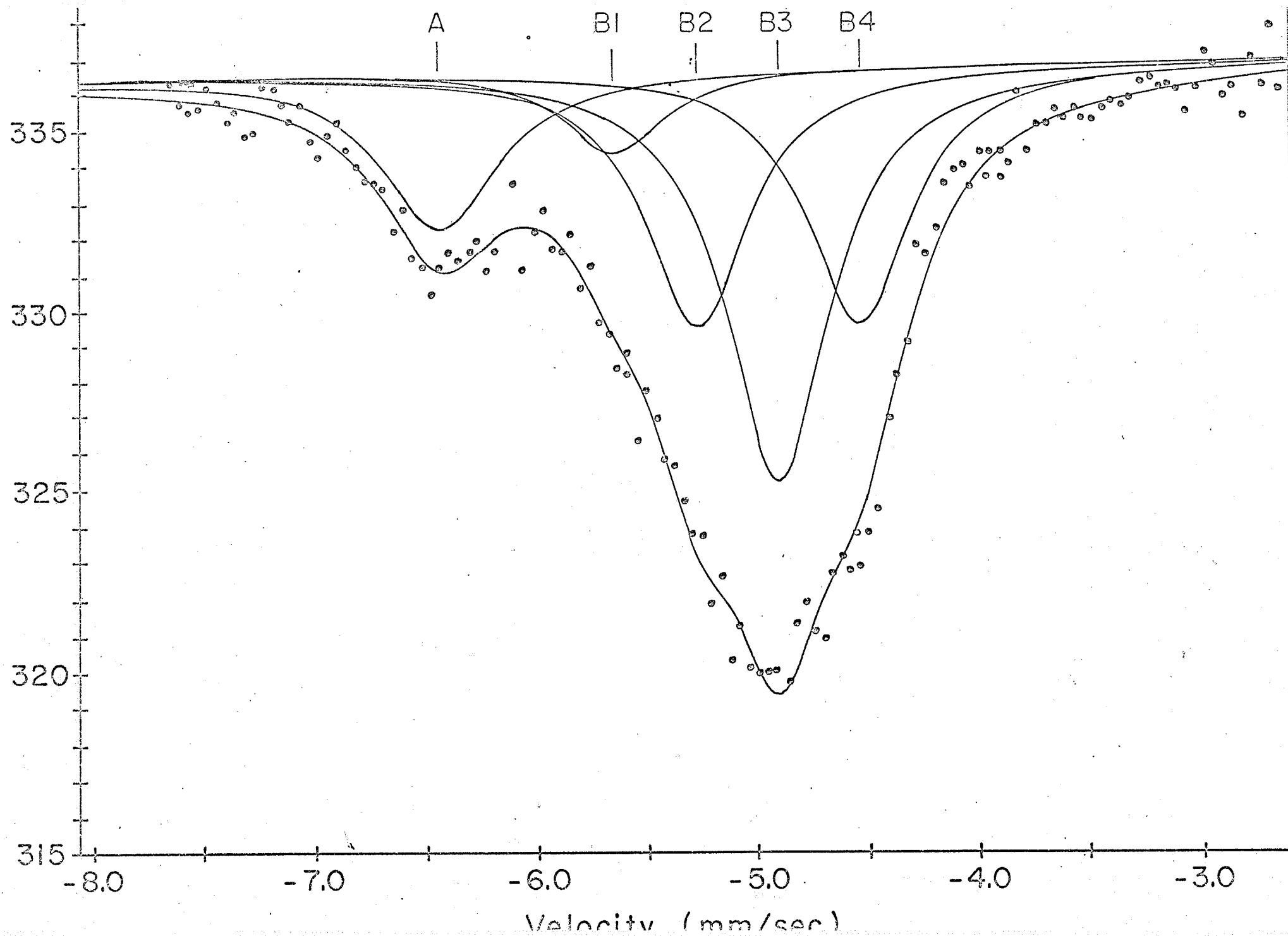
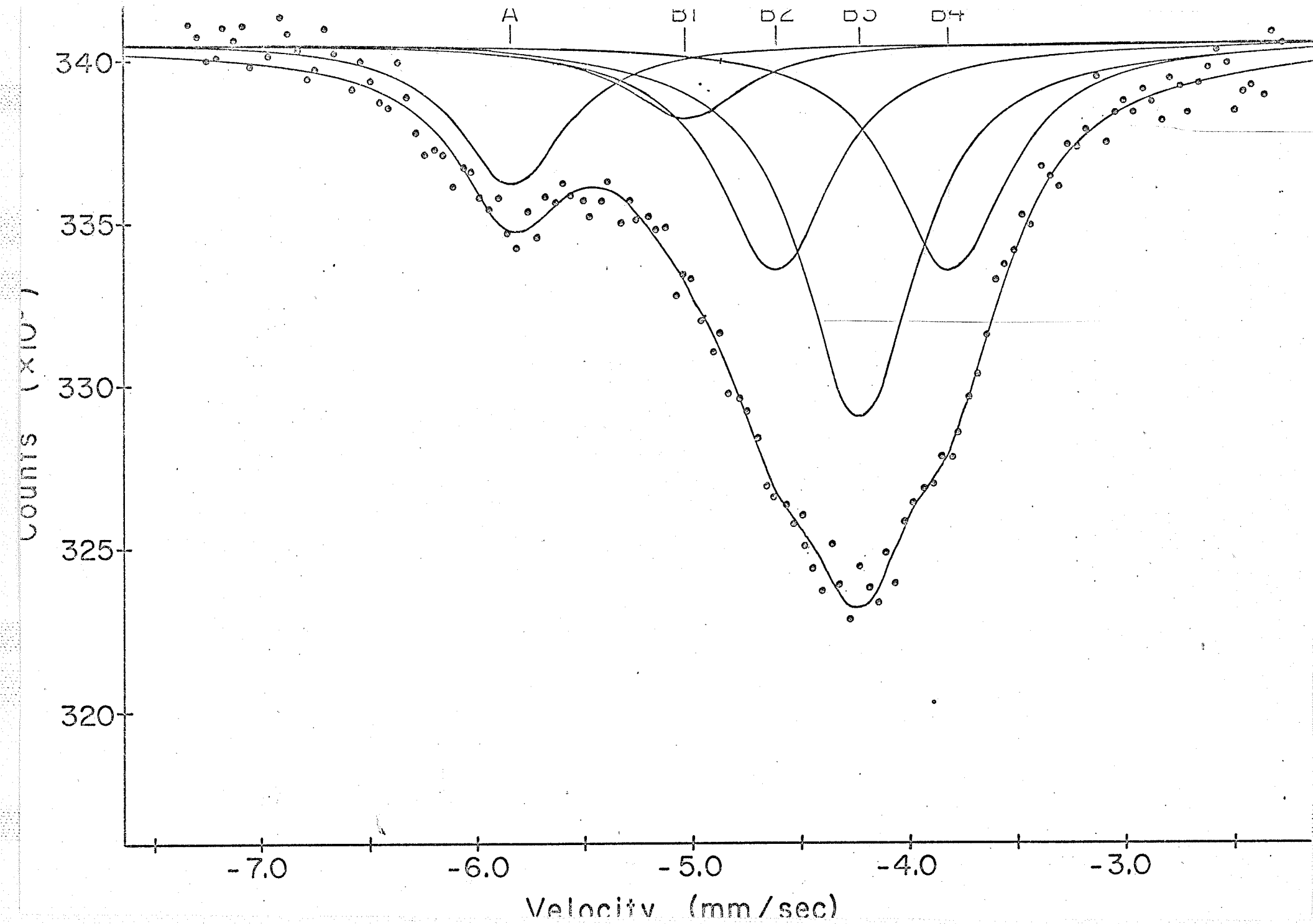


Figure 7-11

Line 1 of the Mössbauer spectrum of MnFe_2O_4 at 475.5°K . A refers to Fe^{57} in A sites. B:1, 2, 3, 4 refer to Fe^{57} in B sites with 3, 4, 5, 6 nearest neighbor Mn A site ions. The Lorentzians shown are those obtained from a least squares fit to the spectrum. Also shown is the envelope of the separate Lorentzians.



pointed out that the B site line widths are wider than those of the A site and increase with increasing temperature. This is probably due to next nearest neighbor effects which have not been considered in the analysis.

In figure 7-12 is shown the temperature dependence of the various hyperfine fields. The ferrimagnetic Néel temperature was determined to be 573° K by the thermal scanning technique. The distribution in the hyperfine fields at 96° K and at 7° K was determined from the width of the B site line. Although these values are not very accurate they indicate that there is a decrease in the hyperfine field of about 6 KOe. at 0° K when an Fe ion in the A sites is replaced by an Mn ion.

