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THE MAGNETIC PROPERTIES OF IRON-ZINC FERRITES

by

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ABSTRACT

Experimental studies of the magnetic properties of mixed Fe-Zn ferrites of the form $Zn_xFe_{3-x}O_4$ are presented. Magnetization measurements were performed as a function of temperature, field, and composition. The value of the moments on different sites of the compound was determined. Mössbauer measurements were taken for various temperatures and fields in order to obtain the temperature and field dependance of the canting angle and hyperfine fields. Relaxation effects were observed for x = 0.8 well below the ordering temperature. These effects were found to be suppressed in a magnetic field.

A modifies version of the localized canting model which considers second and third nearest neighbour interactions for some cases was developed. This model was used with the Mössbauer data to provide a fit of the spin structure to the bulk magnetic properties of the material.

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CHAPTER 1

1-1. INTRODUCTION

Mixed Zn ferrites of the type $Zn_x M_{3-x} O_4$ where M is a magnetic ion have been the subject of numerous investigations in the past, especially with regard to their magnetic properties [1,2]. The metallic ions occupy the tetrahedral A or octahedral B sites in the spinel crystal structure. The Zn ions preferentially occupy the A sites because of their tendency to form covalent bonds involving sp^3 orbitals. The magnetic moments at x = 0 on the A sites are aligned anti-parallel while those on the more numerous B sites are parallel to the magnetization direction. Therefore, the substitution of diamagnetic Zn ions for the M ions on the A sublattice is expected to result in an increase in the magnetic moment of the sample at 0K proportional to the amount of substitution. Such is indeed the case in the region where $x < 0.5$, although the increase is less than expected if free ion magnetic moments for the M ions are assumed. At higher Zn concentrations, i.e., $x \gtrsim 0.5$, the moment begins to decrease and for x = 1.0, an antiferromagnetic structure is observed.[3] Several explanations have been offered for the behaviour of the magnetization for $x \gtrsim 0.5$,[4,5,6] but spin canting has been determined to be primarily responsible. The canting angles have been measured for several systems using

the neutron diffraction[7] or the Mössbauer effect techniques.[8,12] By using the measured values of the canting angles it is possible in principle to fit quantitatively the magnetization results. No such work has yet been done. Magnetization results and Mössbauer results have primarily been determined for different samples, and at differing temperatures and fields. A study to fit quantitatively the canting angles should allow a decision on whether or not the spin canting is solely responsible for the magnetization behaviour. It should be noted that a Mössbauer study can only give information about canting of the Fe magnetic moments. Therefore, the only mixed Zn system for which a correlation between magnetization and Mössbauer effect measurements is possible is the $Zn_x Fe_{3-x} O_4$ system.

Another interesting phenomenon in mixed Zn ferrites is the occurence of relaxation effects in the Mössbauer spectra. This is usually explained as being caused by ionic spin flipping[8,13]; however, superparamagnetic clusters[6] and domain wall oscillations[14,15] have also been proposed. Frequently, one finds that the Curie temperatures, as measured by the Mössbauer effect, neutron diffraction, and magnetization measurements, differ from each other.[16-23] This is probably correlated with the relaxation phenomena in the high Zn region, and the measurement time for each technique.

The present study consists of magnetization and Mössbauer effect measurements for ferrites of the type

$$[Zn_x^{2+} \; Fe_{1-x}^{3+}] \; (Fe_{1-x}^{2+} \; Fe_{1+x}^{3+}) \; O_4$$

The system was first studied by Stuijts et al[24] for $x \lesssim 0.7$. As with other mixed Zn ferrites, the magnetization M was shown to increase with increasing x until $x \simeq 0.5$ after which it began to decrease. Also of interest was a peak in the magnetization versus temperature curve for $x = 0.7$ at 40K. Similar peaks were also observed by Ishikawa[6] in the Ni-Zn system. This maximum has not yet been explained.

