THE UNIVERSITY OF MANITOBA

LOW TEMPERATURE NUCLEAR MAGNETIC RESONANCE

AND RELAXATION IN MANGANESE FERRITE
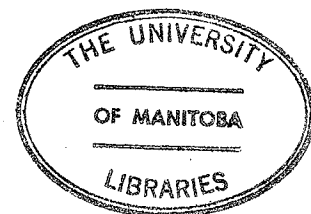

by

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PREFACE

The ^{55}Mn nuclear magnetic resonance of the A-site ions in manganese ferrites provides an opportunity to study many of the features characteristic of magnetic materials. The strong signal and the cubic symmetry of the A-sites make this a relatively easy system to study although the presence of two strongly overlapping signal components and the fairly complex structure of the spinel lattice result in some difficulty in the interpretation of the spectra.

Nuclear magnetic resonance in ordered magnetic materials has many distinctive features and some special problems, these are discussed in Chapter I, as an introduction, with particular reference to the properties of manganese ferrites. The strong magnetic hyperfine interaction, the spin-wave interactions, and the existence of domain-walls lead to most of the interesting properties of this system, including the Suhl-Nakamura or indirect nuclear spin-spin interaction, spin-wave relaxation processes, and the contrast in the behaviour of the two components of the signal (due to nuclei in domains and in domain walls).

Chapter II gives a detailed discussion of the Suhl-Nakamura interaction with particular reference to its role in the formation of multiple echoes following a two pulse rf excitation of the spin system.

Chapter III is a general discussion of relaxation processes in magnetic materials, including dipole-dipole and spin-wave relaxation as well as the dominant Suhl-Nakamura relaxation. The frequency dependent relaxation due to the Suhl-Nakamura interaction is compared to the experimental data for the first three echoes, followed by a discussion of the two-component nature of the spectrum in low external fields.

Chapter IV discusses and compares the temperature and field dependences of the two components of the spectrum. The technique of fitting a set of partially relaxed spectra to a function (made up of two independently relaxing components) of two independent variables, frequency and rf pulse separation, allows the effective separation of the spectrum into its domain and domain-wall components.

Finally, Chapter V gives a brief discussion and conclusion, pointing out some areas where the techniques used here may be usefully applied.

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ABSTRACT

The A-site ^{55}Mn nuclear magnetic resonance at low temperatures con-
sists of two overlapping signal components, one due to nuclei within the
domain walls, the other due to nuclei within the bulk domains. The reson-
ance is inhomogeneously broadened and characterized by strongly frequency
dependent relaxation. Two-pulse spin-echo measurements show that the Suhl-
Nakamura or indirect spin-spin interaction is responsible for most of the
low temperature relaxation near resonance, and provides a mechanism for the
formation of multiple echoes. By studying a series of partially relaxed
spectra it is possible to separate the two signal components leading to
the observation of the different temperature dependences of the frequency-
independent part of the relaxation of the two components. This difference
is felt to be due to the narrowing of the longitudinal dipole-dipole inter-
action's contribution to the homogeneous linewidth of the domain-wall com-
ponent but not of the domain component. Spin-wave scattering, in particu-
lar the dipolar-induced two-magnon process, provides the strongly tempera-
ture dependent contribution to the total relaxation rate.

CHAPTER I

Introduction to NMR in Magnetic Materials

The features that distinguish the nuclear magnetic resonance in magnetic materials from that in other solids are: i) the presence, in the ordered state, of strong magnetic hyperfine fields ($\sim 10^5 - 10^6$ Oe), ii) the distribution of these hyperfine fields and the subsequent severe broadening of the resonance lines, iii) the existence of domain walls in non-saturated samples and the complicated enhancement mechanisms associated with these domain walls, iv) the possibility of the existence of two signal components--one from domain walls, the other from the bulk domains--which strongly overlap each other, and v) the interaction of the nuclear spins with unpaired electronic spins or, in the ordered state, with spin waves. These strictly magnetic effects profoundly alter the nature of the nuclear resonance and, therefore, must be carefully considered and understood before any analysis of the spectra can be attempted.