The quadrupole interaction could not be determined accurately for temperatures below T_{FN} . In figure 7-13 is shown a spectrum obtained at 730° K which is above T_{FN} . From this we see that there is indeed some quadrupole splitting. The splitting given by $\frac{e^2qQ}{2}$ was found to be 0.52 mm/sec.

Since the hyperfine fields will be discussed in detail later, we present here only a short summary of the results.

1. The hyperfine field at 0° K at the B site Fe^{3+} ion seems to decrease with increasing numbers of Mn nearest neighbors.
2. The temperature dependence of the hyperfine field at a B site Fe^{3+} ion increase as the number of Mn nearest neighbors increase.

Figure 7-12

Plot of the hyperfine field versus T/T_{FN} for $MnFe_2O_4$. A refers to Fe^{57} in A sites. B:1, 2, 3, 4 refer to Fe^{57} in B sites with 3, 4, 5, 6 nearest neighbor Mn A site ions.

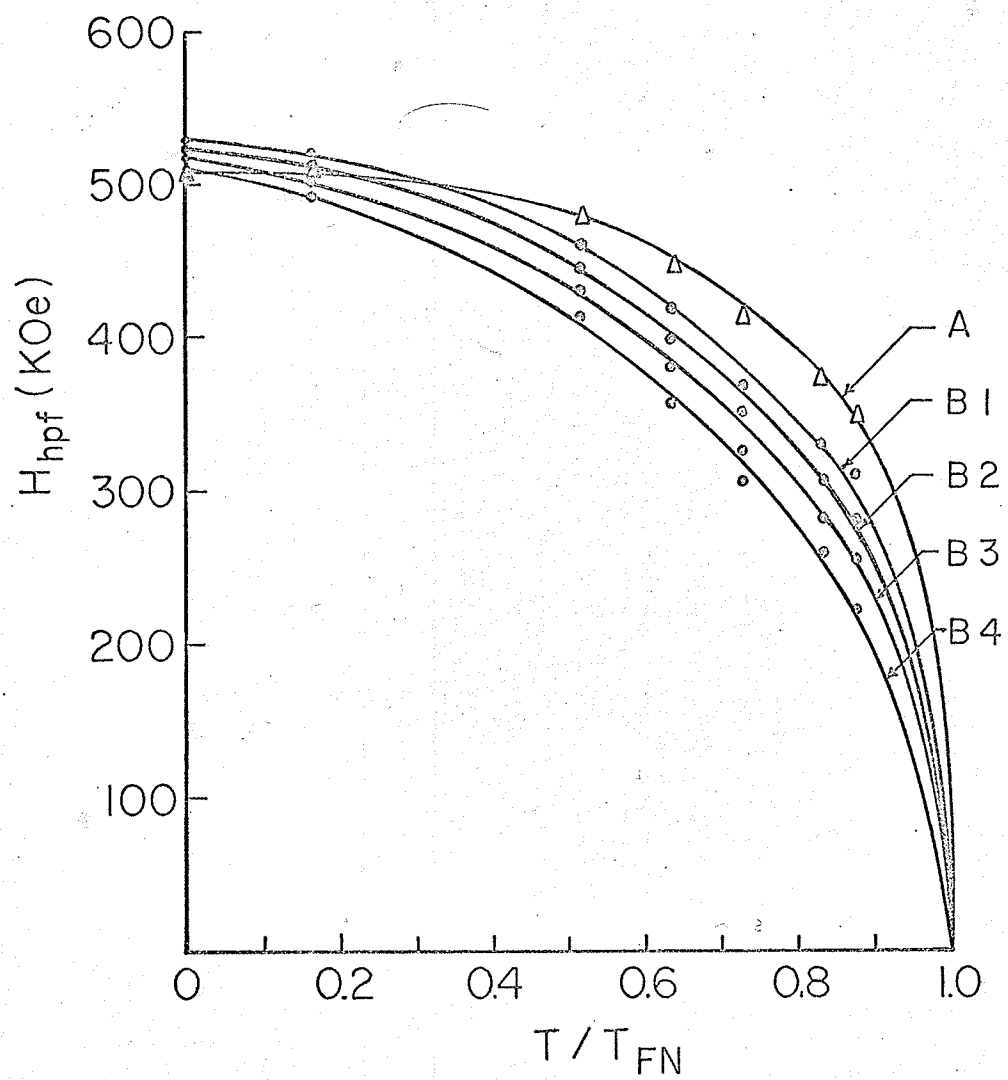
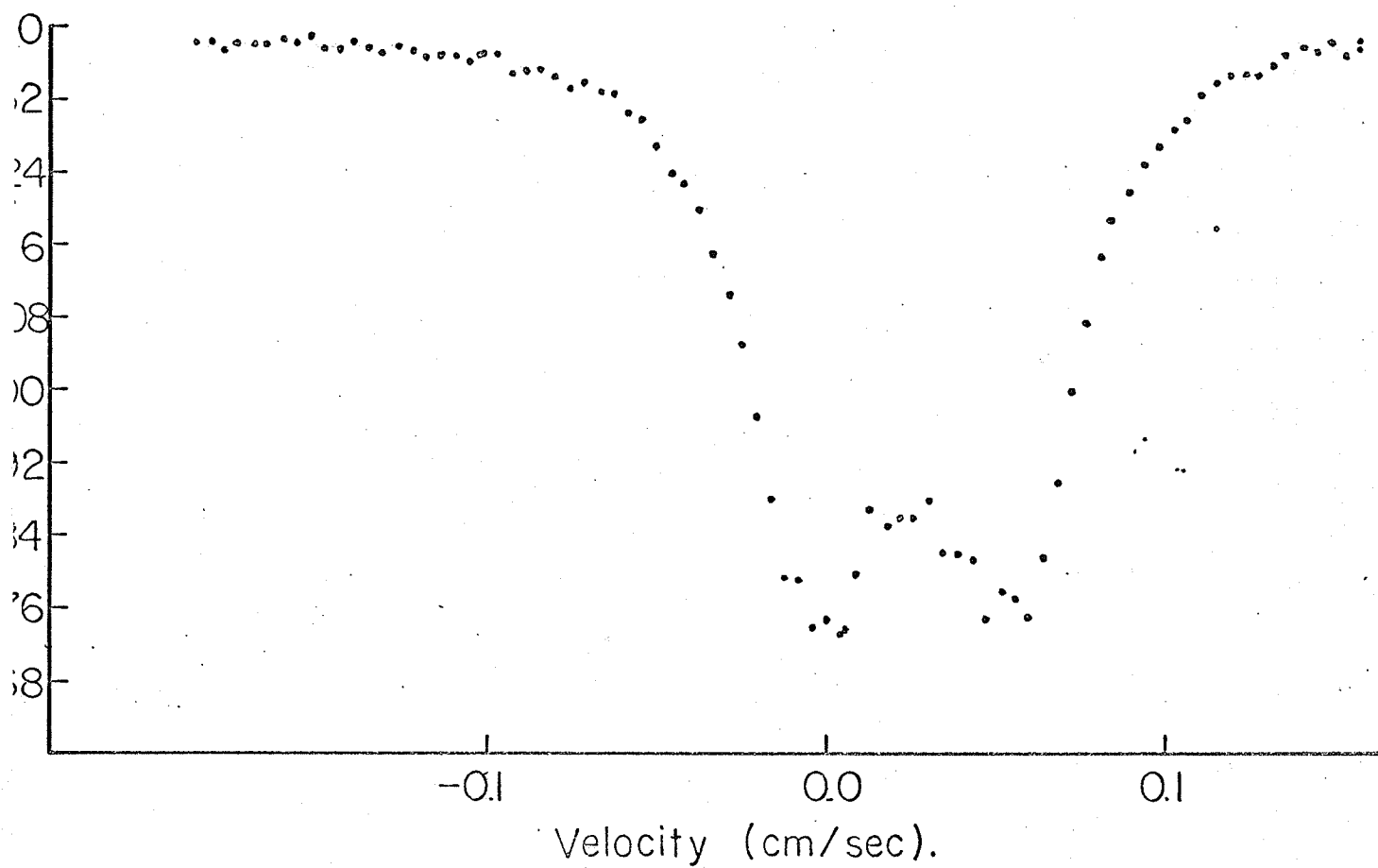


Figure 7-13

Mössbauer spectrum of MnFe_2O_4 at a temperature above the ferrimagnetic Néel temperature.



3. The hyperfine fields and isomer shifts of the A site Fe^{3+} ions are considerably less than those for the B site ions.

These observations are the same as those mentioned in the section on CoFe_2O_4 .