A more recent study has been published by Srivastava et al[14,15] on samples with $x = 0.0, 0.2, 0.4, 0.6$, and 0.8. Their work showed magnetization results from 77K and 300K, and permeability spectra at 300K. The primary focus of their study was the relaxation phenomena which were found to occur well below the Curie temperature at the higher Zn concentrations ($x > 0.5$). These samples were prepared in a way similar to those of Stuijts et al[24], and were generously made available to us for the present study. X-ray diffraction techniques showed the samples to be free of impurity phases. The lattice parameters were measured using a Debye-Scherrer powder diffraction camera, and are plotted as a function of Zn concentration in fig. 1.1. The linear increase in lattice

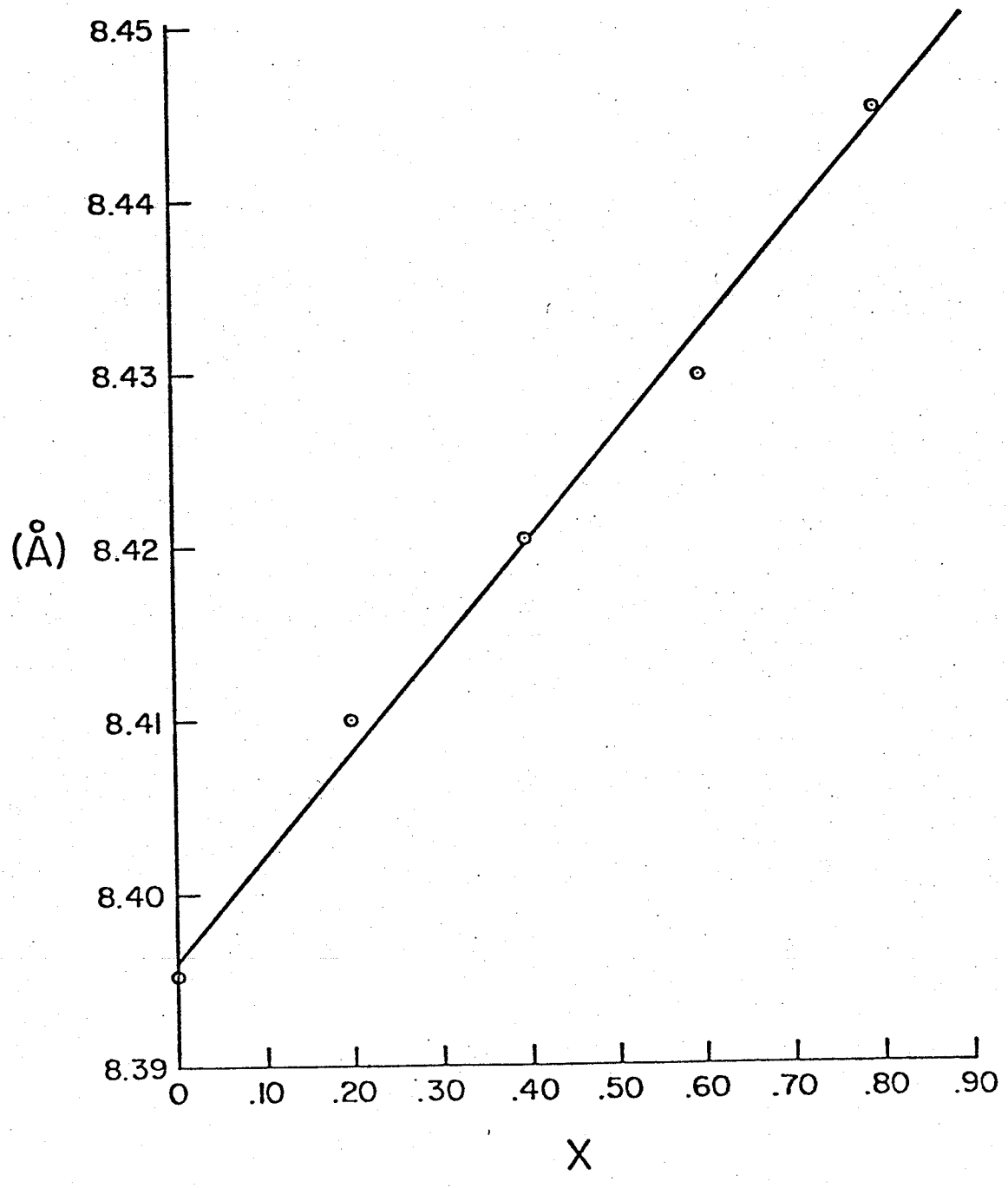

Fig. 1.1 Lattice parameter as a function of Zn concentration.

parameter with Zn concentration derives from the larger size of the Zn^{2+} ions as compared to the Fe^{3+} ions. The high angle lines were not broadened, indicating that the samples had a uniform Zn distribution. This thesis will compare our measured magnetization values with those calculated from the microscopic spin structure as determined from our Mössbauer study.