1. Manganese Ferrite

Manganese ferrite ($MnFe_2O_4$) is a magnetic insulator and has the spinel ($MgAl_2O_4$) structure with the magnetic (Mn, Fe) ions located on two crystallographically inequivalent sites, the tetrahedral A-sites and the octahedral B-sites. The ionic distribution has been studied in some detail[1-4] and can be described by the formula unit $Mn^{2+}_{0.8}Fe_{0.2}$ $[Mn^{3+}_{0.2}Fe_{1.8}]O_4$, where the cations outside the brackets occupy the

tetrahedral sites and the cations inside the brackets occupy the octahedral sites. The nuclear resonance of the ^{55}Mn nuclei on the two different sites have been reported and identified[4] as being from Mn^{2+} ions on the A-sites and Mn^{3+} ions on the B-sites. The B-site resonance will be quadrupolar split into $2I = 5$ components due to the non-cubic symmetry of the octahedral sites (the octahedral symmetry does not extend beyond the O^{2-} ions forming the octahedron), while the A-site, due to its tetrahedral symmetry, has a single resonance line. The work reported here is concerned only with the ^{55}Mn resonance from ions on the A-sites.

The spinel A-site, illustrated in Figure 1, is at the center of a tetrahedron formed by four O^{2-} ions. Each of the oxygen ions is connected to three B-site cations (Mn^{3+}, Fe^{3+}) in such a way as to preserve the tetrahedral symmetry of the A-site. Because of this symmetry, the dipolar field at the A-site is expected to be zero, as is the quadrupole splitting. Some small contribution to the local field may exist due to the presence of different ions on the B-sites, however, there is no indication of this in the nuclear resonance data.
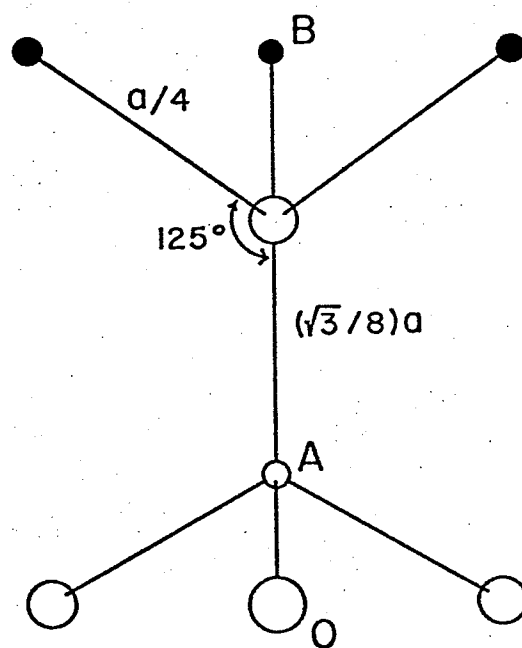
Figure 1. The spinel A-site. Large circles are oxygen ions and the dark circles are B-sites. a = 8.5 Å.

2. The Magnetic Field at the Nucleus

The magnetic field at a nucleus in a magnetic material is the sum of

the externally applied field, the magnetic field due to the distribution
of the magnetic dipoles surrounding the ion containing the nucleus, and
the electronic hyperfine field.

2.1 The dipolar contributions--the Lorentz and demagnetizing fields

The total dipolar contribution to the microscopic magnetic field
at nucleus i in a single domain sample is

$$\vec{h}_{dd} = g\mu_B \sum_j \left(\frac{1}{r_{ij}}\right)^5 (\vec{S}_j r_{ij}^2 - 3\vec{r}_{ij}(\vec{S}_j \cdot \vec{r}_{ij})) \tag{1}$$

where $\sum_j$ is over all spins $\vec{S}_j$ located at position $\vec{r}_{ij}$ with respect to
spin i, g is the electronic spectroscopic splitting factor and μ_B is the
Bohr magneton. (The field due to nuclear dipoles may be neglected.)
This sum may be evaluated by breaking it up into the sums over spins
in two regions separated by a surface, called the Lorentz sphere, such
that the volume enclosed by the sphere is large by atomic dimensions but
small on a macroscopic scale. Then, the sum is evaluated explicitly for
spins inside the sphere and the contribution from spins outside the sphere
can be evaluated as an integral over the volume enclosed by the sample's
surface and the Lorentz sphere. If we define, after Keffer[5]

$$D_V^{IJ} = D_L^{IJ} + D_{V-L}^{IJ} = \sum_\ell (3r_\ell^I r_\ell^J - r_\ell^2 \delta^{IJ}) r_\ell^{-5}$$

for cartesian components I,J of r_ℓ, where D_L^{IJ} is the sum over the interior
of the Lorentz sphere, then,

$$D_{V-L}^{IJ} \rightarrow \delta^{IJ} \int_{V-L} (\partial/\partial r^I)(-r^I/r^3) d\vec{r} = -\delta^{IJ} \int (r^I/r^3)\hat{I} \cdot (d\vec{S}_1 - d\vec{S}_2)$$

where $\delta^{IJ} = 0$ unless I = J, and S_1 is the surface of the sample, and S_2 is

the Lorentz sphere. Then, assuming an ellipsoidal sample,

$$D_{V-L}^{IJ} = (\frac{4\pi}{3} - N^I)\delta^{IJ}$$

The factor $4\pi/3$ is due to the uncompensated poles at the surface of
the Lorentz sphere, while the factor N^I, called the demagnetizing fac-
tor, is due to uncompensated magnetic poles on the surface of the sam-
ple. For a spherical sample, $N^I = 4\pi/3$ and $D_{V-L}^{IJ} = 0$.