Superexchange Interactions

In both the CoFe_2O_4 and MnFe_2O_4 we found that the temperature dependence of the hyperfine field and thus the magnetization depends on the number of Co, Mn or Fe nearest A site neighbors of a B site ion. With the use of molecular field theory we can calculate from the experimental data the Fe(A) - Fe(B), Co(A) - Fe(B) and Mn(A) - Fe(B) superexchange interactions. Although the molecular field theory gives the wrong relation between the transition temperature and the exchange interaction for both ferro and anti-ferro magnets we should however be able to get reasonable values for the ratio of the Co(A) - Fe(B) and Mn(A) - Fe(B) superexchange interactions to the Fe(A) - Fe(B) interactions. These values can then be compared to the values obtained by comparing the ferrimagnetic Néel temperature of CoFe_2O_4 and MnFe_2O_4 to that of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$.

In the molecular field approximation, the molecular field acting on a B site ion can be written as :

$$H(B) = \sum_i N_{A_i B} M_{A_i} + \sum_j N_{B_j B} M_{B_j} \quad [1]$$

where $N_{A_i B}$ and $N_{B_j B}$ are the molecular field coefficients corresponding to A-B and B-B superexchange interactions. The sum is taken over all different kinds of ions in the two sites. Since we are measuring only the temperature dependence of the magnetization for the Fe^{3+} ions we will be concerned with calculating $N_{A_i B}$ where B will refer to an Fe^{3+} ion.

If the molecular fields are due to nearest neighbor interactions only we can write equation [1] in terms of the exchange integrals J .

$$H(B_I) = 2J_1 I \langle S_z(A_1) \rangle + 2J_2 (6 - I) \langle S_z(A_2) \rangle \quad [2]$$

where we have neglected B-B interactions and have assumed that there are only two kinds of ions in the A sites. J_1 and J_2 are then the exchange integrals corresponding to the two types of A site ions. I is the number of nearest neighbor A site ions of type 1 and $(6 - I)$ is the number of nearest neighbor A site ions of type 2. $\langle S_z(A) \rangle$ is the average value of the z component of the spin for the two types of ions referred to with subscripts 1 and 2. From equation [2] we see that if $J_1 \neq J_2$ then the molecular field will depend on I .

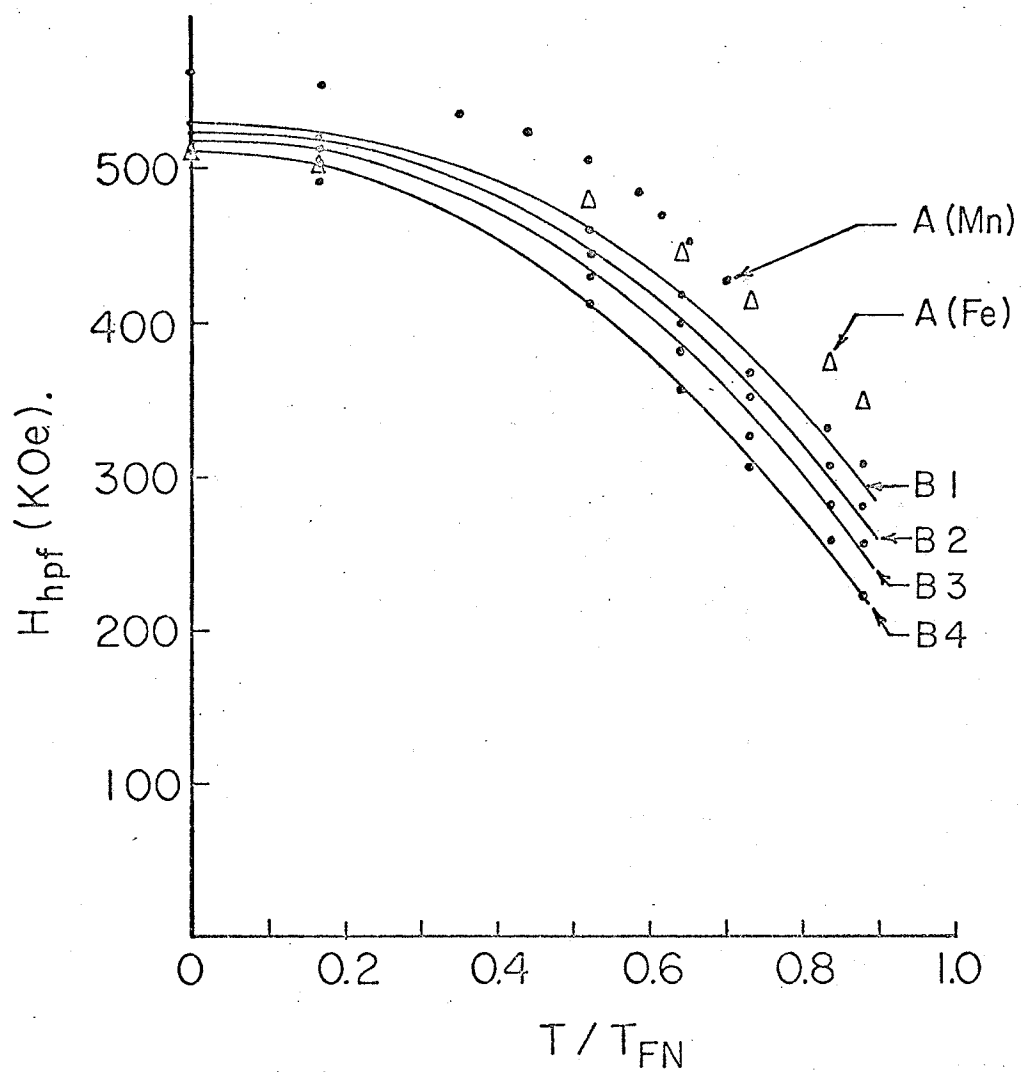
The temperature dependence of the magnetic moment of an Fe ion with I nearest neighbors of type 1 and $(6 - I)$ of type 2 will be given by :

$$\langle S_z(\text{Fe(B)}) \rangle_I = \frac{5}{2} B^{\frac{5}{2}} \left[\frac{2J_1 I \frac{5}{2} \langle S_z(A_1) \rangle + 2J_2 (6 - I) \frac{5}{2} \langle S_z(A_2) \rangle}{kT} \right] \quad [3]$$

Where $B^{\frac{5}{2}}$ is the Brillouin function for spin $\frac{5}{2}$. In figure 8-1 we show again the various magnetization curves as found for MnFe_2O_4 . Also shown is the Mn(A) magnetization curve as found by H. Yasuoka et al (107) using NMR techniques.

Figure 8-1

Plot of the hyperfine fields versus T/T_{FN} for $MnFe_2O_4$.
A refers to Fe^{57} or Mn^{55} in A sites. B:1, 2, 3, 4
refer to Fe^{57} in B sites with 3, 4, 5, 6 nearest
neighbor Mn A site ions respectively. The curves
drawn are theoretically calculated curves as described
in the text.



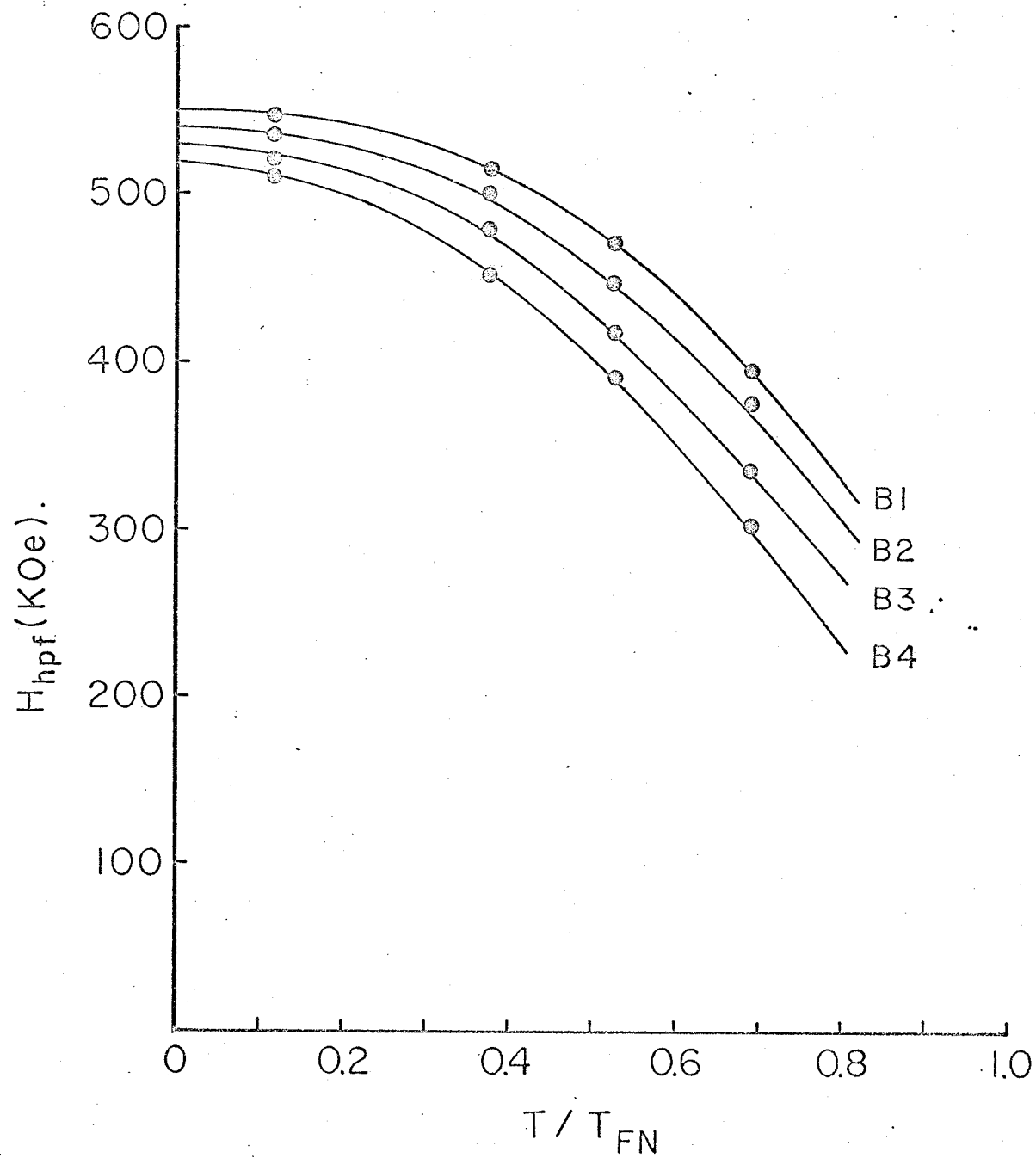
The solid lines drawn are the theoretical curves calculated using equation [3].