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CHAPTER 2

THEORY

2-1. FERRIMAGNETISM IN FERRITES.

Ferrimagnets are ordered magnetic materials having two or more lattices antiferromagnetically aligned with a larger moment in one direction than the others. Ferrites, of which $[Fe^{3+}]\ (Fe^{2+}\ Fe^{3+})\ O_4$ is an example, are a class of ferrimagnetic metal oxides possessing a spinel structure. In this structure, metal ions occupy two different types of sites: A sites, indicated with brackets [ ]; and B sites, indicated with parentheses ( ). The A sites are tetrahedrally coordinated, and the B sites, of which there are twice as many occupied, are octahedrally coordinated as shown in figs. 2.1a and 2.1b.

The exchange interactions in the two lattices can be represented with 3 exchange parameters: J_{AB}, the intersublattice exchange parameter; and J_{BB} and J_{AA}, the intrasublattice exchange parameters. The molecular field for a spin on the ith lattice can then be written as

$$\vec{H}_i = \frac{2}{g\mu_B} \left(\vec{S}_j J_{ij} + \vec{S}_i J_{ii}\right)$$

where $\vec{S}_i$ and $\vec{S}_j$ represent the sum of the 6 neighbouring moments on either lattice, i.e.:

$$\vec{S}_A = \frac{6\mu_\alpha}{g\mu_B} \quad ; \quad \vec{S}_B = \frac{6\mu_\beta}{g\mu_B} \ .$$

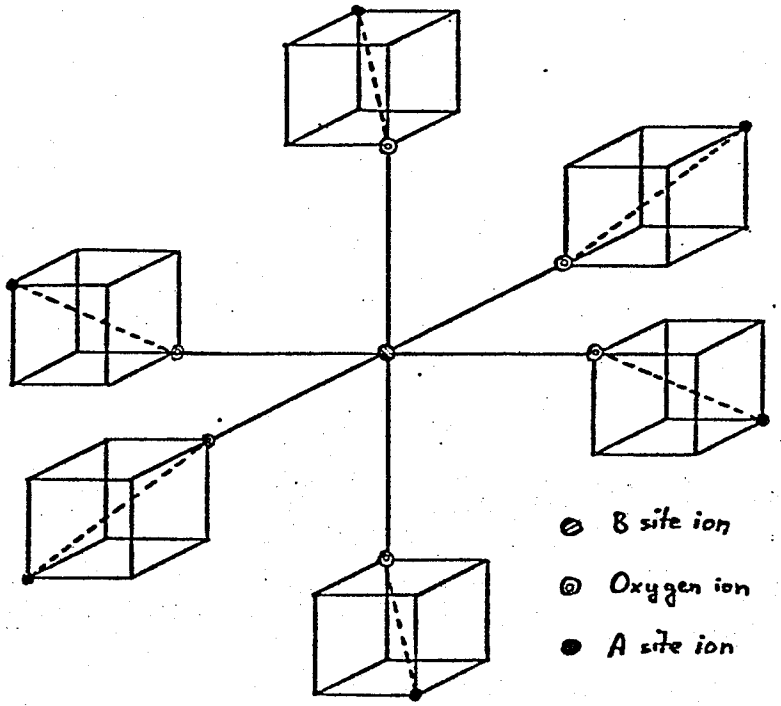

Fig. 2.1a Central B-site iron ion in a spinel structure surrounded by the six nearest oxygen ions and the six nearest A-site metal ions.