The contribution to the field from spins inside the Lorentz sphere
is called the dipolar field and can be readily evaluated by direct sum-
mation over lattice sites. For sites (of the spin i) of cubic symmetry
the dipolar field vanishes.

2.2 The electronic hyperfine field

By far the largest contribution to the magnetic field at the nucleus
is the field produced by it's ion's own electrons--the electronic hyper-
fine field. The magnetic hyperfine interaction can be written as[6]

$$\mathcal{H}_{hf} = - gg_N\mu_B\mu_N \sum_i \left(\frac{8\pi}{3} \delta(r_i)\vec{S}_i\cdot\vec{I} + \frac{(\vec{L}_i - \vec{S}_i)\cdot\vec{I}}{r_i^3} + \frac{3(\vec{S}_i\cdot\vec{r}_i)(\vec{I}\cdot\vec{r}_i)}{r_i^5} \right) \quad (2)$$

where g_N is the nuclear spectroscopic splitting factor, μ_N is the nuclear
magneton; $\vec{L}, \vec{S}, \vec{I}$ are the electronic orbital angular momentum, electronic
spin, and nuclear spin, respectively; r_i is the distance of the ith elec-
tron from the nucleus, and the sum is over all of the ion's electrons.

The term in $\vec{L}_i$ will be neglected here since in many iron-group com-
pounds (as in this case) the orbital angular momentum is almost completely
quenched by the crystal field[6]. The last two terms involving $\vec{S}_i$ are the
dipole-dipole terms and will be non-zero only for unpaired electrons. The

first term, called the Fermi contact term, involves, through the delta

function, the density of electrons at the nucleus. This is non-zero

only for s-electrons and thus should vanish here since all s-electrons

are paired. However, the presence of unpaired d-electrons causes a

polarization[6] of the s-electrons through the exchange interaction and

a substantial hyperfine field results. In fact, the largest contribu-

tion to the field at the nucleus is due to s-electron polarization.

The details of the polarization of the s-electrons are very com-

plicated and include contributions from the unpaired d-electrons of

neighboring ions through polarization by them of the oxygen anions which

in turn polarize the original cation's s-electrons (super-transferred

hyperfine interaction)[7].

The dipolar part of Equation 2 gives rise to an anisotropic hyper-

fine field. For Mn^{3+} ions on the B-sites considerable anisotropy is

observed[4] but for Mn^{2+} ions on the A-sites, since Mn^{2+} is an S-state

ion (five 3-d electrons → half-filled shell), the hyperfine field is

isotropic.

Writing the interaction in Equation 2 in terms of the effective

hyperfine field yields

$$\mathcal{H}_{hf} = - g_N \mu_N \vec{I} \cdot \vec{H}_s = A \vec{I} \cdot \vec{S}$$

(3)

where, $\quad A = - g_N \mu_N \vec{H}_s \cdot \vec{S} / (\vec{S} \cdot \vec{S})$

and S is the total spin of the ion (for Mn^{2+}, S = 5/2). For the iso-

tropic case A is simply a constant while in the anisotropic case A

would be a second rank tensor.

Finally, in manganese ferrite, as in many other magnetic materials,

the hyperfine field at an A- or B-site is anti-parallel to the sublattice magnetization at that site. The A-site hyperfine field has been found to be proportional to the sublattice magnetization at low temperatures[8], and at T = 4.2 ^{o}K has a magnitude of $H_{hf}^{A} \simeq 560$ kOe, while at the same temperature, the B-site hyperfine field is $H_{hf}^{B} \simeq 360$ kOe.

3. Magnetic Ordering

Below a temperature $T_{F} \simeq 600$ ^{o}K the unpaired spins of the magnetic ions in manganese ferrite are spontaneously ordered in such a way that all of the A-site moments are parallel to each other and anti-parallel to the B-site moments. This type of order is called ferrimagnetic and T_{F} is the ferrimagnetic Neel point. The A and B sites can be considered to form sublattices whose magnetizations are oppositely directed but do not have the same magnitude[9]. This results in a net moment of 4.6 μ_{B} per formula unit along the B-site magnetization, since there are twice as many occupied B-sites as there are A-sites. Because of this net moment many of the properties of ferromagnets are present in ferrimagnets; e.g., the existence of domains, magnetic hysteresis, etc.