For $\langle S_z(A_1) \rangle$ we chose the values we measured for Fe in A sites and for $\langle S_z(A_2) \rangle$ we chose the values determined by H. Yasuoka et al (107) for Mn in A sites. The parameters J_1 and J_2 were then varied until the best fit was obtained. The values for the curves drawn in figure 8-1 are $J_1 = 18.4 \pm 0.6^\circ \text{K}$ and $J_2 = 12.1 \pm 0.4^\circ \text{K}$. The ratio of the Mn - Fe to Fe - Fe A-B superexchange interaction is then $\frac{J_2}{J_1} \approx 0.66 \pm 0.04$.

In figure 8-2 we reproduce the CoFe_2O_4 data together with the theoretically calculated curves. Since we did not have any information about the Co A site magnetization curve we used for this the same values as for the Fe A site magnetization except for using a spin $\frac{3}{2}$ for the Co ion. The values of J_1 and J_2 were found to be 20.1 ± 0.6 and $13.7 \pm 0.4^\circ \text{K}$ respectively. The ratio of the Co - Fe to Fe - Fe A-B superexchange interaction is then 0.68 ± 0.04 . It should be noted that the value for J_1 determined for CoFe_2O_4 is close to that determined from the MnFe_2O_4 data. This is expected to be the case because the lattice parameters for MnFe_2O_4 and CoFe_2O_4 are almost the same which would indicate that the Fe - Fe exchange interactions should be nearly the same. The Fe - Fe superexchange interaction calculated from T_{FN} for Li ferrite was $J = 22^\circ \text{K}$. A decrease in J is expected in going from Li to Co to Mn ferrite because of an increase in lattice parameters. The lattice parameters increase from 8.33 to 8.38 to $8.51 \text{ \AA}$ respectively. This shows that the values found for the Fe - Fe superexchange interaction are in qualitative agreement with the Fe - O distances in the materials considered.

Figure 8-2

Plot of the hyperfine fields versus T/T_{FN} for $\text{CoFe}_2\text{O}_4(q)$.
A refers to Fe^{57} in A sites. B:1, 2, 3, 4, refer to
 Fe^{57} in B sites with 0, 1, 2, 3, Co A site nearest
neighbors respectively. The curves shown are theoretically
calculated curves as described in the text.



The ratio of the Co - Fe to Fe - Fe superexchange interaction was found to be 0.68 while the value found by comparing T_{FN} of CoFe_2O_4 to that of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ yielded a ratio of 0.43.

It must, however, be pointed out that the value of 0.68 refers to the Co(A) - Fe(B) interaction while that of 0.43 refers to Co(B) - Fe(A) interaction. That these two values are considerably different is not unexpected because the Co^{2+} orbital levels are very sensitive to the symmetry of the immediate surroundings.

It is rather surprising that the molecular field theory seems to fit the magnetization curves so well since it has been shown in several other cases that the molecular field theory can be quite incorrect in describing quantitatively the magnetization versus temperature data (108,110). It has however, also been found in the case of Mn impurities in Fe metal (111) that the Mn magnetization curve can be quite satisfactorily described by the molecular field theory if one uses the bulk magnetization data of pure Fe metal to determine the molecular field.

It should be pointed out that a more eloquent theory developed by Hone et al. (112) could be used. This theory takes into account the changes in the "host" magnetization where the "host" ion is a nearest neighbor to the "impurity" ion. It was, however, shown in the section on CoFe_2O_4 and MnFe_2O_4 that the A site Fe Mössbauer lines were relatively narrow even at relatively high temperatures. This indicates that these changes in the "host" magnetization, where in our case the "host" is an A site ion, are not very important.

That the A site magnetization curve for Fe^{3+} ions seems to be quite independent of the kind of B site nearest neighbor is evident from the relatively narrow lines found in the Mössbauer spectra for NiFe_2O_4 , CoFe_2O_4 and MnFe_2O_4 . This result is quite unexpected and we do not have a full explanation for this. We must however, remember that since the A site has 12 nearest B site neighbors replacing 1 of these by a different ion will not have as large an effect as replacing 1 of the 6 nearest neighbors of a B site ion by another ion. It seems however unlikely that this can be the sole explanation.

CHAPTER 9

Fields at 0° K

9.1 Introduction

The results on the temperature dependence of the magnetization of the various B site ions indicate that the hyperfine field at 0° K is dependent on the kind of A site nearest neighbors. Also we and others (61) have found that the hyperfine field and isomer shift of Fe^{57} nuclei in A sites are less than those of Fe^{57} nuclei in B sites. In this section we suggest several possible explanations for these observed results also use these ideas to correlate some of the hyperfine field data obtained by other investigators for some materials other than spinels.

There are several mechanisms which could explain the dependence of the hyperfine field (H_{hpf}) on the kind of nearest neighbor effects. If however we assume that the $\text{Fe(B)} - \text{O}$ distance is independent on the kind of A site nearest neighbor in a particular material we can perhaps conclude that this effect is not due to delocalization of the Fe(B) , d electrons or to the number of p electrons transferred from the ligand to the 4s orbitals of the iron ion. These effects would change the hyperfine field but do not seem to explain the dependence of H_{hpf} on the kind of A site ion.

The dependence of H_{hpf} on the kind of A site nearest neighbor can also not be explained by zero point spin deviations. It has been shown by Van de Braak and Caspers (113) that a magnetic vacancy increases

$\langle S_z \rangle$ at 0° K of its neighbors. Although for MnFe_2O_4 or CoFe_2O_4 we are not introducing magnetic vacancies we are however decreasing the A-B superexchange interaction by replacing an Fe(A) ion by a Mn(A) or Co(A) ion. We would thus expect that $\langle S_z \rangle$ at 0° K would increase with the number of Mn or Co A site nearest neighbors an Fe B site ion has. This would mean a corresponding increase in H_{hpf} at 0° K which is in contrast to our results.

9.2 Super-transferred Hyperfine Fields

The concept of covalency may serve as an explanation for the distribution in hyperfine fields at 0° K. This phenomenon has many aspects. In this section I want to discuss the super-transferred hyperfine interactions as a possible explanation for our results at 0° K.

It is known that the Mössbauer effect, NMR and EPR can be used to measure the product $A\langle S_z \rangle$. Locher and Gerschwind (114) have shown that this product is nearly independent of lattice spacings. In a concentrated antiferromagnetic spin system one would expect a value of

$\langle S_z \rangle$ less than that obtained in a dilute paramagnetic system because of zero point spin deviations. Experimentally however an increase in

$\langle S_z \rangle$ was observed (115, 116). Owen and Taylor (117) Orbach, Haung and Simánek (118, 119) have explained this discrepancy in terms of the super-transferred hyperfine fields (STHF). STHF may be described employing the concepts of covalency (117)

$$M_1 - L - M_2$$

assume an ionic configuration metal M_1 - ligand L - metal M_2 as shown above. As a free ion M_1 , has one electron in a singly occupied d_{z^2} orbital with spin up and an empty d_{z^2} orbit. The wave functions are $d\uparrow$ and $d\downarrow$ respectively. The ligand has paired electrons in orbitals $p\uparrow$ and $p\downarrow$. In the actual compound the three electron systems M_1 - L will show overlap and covalency. Because $d\uparrow$ and $p\uparrow$ are wave functions corresponding to different ions the overlap integral $S = \langle p | d \rangle$ will not be zero resulting in an increased spin and charge density at the metal as well as the ligand ion. Covalency i.e. a spin transfer from the $p\uparrow$ orbital into the empty $d\downarrow$ orbital will influence the spin and charge density at M_1 and L in a different way. The new wave functions including overlap and covalency may be written as (120)

$$(1 - S^2)^{-\frac{1}{2}} [d\uparrow - Sp\uparrow] ; p\uparrow ; (1 + 2S\gamma + \gamma^2)^{-\frac{1}{2}} [p\downarrow + \gamma d\downarrow]$$

The overlap is given by $S = \langle d\uparrow | p\uparrow \rangle$ and γ is the covalency factor. The influence of overlap and covalency on the spin and charge density at M_1 and L are shown in table 9-1.