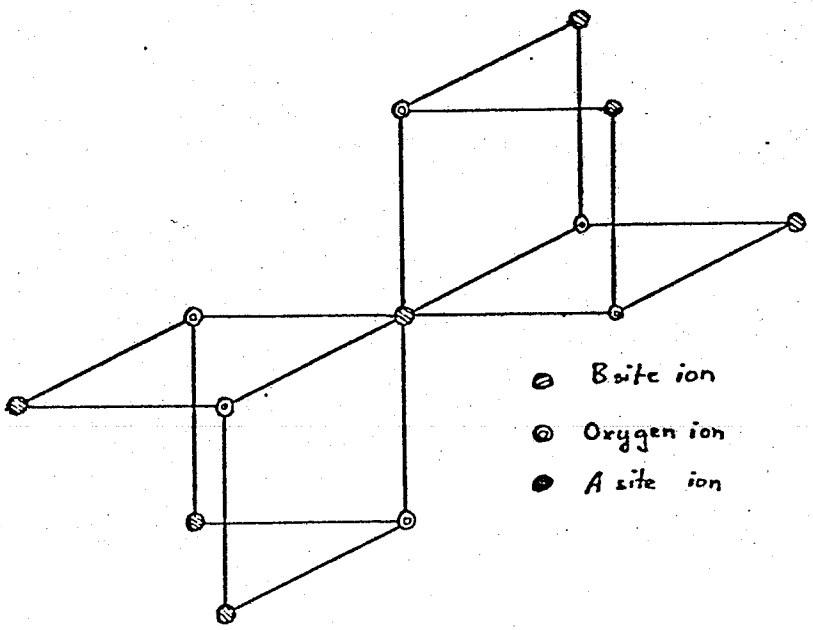

Fig. 2.1b Central B-site iron ion in a spinel structure surrounded by the six nearest oxygen ions and the six nearest B-site iron ions.

Here μ_α and μ_β are the magnetic moments of spins on the A and B lattices respectively. From the chemical formula of the example above, and using the free ion magnetic moments of $5\mu_B$ for Fe^{3+} ions and $4\mu_B$ for Fe^{2+} ions, we get $\mu_\alpha = 5\mu_B$ and $\mu_\beta = 4.5\mu_B$. As $|J_{AB}| > |J_{BB}| > |J_{AA}|$, and the exchange parameter J_{AB} is negative because of the antiferromagnetic nature of the superexchange interaction in ferrites, the two sublattices are arranged in an antiparallel fashion as shown in figure 2.2.

In $[Zn^{2+}_{x}\ Fe^{3+}_{1-x}]\ (Fe^{2+}_{1-x}\ Fe^{3+}_{1+x})O_4$, diamagnetic Zn^{2+} ions are randomly substituted onto the A sublattice, resulting in a change in $\vec{S}_A$ and $\vec{S}_B$, and in a breaking of exchange interactions. Geller et al[1] proposed that random canting occurred on the unsubstituted lattice under these conditions, on the basis of their experimental data. This proposal was mathematically developed by Rosencwaig[2], and is outlined here.

Random substitution of diamagnetic ions is assumed on the A site, and some average canting angle ϕ, with respect to the magnetization direction, is assumed for the B site. This allows us to write the local molecular field for a given B site ion called B_i, as

$$\vec{H}_i = \frac{2}{g\mu_B}\left(\vec{S}_A\, J_{AB} + \vec{S}_B\, J_{BB}\right).$$

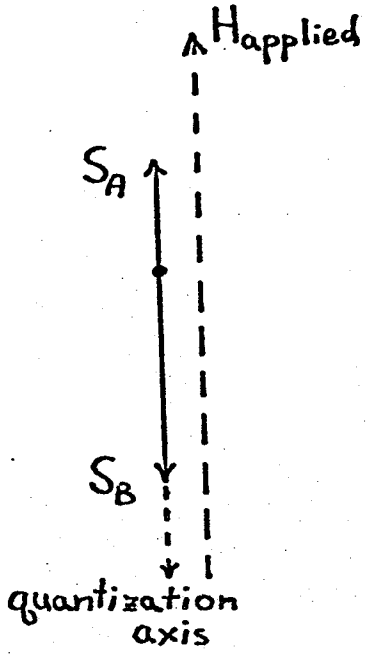

Fig. 2.2 Ferrimagnetic spin structure of Fe_3O_4.