3.1 The exchange interaction

The interaction responsible for the spontaneous ordering of the magnetic ions' spins is the exchange interaction, which can be described in insulators by the Heisenberg exchange Hamiltonian

$$\mathcal{H}_{ex} = - \sum_{i<j} J_{ij} \vec{S}_{i} \cdot \vec{S}_{j} \qquad (4)$$

where $\vec{S}_{i}$ is the spin of the ith ion, and J_{ij} is the exchange constant representing the strength of the interaction between ions i and j. In

these materials, as mentioned earlier in connection with the hyperfine

interaction, the orbital contribution to the magnetic moment is quenched

and therefore the contribution of the orbital angular momentum to the

exchange interaction will be neglected. The exchange interaction is very

short ranged and only very near neighbors in the sums over i and j in

Equation 4 need to be considered.

As shown in Figure 1 there is an oxygen anion between an A-site ion

and each of its nearest B-site neighbors. The exchange interaction must

proceed via a polarization of the anion's electronic p-orbitals[10]. Such

an interaction is called superexchange (analagous to the super-transferred

hyperfine fields mentioned earlier) and is found to be very common in iron-

group salts[11]. Superexchange allows the exchange interaction to be ef-

fective over quite large distances when compared with direct exchange[10]

which would require significant overlap of the magnetic ions' d-orbitals.

Even so, the strength of the superexchange is strongly dependent on dis-

tance between cations and on the angle formed by the cation-anion-cation

system[11]. Table 1 gives a list of the possible exchange couplings bet-

ween cations in a spinel together with the distances and angles between

the cations.[12]

Table 1: Superexchange in Spinels

Interaction	Angle	Distance	Sign
A-O-B	125° 9'	$\sqrt{11}a/8$	–
A-O-B	154° 34'	$3\sqrt{3}a/8$	–
A-O-A	79° 38'	$\sqrt{3}a/4$	+
B-O-B	90°	$\sqrt{2}a/4$	+
B-O-B	125° 2'	$\sqrt{6}a/4$	+

The minus sign corresponds to antiparallel or antiferromagnetic exchange and the plus sign to parallel or ferromagnetic exchange.

The superexchange interaction is strongest for short distances and for angles closest to 180° [11], thus the A-B exchange (especially the first type shown in Table 1) is the strongest in these materials [12] and is responsible for the antiparallel alignment of the two sublattices. The other contributions (of which the 125° B-B is the largest) can be safely neglected [12] in many instances.

3.2 Molecular field theory

As postulated by Weiss [13] the exchange interaction in a ferromagnetic material can be represented by an effective magnetic field $H_{ex} = \lambda M$, where M is the sample magnetization and λ is the molecular field constant. Extending this concept to the ferrimagnetic case [9,14] one obtains an exchange field acting on A-site spins due to the B-sublattice magnetization and a similar field on the B-site spins due to the A-sublattice magnetization (neglecting intrasublattice interactions).

$$H^A_{ex} = \lambda M_B \qquad , \qquad H^B_{ex} = \lambda M_A$$

where the molecular field constant λ represents the same quantity in both cases and is given by

$$\lambda = 3k_B T_F / N g^2 \mu_B^2 (S_A(S_A + 1)S_B(S_B + 1))^{\frac{1}{2}} \qquad (5)$$

where $S_A = 5/2$ is the A-site spin (both Mn^{2+} and Fe^{3+} have spin 5/2) and $S_B = 2.40$ is the average B-site spin. N is the total number of magnetic ions, k_B is the Boltzmann constant, and T_F is the ferrimagnetic ordering temperature.

Since $M_B = N_B g\mu_B S_B$ and $N_B = \frac{2}{3} N$, the exchange field acting on the A-site ions is

$$H^A_{ex} = \frac{2}{3} S_B \left(\frac{3k_B T_F}{g\mu_B (S_A(S_A+1)S_B(S_B+1))^{\frac{1}{2}}} \right) \qquad (6)$$

Then, for $g = 2$ and $T_F = 600\ {}^{\circ}K$, the exchange field is

$$H^A_{ex} = (2zS_B/g\mu_B)J \simeq 2.6 \times 10^6\ Oe$$

where $z = 12$ is the number of magnetic nearest neighbors of the A-site ion and J is the A-B exchange constant as used in Equation 4.