Overlap and covalency, both create a spin density at the ligand which can be measured with NMR or ME as a so called transferred hyperfine field. The transferred spin $\uparrow$ density at L will produce via overlap and covalency with 1, 2 or 3 electrons of M_2 a spin density at M_2 . The moment of this spin density at M_2 is parallel to the moment of M_1 , and consequently this supertransferred hyperfine field is parallel to the magnetic dipole moment of M_1 . In an antiferromagnetic material the magnetic moments of M_1 and M_2 are antiparallel. The effective magnetic

Table 9-1

Change in the spin and charge density at the ligand (L) and metal (M) due to covalency and overlap.

+ indicates an increase and - indicates a decrease in spin or charge density.

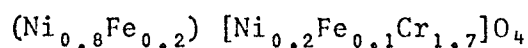
	<u>M₁</u>		<u>L</u>	
	<u>Charge</u>	<u>Spin</u>	<u>Charge</u>	<u>Spin</u>
Overlap	+	+	+	+
Covalency	+	-	-	+
	—	—	—	—
Total Effect	++	+-	+-	++

field H_{hpf} produced by the contact interaction at the nucleus of M_2 , is antiparallel to the magnetic moment of M_2 , so parallel to the magnetic moment of M_1 . Thus H_{hpf} is increased by STHF and this field is usually considered as an extra contribution to the hyperfine coupling constant A . This means that A_2 of an antiferromagnetic material is larger than A_2 of a diluted material. Besides this indirect process also a direct spin transfer $3d(M_1) \rightarrow 4f(M_2)$ may occur with the same sign for STHF.

Beside the dominant negative A-B superexchange interactions in ferrimagnetic spinels there are also present the weaker positive or negative B-B superexchange and the much weaker A-A superexchange interactions. The last one will be left out of the discussion. The effective magnetic field at a B site nucleus can be written as a sum of the contact term and super-transferred hyperfine terms :

$$\text{STHF}(B) = A_0 \langle S_B \rangle + \sum_i A_{1i} \langle S_{Ai} \rangle + \sum_j A_{2j} \langle S_{Bj} \rangle .$$

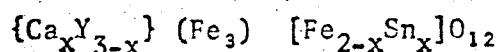
A relatively strong B-B interaction will lead to a smaller $H_{\text{hpf}}(B)$ and in case this interaction is negative, it may also lead to complicated spin configurations. Both effects have been observed by Chappert and Frankle (88) in



where they found $H_{\text{hpf}}(A) = H_{\text{hpf}}(B) = 498 \pm 5 \text{ KOe}$. A triangular spin configuration in which the magnetic moments at the two B sites are not parallel to each other will show a smaller total magnetic moment. As long as the individual moments are not affected, a reduction in H_{hpf} would not

be expected. But a super-transferred field from the B site should reduce $H_{\text{hpf}}(\text{B})$. Also since the STHF from the A site to the B site is parallel to $M(\text{A})$, this field will also be reduced in a triangular spin arrangement because of the angle between $M(\text{A})$ and $M(\text{B})$.

A direct observation of a field (STHF = 210 KOe.) has been reported by Belov et al. (121) in ^{117}Sn in



and more recently Evans et al. (122) have found STHF of 300 Koe. for Sb in Sb substituted ferrites. Goldanski (123) et al. have shown that the direction of the super-transferred hyperfine field at octahedral Sn^{117} nuclei is indeed parallel to the magnetic moments of ions in tetrahedral sites. Previously we have shown that the total superexchange strength felt by a central octahedral ion is reduced by replacing an Fe^{3+} ion in a neighboring tetrahedral position by a Co or Mn ion. Or in other words spin density transferred from Co or Mn to the ligand via overlap and covalency has decreased and consequently STHF(B) has decreased. Since STHF and H_{hpf} have the same sign, smaller magnetic fields will be found at octahedral ion nuclei having more Co or Mn ions in the nearest neighbor tetrahedral positions. The A-B superexchange strengths of the Co-O-Fe, Mn-O-Fe bonds relative to the Fe-O-Fe superexchange strengths can be used to calculate STHF in the following way. By using the notation of Simánek (118) we can write :

$$\text{STHF} = Z_{\frac{8}{3}}^g \pi g \mu_B M_s [-\sum_{\text{ns}} \phi_{\text{ns}}(0)]^2$$

where Z is the number of nearest neighbors, $g\mu_B M_S$ is the magnetic moment for spin $\frac{1}{2}$, μ_{ns} is defined by the orthogonality of the antibonding orbital to the core orbitals to be

$$\mu_{ns} = S_{p,ns} A_{\sigma} - S_{s,ns} A_s$$

where

$$S_{p,ns} = \langle p | \phi_{ns} \rangle \quad \text{and} \quad S_{s,ns} = \langle s | \phi_{ns} \rangle$$

where p and s refer to the ligand orbitals. $\phi_{ns}(0)$ are the core orbitals evaluated at the nucleus. The term in $a_s \phi_{4s}(0)$ present in the paper by Simánek (118) has been neglected. For the ferrites we want to calculate $H_{\text{hpf}}(B)$. This will be given by :

$$\text{STHF}(B) = \frac{8}{3} \pi g \mu_B \sum_{i=1}^6 M_{S_i}(A) A_{\sigma i}^2(A) \left[- \sum_{n=1}^3 \langle p | \phi_{ns}^B \phi_{ns}^B(0) \rangle^2 \right] \quad [1]$$

where we have neglected any effect from the neighboring B site ions. Also we have assumed that the $3d^A \rightarrow 4s^B$ transfer is negligible and that $A_s \langle s | \phi_{ns} \rangle$ is small compared to $A_{\sigma} \langle p | \phi_{ns} \rangle$. The sum is taken over all nearest neighbor A site ions which have covalency factors $A_{\sigma i}(A)$ and the directions of the magnetic moment given by $M_{S_i}(A)$. For CoFe_2O_4 and MnFe_2O_4 there are several different kinds of nearest A site neighbors. If we assume that each kind of nearest neighbor contributes to STHF in the same way we can write :

$$\text{STHF}(B) = \frac{8}{3} \pi g \mu_B \left[I M_S(A_1) A_{\sigma}^2(A_1) + (6 - I) M_S(A_2) A_{\sigma}^2(A_2) \right] \left[- \sum_{n=1}^3 \langle p | \phi_{ns}^B \phi_{ns}^B(0) \rangle^2 \right] \quad [2]$$

where we have assumed that $\langle p | \phi_{ns}(B) \rangle$ is independent of the nearest A site neighbor. I denotes the number of A site neighbors of type 1 and $(6 - I)$ is the number of A site neighbors of type 2.

From equation [2] it is easy to see first of all how the hyperfine field at $\text{Fe}^{57}(\text{B})$ at 0°K can be nearest neighbor dependent.

If in fact the neighbors of type 1 are diamagnetic then $M_s(A_1) = 0$ and one should observe a decrease in the hyperfine field of

$$\frac{8}{3} \pi g \mu_B M_s(A_2) A_O^2(A_2) \left[- \sum_{n=1}^3 \langle p | \phi_{ns}^B \rangle \phi_{ns}^B(0) \right]^2$$

for each ion of type 2 replaced by a diamagnetic ion. This reduction in hyperfine field has been observed in NMR studies of $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ (124), where a decrease in hyperfine field at the $\text{Fe}(\text{B})$ nucleus of 12 KOe. per Zn nearest neighbor was observed. This then corresponds to a STHF of 12 KOe. per $\text{Fe}(\text{A})$ ion or 72 KOe. for the total STHF in $(\text{Fe})[\text{NiFe}]_2\text{O}_4$. Taking a hyperfine field of 555 KOe. for $\text{Fe}(\text{B})$ in NiFe_2O_4 one then expects a hyperfine field of 483 KOe. for ZnFe_2O_4 . This is in good agreement with the value of 485 KOe. as observed for ZnFe_2O_4 (125). Also in the case of $\text{Ca}_2\text{Fe}_{2-x}\text{M}_x\text{O}_5$ (126) where M refers to Ga^{3+} or Sc^{3+} a decrease in hyperfine field at 5°K with increasing x was observed. This effect has also been observed in Ga substituted YIG (127). One must however be careful in interpreting the decrease in hyperfine fields as being solely due to STHF since when diamagnetic ions are substituted for magnetic ones, one can also get changes in the dipole fields.