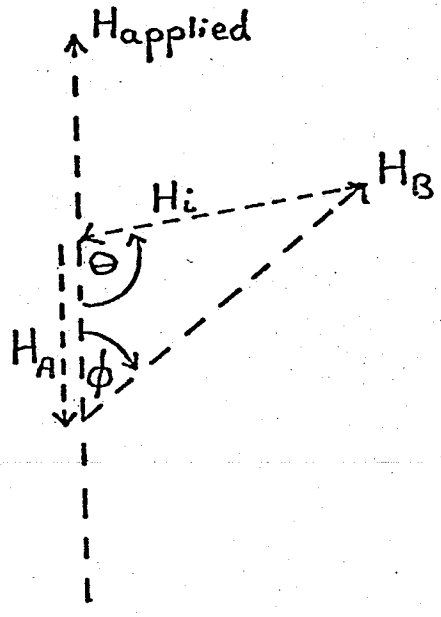

Fig. 2.3a Angular relationship between magnetic and hyperfine fields.

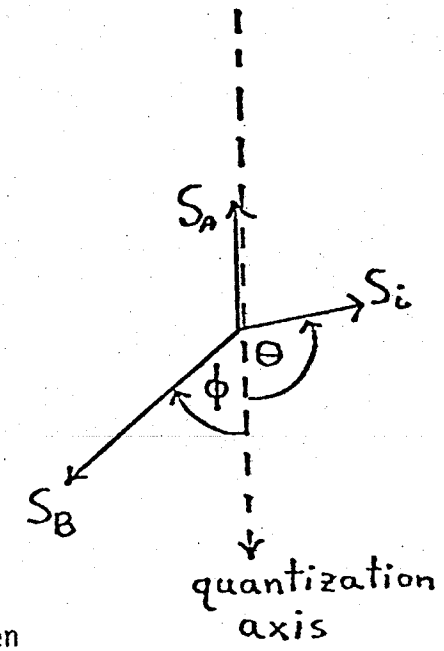

Fig. 2.3b Angular relationship of spins in fields of fig. 2.3a.

Since there is diamagnetic substitution on the A lattice, we may write

$$|\vec{S}_A| = \frac{(6-m)\mu_\alpha}{g\mu_B}$$

where m is the number of neighbouring A sites occupied by diamagnetic ions. Similarily, we have

$$|\vec{S}_B| = \frac{6\mu_\beta(x)}{g\mu_B} ,$$

where

$$\mu_\beta(x) = (1-x)\ \mu_\beta^{2+} + (1+x)\ \mu_\beta^{3+} ,$$

and μ_β^{2+} and μ_β^{3+} represent the moments of the B site Fe^{2+} and Fe^{3+} ions respectively. In fig. 2.3a, $\vec{H}_i$ as well as the component terms $\vec{H}_A$ and $\vec{H}_B$ are shown. The resultant spin structure, with the moment S_i taking a canting angle of θ with respect to the magnetization direction, is shown in fig. 2.3b. By using fig. 2.3a, and the formula for the local molecular field, we may write

$$\cos\theta = \frac{S_A - S_B\delta\cos\phi}{[S_A^2 + (S_B\delta)^2 + 2S_A S_B\cos\phi]^{\frac{1}{2}}}$$

where

$$\delta = \frac{J_{BB}}{J_{AB}} .$$

It is clear that θ can take on any value between 0^0 and 180^0 depending on the value of the term $S_A - S_B\delta\cos\phi$. If

$S_A > S_B\delta \cos \phi$, i.e., if the net intersublattice interaction on a spin is greater than the net intrasublattice interaction, then θ will be smaller than the average canting angle ϕ. If $S_A < S_B\delta \cos \phi$, then θ will be larger than the average canting angle ϕ, and if $S_A = 0$, then the B_i spin will be aligned antiparallel to the B sublattice and the magnetization direction.

In order to calculate any bulk properties of the mixed Zn ferrite, we must calculate the probability of a spin having m of its six A sites occupied by Zn^{2+} ions. This is determined by the binomial distribution:

$$P(x,m) = \binom{6}{m} x^{6-m} (1-x)^m$$

which allows us to write the 0 K magnetic moment as

$$\mu(x,T=0) = 2\sum_{m=0}^{6} P(x,m) \cos [\theta(x,m)]\mu_\beta(x)-(1-x)\mu_\alpha .$$

The first term indicates the decrease in moment due to random canting on the B sublattice, and the second represents the increase in moment due to diamagnetic substitution on the antiparallel A sublattice.