4. Spin Waves

The Hamiltonian of a ferromagnet including only an isotropic exchange interaction and the electronic Zeeman interaction with an external field H_o is

$$\mathcal{H} = - \sum_{(i,j)} J_{ij} \vec{S}_i \cdot \vec{S}_j - g\mu_B H_o \sum_i S^z_i \qquad (7)$$

where $\sum_{(i,j)}$ is the sum over all "distinct" pairs of spins. The ground state of a ferromagnet, denoted by $|\!\uparrow>$, is the state with all spins aligned parallel. Introducing the spin raising and lowering operators $S^{\pm} = S^x \pm iS^y$ the Hamiltonian can be written as

$$\mathcal{H} = - \sum_{(i,j)} J_{ij} (S^z_i S^z_j + \tfrac{1}{2} S^+_i S^-_j + \tfrac{1}{2} S^-_i S^+_j) - g\mu_B H_o \sum_i S^z_i$$

Then, the ground state energy is given by

$$\mathcal{H} |\!\uparrow> = - N(g\mu_B H_o S + \tfrac{1}{2} S^2 \sum_j J_{ij}) |\!\uparrow> \qquad (8)$$

since $S_i^z|\uparrow> = S$, $S_i^+|\uparrow> = 0$. The factor of 1/2 preceding Σ_j is to in-
sure that the contribution from each pair of spins is counted only once.

Then, taking the commutator of $\mathcal{H}$ and the spin lowering operator
S_i^- and applying it to $|\uparrow>$ yields

$$\left[\mathcal{H}, S_i^-\right]|\uparrow> = \left(g\mu_B H_o S_i^- + \sum_j J_{ij}(S_i^- S_j^z - S_i^z S_j^-)\right)|\uparrow>$$

$$= \left(g\mu_B H_o S_i^- + S\sum_j J_{ij}(S_i^- - S_j^-)\right)|\uparrow> \tag{9}$$

This forms a new state which is a linear combination of states where a
spin i has been flipped, $(S_i^-|\uparrow>)$. Then, replacing S_i^- by its Fourier
transform $\Sigma_i \exp(i\vec{k}\cdot\vec{r}_i)S_i^-$,

$$\left[\mathcal{H}, \sum_i \exp(i\vec{k}\cdot\vec{r}_i)S_i^-\right]|\uparrow>$$

$$= \left(g\mu_B H_o + S\sum_j J_{ij}(1 - \exp(i\vec{k}\cdot(\vec{r}_i - \vec{r}_j)))\right)\sum_i \exp(i\vec{k}\cdot\vec{r}_i)S_i^-|\uparrow> \tag{10}$$

it can be seen that the states

$$|k> = \frac{1}{\sqrt{2SN}}\sum_i \exp(i\vec{k}\cdot\vec{r}_i)S_i^-|\uparrow> \tag{11}$$

are the normalized eigenstates of the Hamiltonian $\mathcal{H}$ with eigenvalues
given by

$$E_k = E_o + g\mu_B H_o + S\sum_i J_{ij}\{1 - \exp(i\vec{k}\cdot(\vec{r}_i - \vec{r}_j))\} \tag{12}$$

where E_o is the ground state energy. These new states $|k>$ are called
Bloch spin-wave states[15,16] and the excitations of wavevector $\vec{k}$ are cal-
led spin waves.

The minimum energy required to excite a spin wave $(E - E_o = g\mu_B H_o)$
is much lower than that required to flip a single spin since, for a
spin-wave excitation, neighboring spins are still very nearly parallel

(on the average) and their exchange energy is only slightly increased.

The interaction of the ^{55}Mn nuclear moments with these spin waves via the hyperfine ($A\vec{I}\cdot\vec{S}$) interaction and the effective nuclear spin-spin interaction—the Suhl-Nakamura interaction—which is a result of the virtual excitation, by the hyperfine interaction, of electronic spin waves as intermediate states, require a detailed understanding of these excitations.

4.1 Holstein-Primakoff diagonalization

The eigenstates of the Hamiltonian are expanded in terms of the eigenstates $|n_\ell>$ of the spin-deviation operator n_ℓ defined by

$$n_\ell|n_\ell> = (S - S_\ell^z)|n_\ell> = n_\ell|n_\ell>$$

In this notation, the ferromagnetic ground state is $|0>$, the state of zero spin deviation. Then the raising and lowering operators acting on these states give[17]

$$S_\ell^+|n_\ell> = \{(S - S_\ell^z)(S + S_\ell^z + 1)\}^{\frac{1}{2}}|n_\ell - 1>$$

$$S_\ell^-|n_\ell> = \{(S + S_\ell^z)(S - S_\ell^z + 1)\}^{\frac{1}{2}}|n_\ell + 1>$$

$$(13)$$

The spin-deviation operator n_ℓ is actually the boson occupation number operator defined by