Also in the case of Ga substituted YIG one can have a non-colinear spin arrangement at high Ga concentrations which will also effect the STHF.

For CoFe_2O_4 and MnFe_2O_4 the situation is slightly more complex because the Co and Mn ions will contribute to the STHF as well as the Fe ions. Here we find a decrease in hyperfine field of 6-10 KOe. per Mn or Co ion. This is consistent with a hyperfine field of 525 KOe. at 0°K for $\text{Fe}^{57}(\text{B})$ in MnFe_2O_4 since the average number of Mn A site nearest neighbors is 4.8. Since in NiFe_2O_4 there are all Fe A site nearest neighbors one would expect a field at $\text{Fe}^{57}(\text{B})$ in MnFe_2O_4 to be $555 - (4.8) 6 = 526 \text{ KOe.}$ in agreement with the observed value. MnFe_2O_4 is perhaps the most suitable to discuss in this way because the Mn^{2+} has the same moment as Fe^{3+} so dipolar effects should be negligible.

Although our results are not accurate enough to compare the superexchange interactions to the STHF it is interesting to note that under certain conditions such a relationship does exist. If we assume that the A-B superexchange interaction is given by 132

$$E \propto A_{\text{O}}^2(\text{A}) A_{\text{O}}^2(\text{B}).$$

$$\text{Then } \frac{E_{\text{Mn} - \text{Fe}}}{E_{\text{Fe} - \text{Fe}}} = \frac{A_{\text{O}}^2(\text{Mn}(\text{A}))}{A_{\text{O}}^2(\text{Fe}(\text{A}))}$$

Assuming the proportionality constants to be the same. The ratio of the two STHF's is also

$$\frac{A_{\text{O}}^2(\text{Mn}(\text{A}))}{A_{\text{O}}^2(\text{Fe}(\text{A}))}$$

This relation of course holds only in the special example where

$\langle p | \phi_{ns}^B \rangle$ is independent of the kind of A site nearest neighbor and $a_{4s}(B)$ is negligible. The ratio of Mn - Fe to Fe - Fe superexchange interactions was found to be 0.66 i.e. see section 8. The ratio of STHF is $\frac{6 \leftrightarrow 10}{12} = 0.5 \leftrightarrow 0.87$

So far we have only considered the B site fields. It is seen from table 9-2 that the A site hyperfine field seems to be insensitive to the kind of B site nearest neighbor. This is rather surprising because the A site has 12 nearest neighbor B site ions and also the Fe - O distance is shorter for the A site so one may expect

$$\langle p | \phi_{ns}^A \rangle > \langle p | \phi_{ns}^B \rangle$$

However the STHF is given by the product

$$\Delta H_{\text{hpf}} \propto \langle p | \phi_{ns}^A \rangle^2 A_O^2(B)$$

We expect again from Fe - O distance considerations that $A_O^2(B) < A_O^2(A)$. It is therefore difficult to say whether or not we would expect $\text{STHF}(A) < \text{STHF}(B)$, this however would be the case if we use Simánek's (128) suggestion that $\langle p | \phi_{ns}^A \rangle \approx \langle p | \phi_{ns}^B \rangle$ which comes about because of the overlap repulsion of the s and p electrons.

So far we have shown that the hyperfine field could be related to the number of magnetic nearest neighbors in the case of diamagnetic substitution. If one could assume that the dipolar fields and contact

Table 9-2

List of A site Fe^{57} hyperfine fields extrapolated
to 0° K for several ferrites.

MaterialH_{hpf}(A) (KOe.)

Li _{0.5} Fe _{2.5} O ₄	518
NiFe ₂ O ₄	515
Ni _{0.9} Zn _{0.1} Fe ₂ O ₄	515
CoFe ₂ O ₄	510
MgFe ₂ O ₄	495, 505
Fe ₃ O ₄	508
MnFe ₂ O ₄	511

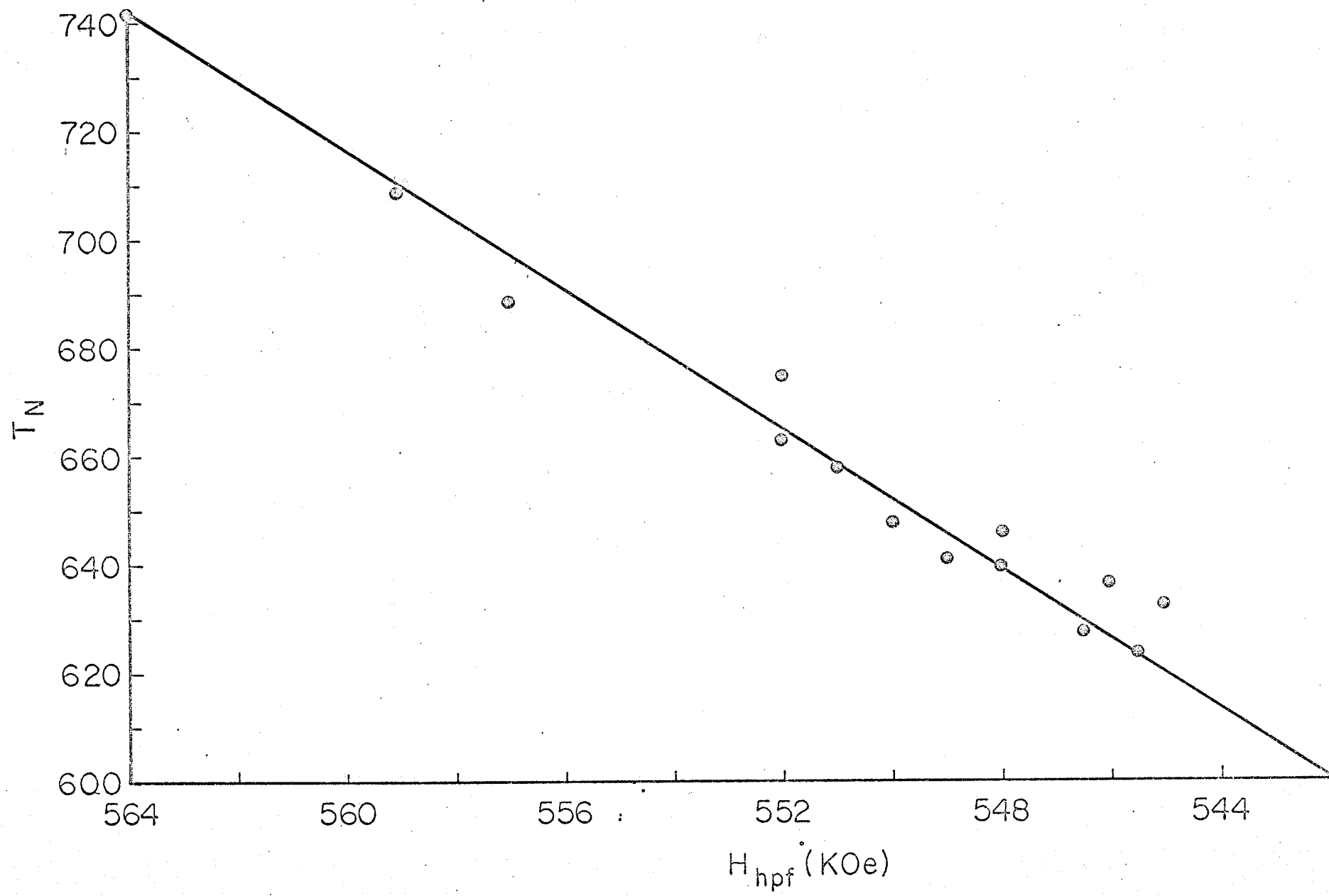
field were independent of the number of diamagnetic nearest neighbors one can determine the STHF by measuring the hyperfine field as the function of the number of diamagnetic nearest neighbors. In the case of MnFe_2O_4 we showed that the STHF field was related to the superexchange interaction if one assumed that the strength of the superexchange interaction was proportional to the product of the covalency factors of the two ions involved.

The ferrites and the diamagnetically substituted garnets are however a special case because only one of the two cations involved in the STHF and superexchange have been changed. The relations between the STHF and the superexchange interactions seems however to be more general. In figure 9-1 we have plotted H_{hpf} versus T_N for the orthoferrites (129). The interesting characteristics are that H_{hpf} decreases in a linear manner with the Néel temperature. Since the isomer shift remains constant in going from La to Lu orthoferrite this decrease in hyperfine field cannot be attributed to an increase in the 4s contribution.