This model has been successfully applied to the substituted Yttrium Iron Garnets, and gives a qualitative agreement with the experimental data for Zn substituted ferrites. Neutron diffraction[3] and Mössbauer effect[4] data show canting angles in these systems for Zn substitution in excess of $x \simeq 0.5$.

However, no quantitative correlation has been published as yet. Reasons for this include the facts that magnetization, neutron diffraction and Mössbauer results have largely come from different samples. Also, canting angles, as determined by the Mössbauer effect, have been measured in relatively large fields and not compared with magnetization results in the same field.

2.2 MODEL REVISIONS

The major flaw of the localized canting model is that only first nearest neighbour interactions are considered. In most cases, this is a justifiable approximation, but for cases in which there are spins having canting angles $\theta > 90^0$, a revision is required, considering second and even third nearest neighbour interactions.

Spins which have canting angles $\theta > 90^0$ will be referred to as "reversed" spins. If all or nearly all of the B site neighbours of one of these reversed spins are themselves reversed, then that spin will have been reversed twice. Similarily, if all the neighbours to a reversed spin are themselves doubly reversed, that spin will have been triply reversed. Since $|J_{AB}|$ is known to be much larger than $|J_{BB}|$ we will assume that only those spins with all six nearest neighbour A sites occupied by Zn ions can be reversed. The probabilities for such multiple reversals occurring are higher than might at first be expected. This is because the B site nearest neighbours of a spin having six

Zn A site nearest neighbours each have three Zn A site nearest neighbours which are shared with the central spin. The remaining A site neighbours are shared among each other. The calculations for multiple reversal (single and double reversal for x = 0.6 and single and triple reversal for x = 0.8) are given in Appendix A, where the notation used in the following discussion is defined. The probabilities for multiple reversals are extremely small for all other cases. The results of these calculations are as shown in table 2.1.

TABLE 2.1

Multiple reversal probabilities for x = 0.6 and x = 0.8.

Sample	Unreversed (B_0-B_5)	Single Reversal B_6	Double Reversal B_6	Triple Reversal B_6
x = 0.6	0.95334	0.04274	0.00392	---
x = 0.8	0.73786	0.15219	0.08121	0.02874

This allows determination of the total number of spins reversed or unreversed with respect to the magnetization direction, as shown in table 2.2.

TABLE 2.2

Probabilities for reversed and unreversed spins in samples with x = 0.6 and x = 0.8.

Sample	Unreversed (B_{05})	Reversed (B_6')	Unreversed (B_6)
x = 0.6	0.95334	0.00392	0.04274
x = 0.8	0.73786	0.08121	0.18093

The bulk magnetic moment at T = 0 K may now be written as

$$\mu(x,T=0)= \sum_{m=0}^{5} \{P(m,x)\cos[\theta(m,x)]+P(6',x)\cos[\theta(6',x)] + P(6,x)\cos[\theta(6,x)]\}2\mu_\beta-(1-x)\mu_\alpha$$

One would expect $\theta(6,x)$ to be quite close to zero, since the only interaction that a B_6 site has is with B_6' sites, each having the same canting angle with respect to the quantization axis. An average of the six B_6' spins, will therefore be of the form:

$$\overline{S}_{6'} = S\,\frac{\cos\theta}{6}\sum_{i=1}^{6}\cos\psi_i\,\hat{x} + S\,\frac{\cos\theta}{6}\sum_{i=1}^{6}\sin\psi_i\,\hat{x} + S\sin\theta\,\hat{y}.$$

Since the spins will be randomly distributed over the azimuthal angle ψ_i, the first two terms will be close to zero.

This analysis will be used in Chapter 5 of this thesis to compare the Mössbauer and magnetization results.

2.3 MÖSSBAUER EFFECT

General Theory

The energy difference for a given nuclear transition is a well defined quantity, but in general, the energy distribution of gamma rays emitted or absorbed in such a transition is quite broad due to the recoil of the nucleus involved. In solids however,