$$n_\ell = a_\ell^+ a_\ell \quad\text{, with}\quad \left[a_\ell, a_m^+\right] = \delta_{\ell,m} \quad\text{, all others zero}$$

where the a_ℓ^+ and a_ℓ are the spin-deviation creation and annihilation operators. Then, since

$$a_\ell^+|n_\ell> = (n_\ell + 1)^{\frac{1}{2}}|n_\ell + 1>$$

and,   (14)

$$a_\ell |n_\ell> = (n_\ell)^{\frac{1}{2}} |n_\ell - 1>$$

we may express the spin operators in the Hamiltonian in terms of these

operators as

$$S_\ell^+ = (2S)^{\frac{1}{2}}(1 - a_\ell^+ a_\ell / 2S)^{\frac{1}{2}} a_\ell$$

$$S_\ell^- = (2S)^{\frac{1}{2}} a_\ell (1 - a_\ell^+ a_\ell / 2S)^{\frac{1}{2}} \qquad\qquad (15)$$

$$S_\ell^z = S - a_\ell^+ a_\ell$$

Expanding these expressions for S_ℓ^+, S_ℓ^- in powers of $(1/S)$ yields

$$S_\ell^+ = (2S)^{\frac{1}{2}} \left(1 - \frac{a_\ell^+ a_\ell}{4S} - \frac{a_\ell^+ a_\ell a_\ell^+ a_\ell}{32S^2} - \cdot\cdot\right) a_\ell$$

$$S_\ell^- = (2S)^{\frac{1}{2}} a_\ell^+ \left(1 - \frac{a_\ell^+ a_\ell}{4S} - \frac{a_\ell^+ a_\ell a_\ell^+ a_\ell}{32S^2} - \cdot\cdot\right)$$

where for many applications only the terms linear in the spin-deviation

operators need to be retained[5,18,19]. When spin wave scattering becomes

important, as in the derivation of spin-wave relaxation processes, higher

order terms may be necessary.

For a two sublattice system, with the B-sublattice aligned along

the positive z-axis (the direction of H_o), the spin operators are given

by[20]

$$S_{B_j}^+ = (2S_B)^{\frac{1}{2}} (1 - b_j^+ b_j / 2S_B)^{\frac{1}{2}} b_j$$

,(plus complex conjugates)

$$S_{A_i}^+ = (2S_A)^{\frac{1}{2}} a_i^+ (1 - a_i^+ a_i / 2S_A)^{\frac{1}{2}} \qquad\qquad (16)$$

$$S_{B_j}^z = S_B - b_j^+ b_j \quad , \qquad S_{A_i}^z = -S_A + a_i^+ a_i$$

where S_A and S_B are the A- and B-site spin and the operators a_i^+, b_j^+ create a spin-deviation on their respective sublattices.

The next step in diagonalizing the Hamiltonian is to Fourier transform the spin-deviation operators, which become

$$a_i = (N_A)^{-\frac{1}{2}} \sum_k \exp(i\vec{k}\cdot\vec{r}_i) a_k$$

$$b_j = (N_B)^{-\frac{1}{2}} \sum_k \exp(-i\vec{k}\cdot\vec{r}_j) b_k$$

4.2 The diagonalized Hamiltonian

The Hamiltonian we wish to consider is

$$
\begin{aligned}
\mathcal{H} &= \mathcal{H}_A^z + \mathcal{H}_B^z + \mathcal{H}_{A-B}^{ex} + \mathcal{H}^{dd} \\
&= -g\mu_B H \sum_i^A S_{A_i}^z - g\mu_B H \sum_j^B S_{B_j}^z + \frac{1}{2} J \sum_{i,j}^{nn} \vec{S}_i \cdot \vec{S}_j \\
&\quad + \frac{1}{2} \sum_{i,j} \frac{g^2\mu_B^2}{R_{ij}^5} \left(R_{ij}^2 \{\vec{S}_i \cdot \vec{S}_j - 3(\vec{R}_{ij}\cdot\vec{S}_i)(\vec{R}_{ij}\cdot\vec{S}_j)\} \right)
\end{aligned}
\tag{17}
$$