Since it has been shown by Locher et al. (114) that the hyperfine coupling constant is nearly independent of Fe - O distance we conclude that the decrease in hyperfine field is primarily due to a decrease in STHF. As pointed out by Simánek (118) one might expect an increase in going from La to Lu because of the decrease in lattice parameters, which suggests an increase in $\langle \phi_{\text{ns}} | p \rangle$. One must however take into account the angle between the $\text{Fe}_1 - \text{O}$ and $\text{Fe}_2 - \text{O}$ bonds. This angle changes in going from La to Lu and it has been suggested by Eibschütz et al. (129) that this is the cause of the decrease in the superexchange interactions.

Figure 9-1

Plot of the hyperfine field versus T_N for the orthogerrites. The values are taken from ref. 129.



The linear relationship between H_{hpf} and T_N could then be explained if the transfer from $d(M_1)$ to $s(M_2)$ was proportional to the transfer from $d(M_1)$ to $d(M_2)$ where the former is responsible for the STHF and the latter for superexchange. By using this relationship we can calculate STHF for LaFeO_3 by extrapolating H_{hpf} to $T_N = 0^\circ \text{ K}$. This gives us the value of $110 \pm 20 \text{ KOe}$, which is a factor of two larger than that calculated by Simánek (118). This suggests that the assumed linear relationship is probably an oversimplification. That the linear relationship does not work is probably due to the different angular dependence of $\langle p|\phi_{\text{ns}} \rangle$ than the $p \rightarrow d$ transfer.

9.3 Other Contributions to H_{hpf}

Iron ions at A and B sites show many distinct properties viz. $H_{\text{hpf}}(\text{A}) < H_{\text{hpf}}(\text{B})$, $\text{IS}(\text{A}) < \text{IS}(\text{B})$, $f_A > f_B$ and also the iron oxygen distances in the tetrahedron are shorter than in the octahedron. This is frequently expressed by calling the A site ions more covalent. Van Loef (61) has interpreted the differences between A and B sites using volume and pressure effects. We prefer to discuss these from different aspects of covalency.

It may be mentioned that overlap and covalency have different effects on the spin density, which means that $\langle S_z \rangle$ may also depend on the degree of covalency. This of course will be reflected in H_{hpf} since $H_{\text{hp}} = A\langle S_z \rangle$.

Another aspect of covalency viz. the influence of overlap has been emphasized by Marshall and Stuart (130). The overlap of the 2p ligand electrons and the 3d metal electrons produce a 2p electron density at the metal nucleus. This effect screens the 3d electrons from the parent nucleus and these will consequently move radially outwards. In this picture $r_{\max}$ (3d) is larger for A site ions than for B site ions. It is difficult to estimate what the results on $H_{\text{hpf}}(\text{A})$ and $H_{\text{hpf}}(\text{B})$ will be. The 1s and 2s contributions will become smaller negative and the 3s contribution smaller positive or even negative for the A sites. Because $r_{\max}$ (3s) is close to $r_{\max}$ (3d) a change in $r_{\max}$ (3d) may be more strongly reflected in the 3s contribution. This however would result in a larger negative field at the A sites, in disagreement with the experimental results. On the other hand the effect on the isomer shift would be correct. A more delocalised 3d electron cloud at the A site will produce weaker shielding for the s electrons, so a higher s electron density will be measured.

Simánek and Sroubek (128) have calculated from IS data the electronic configurations $3d^5 4s^0$ and $3d^5 4s^0$ for B and A site Fe^{3+} ions respectively. Interpreting these densities in STHF terms as originating from a direct $3d(M_1) \rightarrow 4s(M_2)$ and $3d(M_2) \rightarrow 4s(M_1)$ spin transfer would give $|H_{\text{hpf}}(\text{A})| > |H_{\text{hpf}}(\text{B})|$. This is in contradiction with the observed fields. However in addition to the above mentioned and the $2p(L) \uparrow \rightarrow 3d(M) \downarrow$ spin transfers there are also spin transfers to the 4s(M) orbits possible. Let us assume that $2p \uparrow(L) \rightarrow 4s \uparrow(M)$ and $2p \downarrow(L) \rightarrow 4s \downarrow(M)$ are equally probable. Thus from the contribution to the

contact field as calculated by Watson and Freeman (19) we estimate a value of +1000 KOe. for a closed 4s shell i.e. for two electrons. Consequently the 4s electrons contribute + 100 and + 160 KOe. to H_{hpf} for B and A sites respectively. The difference in 4s contributions together with the difference in STHF could explain the observed difference. Combining the estimated contributions from STHF and the 4s electrons we obtain from the measured effective fields the Fermi contact contributions $H_c(A) = - 590$ KOe. This value comes close to $H_{\text{hpf}} = - 630$ in FeF_3 (131) a highly ionic material and consequently with much smaller covalency effects.

For the garnets we found that the difference in A and B site isomer shifts was about 0.21 mm/sec. This is considerably larger than the difference of 0.13 mm/sec found for NiFe_2O_4 . We thus expect that the electronic configuration is $3d^5 4s^{0.4}$ for Fe^{3+} in tetrahedral sites of the garnets. Since the isomer shift of the octahedrally situated nuclei in the garnets is approximately the same as that for the ferrites we expect the electronic configuration of these ions to be $3d^5 4s^{0.20}$. The difference in the A and B site hyperfine fields would then be 100 KOe. This value is in reasonable agreement with the value of 90 KOe. we obtained for YIG.

We think that an important conclusion from the discussion on the differences between A and B site properties is that the occupation of the 4s(M) levels explains qualitatively the differences in H_{hpf} . This aspect of covalency viz. the $2p(L) \rightarrow 4s(M)$ spin transfer has usually been neglected.

In the discussion of STHF we have assumed that the superexchange interaction is proportional to the product of the covalency factors of the two ions involved. If this would be so simple then one would expect an increase of T_{FN} in going from fluorides via oxides, sulfides to chlorides and so on. In this sequence the tendency to transfer electrons to the metal ions increases. Consequently the covalency and also T_{FN} increases. It is well known however that this is not the general trend in fact only the oxides have a higher T_{FN} than the fluorides. Here it seems indeed correct to consider the metal-oxygen bonds more covalent than the metal-fluoride bond. However the effective fields are larger negative in the fluorides compared to the oxides.

As we have shown in the foregoing paragraph not only the overlap and covalency between $3d(M)$ and $2p(L)$ electrons are larger in more covalent materials but also the transfer $2p(L) \rightarrow 4s(M)$ is larger causing a decrease in H_{hpf} .

The breakdown of the covalency superexchange relation for more polarizable ligands is evident. This breakdown may be due to several effects. First, in going to more polarizable ligands the π bonding will increase as well as the σ bonding. This can eventually lead to ferromagnetism if the π and σ bonding become comparable. Also the $2p \rightarrow 4s$ transfer will increase in going to more polarizable ligands which will decrease the hyperfine fields and the isomer shift. Also the s electrons in the $4s$ level can eventually form a conduction band which can lead to a ferromagnetic direct exchange interaction via s - d exchange. This may lead to metamagnetism as in $FeCl_3$, or even ferromagnetism as in $MnSb$.

9.4 Summary of Various Contributions to the Hyperfine Field

The hyperfine field at 0° K of Fe^{3+} in antiferromagnetic insulators will be due to several contributions, first of all there is the contact term $H = A\langle S_z \rangle$ which takes into account zero point spin deviations and also the spatial d electron spin distribution. The latter will depend on covalency and overlap between the d orbits and the ligand. The effect of this delocalization of the electrons is difficult to estimate because as was pointed out above, there will be both positive and negative contributions.

Another contribution to the hyperfine field is the STHF. This we have shown is related to the superexchange since both effects depend on the $L \leftrightarrow d$ spin transfer. In the case of diamagnetic substitution the STHF would be simply proportioned to the number of nearest neighbor magnetic ions. In this case diamagnetic substitution can provide us with a means for measuring the STHF.

Another contribution to the hyperfine field is the contact field produced by spin polarization of the 4s electrons. These 4s electrons come from $p \rightarrow 4s$ transfer. The effect of this can be found from the IS data which provides, in principle at least, a measure of the number of 4s electrons present.

CHAPTER 10

Summary of Conclusions and Suggestions for Further Investigations

10.1 Summary of Conclusions

1. We have shown in section 3 that the recoilless fractions for Fe^{57} nuclei in A and B sites in both Fe_3O_4 and YIG are different. The values we obtained for $\frac{f'_B}{f'_A}$ at various temperatures can be used in conjunction with area ratio measurements to determine the cation distribution in ferrites and garnets. We also describe a method of obtaining the cation distribution in crystallographically inequivalent sites without knowledge of the ratio of recoilless fractions. This is done by extrapolating high temperature measurements ($T > \theta_D$) of the area ratios to 0° K . In this way the zero point motion of the nucleus is corrected for.

2. In section 4 we have shown that the hyperfine coupling constant for iron ions in both A and B sites of Fe_3O_4 is temperature independent over a 500° K temperature interval. This is done by comparing the Mössbauer effect hyperfine field data to the sublattice magnetization as determined by neutron diffraction measurements.

Since the crystal structure of other ferrites is similar to that of Fe_3O_4 , we use this result to determine in part the sublattice magnetizations in other ferrites.

3. In section 5 we have shown that NiFe_2O_4 is an inverse spinel and the Mössbauer spectrum can be explained in terms of two six line hyperfine patterns corresponding to Fe^{57} in A and B sites.

4. In section 6 we have shown that CoFe_2O_4 is not a completely inverse spinel and that the degree of inversion depends on the heat treatment. The usefulness of the Mössbauer effect in determining the cation distribution is displayed. The cation distribution is found for two materials which have experienced different heat treatment. Magnetic moment measurements together with the measured cation distribution are used to calculate the magnetic moment of $\text{Co}^{2+}(\text{B})$. The low value of $3.1 \leftrightarrow 3.2 \mu_B$ is explained in terms of covalency effects on the effective orbital angular momentum and the reduction of the spin contribution due to spin orbit coupling.

5. The cation distribution of MnFe_2O_4 is found using the Mössbauer effect. The distribution obtained agrees with that found by neutron diffraction techniques.

6. Mössbauer spectra of MnFe_2O_4 at 7°K in an applied field of 55 KOe. show no evidence of any Fe^{2+} in the B sites. These spectra also show no evidence of a $\Delta m = 0$ transition. Therefore it is concluded that the low observed magnetic moment cannot be explained by the presence of Fe^{2+} or by a canting of the $\text{Fe}(\text{B})$ spins with respect to the $\text{Mn}(\text{A})$ spins.

7. Using free energy calculations we have shown that a spin arrangement where the $\text{Fe}(\text{B})$ and $\text{Mn}(\text{A})$ moments are nearly colinear and the $\text{Mn}(\text{B})$ moments make an angle θ with respect to these is energetically possible. In order to stabilize such a ground state, however, the $\text{Fe}(\text{B})$ moments must make a small angle with respect to the $\text{Mn}(\text{A})$ moments. In order to justify this model we need, however, information about the

Mn(A) - Mn(B) and Mn(B) - Fe(B) superexchange interactions.

8. The broadening of the B site lines in CoFe_2O_4 and MnFe_2O_4 is explained as being due to several kinds of A site ions. The details of these spectra can be explained by assuming several different B site lines with intensities proportional to the probabilities of having various distributions of A site nearest neighbors.

9. From the temperature dependence of the various B site hyperfine fields and also of the A site hyperfine fields we have calculated the Fe(A) - Fe(B), Co(A) - Fe(B) and Mn(A) - Fe(B) superexchange interactions using a simple extension to the molecular field theory.

10. The distribution in B site hyperfine fields at 0°K can be explained by using super-transferred hyperfine fields which are dependent on the amount of spin transferred from the ligand to an A site ion. The amount of spin transferred will depend on the type of A site ion so that the B site hyperfine field will depend on the kind of nearest neighbor A site ions it has.

11. It is shown that reasonable values for STHF can be found by measuring the hyperfine field at 0°K as a function of the amount of substitution of magnetic ions by diamagnetic ions. It is also shown that under certain conditions the STHF can be used as a measure of the superexchange interaction. This property is used to attempt to explain the hyperfine field data at 0°K for the orthoferrites.

12. It is shown that the difference in hyperfine fields at 0° K of Fe^{57} in A and B sites can be explained at least in part by the presence of 4s electrons transferred from the ligand. A measure of the number of 4s electrons can be obtained from the isomer shift data.

10.2 Suggestions for Further Investigations

Since the ferrites and garnets are quite complicated systems as far as the Mössbauer effect is concerned a lot of the data cannot be obtained accurately enough to discuss the hyperfine fields at 0° K quantitatively. It would be interesting to study simpler systems like say $(\text{Rh}_2\text{O}_3)_x (\text{Fe}_2\text{O}_3)_{1-x}$ where the Mössbauer spectrum is quite simple and the lines in pure Fe_2O_3 are quite narrow. A study of this system at low temperatures should yield information about STHF since as found in the ferrites the hyperfine field depends on the number and kind of nearest neighbors.

Since this would be an obvious suggestion for further study it should be pointed out here that we have also studied MgFe_2O_4 and $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ for $x = 0.25$ and 0.50 . The Mössbauer spectra are however very complicated in that the A site lines are also broadened especially at higher temperatures. Qualitatively the spectra could be explained in the same way as was done for CoFe_2O_4 and MnFe_2O_4 .

A more detailed study of the temperature dependence of the hyperfine fields in ferrites and garnets near the critical point could be quite interesting. The question is do the hyperfine fields at the two sites

eventually have the same temperature dependence and how close to the critical temperature must one be before this is so. Fe_3O_4 and some garnets would be suitable materials for such a study.

I would also like to suggest a careful study of the diamagnetically substituted garnets. The reason for studying these materials is to obtain information about the spin arrangement. With the Mössbauer effect one can obtain the cation distribution and also the average canting angle can be obtained from experiments in an applied field. These data can be easily checked with magnetic moment measurements. A detailed crystallographic and magnetic moment study of some such materials has been made by Geller (133). He found that the experimental data did not agree with the Yafet-Kittel theory. This is not surprising since the Yafet-Kittel theory essentially assumes that all the ions have an average number of magnetic nearest neighbors. The Yafet-Kittel theory will then give the same magnetic moment as the Néel theory until enough magnetic ions have been replaced by diamagnetic ones so that canting can occur. It is easy to see that this theory is not quite correct. Even at a fairly small concentration of diamagnetic ions there is a finite probability that a magnetic ion say in an A site has all diamagnetic nearest neighbors in the B sites. Any ions like this will then have magnetic moments antiparallel to the other A site moments because of the antiferromagnetic A-A superexchange interaction. In an exact theory then one must take into account all the possible combinations of nearest neighbors and take into account that each of these moments can have a different spin orientation when one minimizes the free energy in an attempt to determine the ground state spin arrangement.

It should be mentioned that these experiments would also show whether or not the Gilleo theory (134) is correct. Gilleo assumes that any magnetic ion in the A or B site with only zero or one magnetic nearest neighbors in the B or A sites respectively will be paramagnetic. One should then observe a paramagnetic peak in the Mössbauer spectrum the intensity of which would be proportional to the sum of the probabilities that an ion has zero or one magnetic nearest neighbors. The Gilleo theory is however based on the assumption that the intrasublattice exchange interaction is zero which is probably not the case for most ferrites and garnets.

APPENDIX A

Here we have tabulated the probabilities that an ion has I nearest neighbor ions of type 1 and $6 - I$ nearest neighbors of type 2. The probability is given by :

$$P(I) = \frac{6!}{(6-I)! I!} (1-x)^{6-I} x^I$$

where x is the concentration of ions of type 1.

P(I)

<u>x</u>	<u>I=0</u>	<u>I=1</u>	<u>I=2</u>	<u>I=3</u>	<u>I=4</u>	<u>I=5</u>	<u>I=6</u>
0.02	0.89	0.11	0.055	1.5 -04	2.4 -05	1.9 -08	6.4 -11
0.04	0.78	0.20	0.020	1.1 -03	3.5 -05	5.9 -07	4.1 -09
0.06	0.69	0.26	0.042	3.6 -03	1.7 -04	4.4 -06	4.7 -08
0.08	0.61	0.32	0.069	8.0 -03	5.2 -04	1.8 -05	2.6 -07
0.10	0.53	0.35	0.098	0.015	1.2 -03	5.4 -05	1.0 -06
0.12	0.46	0.38	0.13	0.024	2.4 -03	1.3 -04	3.0 -06
0.14	0.40	0.40	0.16	0.035	4.3 -03	2.8 -04	7.5 -06
0.16	0.35	0.40	0.19	0.049	6.9 -03	5.3 -04	1.7 -05
0.18	0.30	0.30	0.22	0.064	0.011	9.3 -04	3.4 -05
0.20	0.26	0.39	0.25	0.082	0.015	1.5 -03	6.4 -05
0.22	0.23	0.38	0.27	0.10	0.021	2.4 -03	1.1 -04
0.24	0.19	0.37	0.29	0.12	0.029	3.6 -03	1.9 -04
0.26	0.16	0.35	0.30	0.14	0.038	5.3 -03	3.1 -04
0.28	0.14	0.33	0.32	0.16	0.048	7.4 -03	4.8 -04
0.30	0.12	0.30	0.32	0.19	0.060	0.010	7.3 -04

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