This Hamiltonian consists of Zeeman, exchange, and dipole-dipole terms. The sum Σ_i^A is over all spins on the A-sublattice, Σ_j^B is over all spins on the B-sublattice, $\Sigma_{i,j}^{nn}$ is over all pairs (i,j) of nearest neighbor spins, and $\Sigma_{i,j}$ is over all spins (i ≠ j). When the spin has a subscript it refers to a particular sublattice and when no subscript is present, S can refer to either sublattice. Thus, for example,

$$
\frac{1}{2} J \sum_{i,j}^{nn} \vec{S}_i \cdot \vec{S}_j = \frac{1}{2} J \left(\sum_i^A \sum_{i+\delta}^B \vec{S}_{A_i} \cdot \vec{S}_{B_{i+\delta}} + \sum_j^B \sum_{j+\delta}^A \vec{S}_{B_j} \cdot \vec{S}_{A_{j+\delta}} \right)
$$

where $\vec{\delta}$ is the vector joining nearest neighbors. Similarly, the dipole-

dipole part of the Hamiltonian can be written as

$$\frac{1}{2} \sum_{i \neq j} \mathcal{H}^{dd}_{i,j}(\vec{S}_i, \vec{S}_j) = \frac{1}{2}\Bigg(\sum_{i \neq \ell}^{A} \mathcal{H}^{dd}_{i,\ell}(\vec{S}_{A_i}, \vec{S}_{A_\ell})$$

$$+ \sum_{i}^{A} \sum_{j}^{B} \mathcal{H}^{dd}_{i,j}(\vec{S}_{A_i}, \vec{S}_{B_j}) + \sum_{j}^{B} \sum_{\ell}^{A} \mathcal{H}^{dd}_{j,\ell}(\vec{S}_{B_j}, \vec{S}_{A_\ell})$$

$$+ \sum_{j \neq m}^{B} \mathcal{H}^{dd}_{j,m}(\vec{S}_{B_j}, \vec{S}_{B_m})\Bigg)$$

The factor of $\frac{1}{2}$ on both sides of these equations is to insure that the interaction between any two spins is included only once.

By breaking up the Hamiltonian in this manner we can more easily carry out the steps in diagonalization of the total Hamiltonian. The dipole-dipole Hamiltonian can be written in terms of spin operators S^+, S^-, and S^z as

$$\mathcal{H}_{dd} = \frac{1}{2} \sum_{i \neq j} \Bigg[A^{(z,z)}_{i,j} S^z_i S^z_j + A^{(+,-)}_{i,j}(S^+_i S^-_j + S^-_i S^+_j)$$

$$- A^{(z,+)}_{i,j}(S^z_i S^+_j + S^+_i S^z_j) - A^{(z,-)}_{i,j}(S^z_i S^-_j + S^-_i S^z_j) \qquad (18)$$

$$- A^{(+,+)}_{i,j} S^+_i S^+_j - A^{(-,-)}_{i,j} S^-_i S^-_j \Bigg]$$

where,

$$A^{(z,z)}_{i,j} = \frac{g^2 \mu_B^2}{R^5_{ij}} \left(R^2_{ij} - 3(R^z_{ij})^2 \right)$$

$$A^{(+,-)}_{i,j} = \frac{1}{2} \frac{g^2 \mu_B^2}{R^5_{ij}} \left(R^2_{ij} - \frac{3}{2} R^+_{ij} R^-_{ij} \right) \qquad (19)$$

$$A^{(z,\pm)}_{i,j} = \frac{3}{2} \frac{g^2 \mu_B^2}{R^5_{ij}} R^z_{ij} R^{\mp}_{ij}$$

$$A_{i,j}^{(\pm,\pm)} = \frac{3}{4} \frac{g^2 \mu_B^2}{R_{ij}^5} (R_{ij}^{\mp})^2$$

Each of the four parts (A-A, A-B, B-A, B-B) of the dipole-dipole Hamiltonian will be written in this fashion, where the sums involved will be over a particular sublattice.

Applying the Holstein-Primakoff transformation to the Zeeman and exchange terms leads, to second order in magnon operators, to

$$\mathcal{H}^{'(2)} = \sum_k (\mu_{AA}^o a_k^+ a_k + \mu_{AB}^o a_k^+ b_k^+ + \mu_{BA}^o a_k b_k + \mu_{BB}^o b_k^+ b_k) + \text{const.} \quad (20)$$

where,

$$\mu_{AA}^o = -g\mu_B H + \hat{z} J S_B (N_B/N_A)^{\frac{1}{2}}$$

$$\mu_{AB}^o = \frac{1}{2} J (S_A S_B)^{\frac{1}{2}} \{ Z_B (N_B/N_A)^{\frac{1}{2}} \gamma_{-k}^B + Z_A (N_A/N_B)^{\frac{1}{2}} \gamma_{-k}^A \}$$

$$\mu_{BA}^o = \frac{1}{2} J (S_A S_B)^{\frac{1}{2}} \{ Z_B (N_B/N_A)^{\frac{1}{2}} \gamma_k^B + Z_A (N_A/N_B)^{\frac{1}{2}} \gamma_k^A \} \quad (21)$$

$$\mu_{BB}^o = g\mu_B H + \hat{z} J S_A (N_A/N_B)^{\frac{1}{2}}$$

with, $\quad \hat{z} = \frac{1}{2} \{ (N_B/N_A)^{\frac{1}{2}} Z_B + (N_A/N_B)^{\frac{1}{2}} Z_A \}$

and $\quad \gamma_k^{A,B} = Z_{A,B}^{-1} \sum_\delta^{A,B} \exp(i\vec{k}\cdot\vec{\delta})$

where $\vec{\delta}$ is the vector joining nearest neighbors and N_A, N_B, Z_A, Z_B are the numbers of A-, B-site ions and the number of A-, B-site nearest neighbors.

The dipole-dipole Hamiltonian can be transformed in the same fashion to obtain the total Hamiltonian to second-order in magnon operators

$$\mathcal{H}^{(2)} = \sum_k (\mu_{AA} a_k^+ a_k + \mu_{AB} a_k^+ b_k^+ + \mu_{BA} a_k b_k + \mu_{BB} b_k^+ b_k) \quad (23)$$

In this equation we have neglected terms such as $a_k a_{-k}$, $a_k^+ b_{-k}$, $b_k^+ b_{-k}$,

etc., which arise from terms in S^+S^+, S^-S^- and are expected to be small compared to the remaining terms[5,20]. The coefficients in this Hamiltonian are

$$\mu_{AA} = \mu_{AA}^o + \mu_{AA}^{dd} , \qquad \mu_{AB} = \mu_{AB}^o + \mu_{AB}^{dd} , \qquad \text{etc., and}$$

$$\mu_{AA}^{dd} = S_A\{(C_{AA}^{(+,-)}(-\vec{k}) + C_{AA}^{(+,-)}(\vec{k})) - C_{AA}^{(z,z)}(0)\}$$

$$+ (S_A S_B)^{\frac{1}{2}} (N_B/N_A)^{\frac{1}{2}} \{(N_A/N_B)^{\frac{1}{2}} C_{AB}^{(z,z)}(0) + (N_B/N_A)^{\frac{1}{2}} C_{BA}^{(z,z)}(0)\}$$

$$\mu_{AB}^{dd} = (S_A S_B)^{\frac{1}{2}} \{(N_A/N_B)^{\frac{1}{2}} C_{AB}^{(+,-)}(-\vec{k}) + (N_B/N_A)^{\frac{1}{2}} C_{BA}^{(+,-)}(\vec{k})\}$$

$$(24)$$

$$\mu_{BA}^{dd} = (S_A S_B)^{\frac{1}{2}} \{(N_A/N_B)^{\frac{1}{2}} C_{AB}^{(+,-)}(\vec{k}) + (N_B/N_A)^{\frac{1}{2}} C_{BA}^{(+,-)}(-\vec{k})\}$$

$$\mu_{BB}^{dd} = S_B\{(C_{BB}^{(+,-)}(\vec{k}) + C_{BB}^{(+,-)}(-\vec{k})) - C_{BB}^{(z,z)}(0)\}$$

$$+ (S_A S_B)^{\frac{1}{2}}(N_A/N_B)^{\frac{1}{2}} \{(N_A/N_B)^{\frac{1}{2}} C_{AB}^{(z,z)}(0) + (N_B/N_A)^{\frac{1}{2}} C_{BA}^{(z,z)}(0)\}$$

Here we have defined the expressions $C_{XY}^{(\mu,\nu)}$ by

$$C_{XY}^{(\mu,\nu)}(\vec{k}) = \sum_{\delta_X}^{Y} A_{\delta_X}^{(\mu,\nu)} \exp(i\vec{k}\cdot\vec{\delta}_X) \qquad (25)$$

where the sum $\sum_{\delta_X}^{Y}$ is over all vectors $\vec{\delta}_X$ originating on a site on the X-sublattice (X = A or B) and terminating on the Y-sublattice, and the $A_{\delta}^{(\mu,\nu)}$ are as defined in Equation 19 with $\vec{\delta} = R_{ij}$.

The Hamiltonian in Equation 23 is still not diagonal since it contains terms coupling the operators a_k and b_k . To bring the Hamiltonian into normal-mode form, the transformation to normal-mode operators α_k , β_k is made.

$$b_k = u_k \alpha_k - v_k \beta_k^\dagger$$

$$a_k = -v_k \alpha_k^+ + u_k \beta_k \tag{26}$$

$$[\alpha_k, \alpha_k^+] = [\beta_k, \beta_k^+] = 1, \text{ all others zero.}$$

The transformation coefficients u_k, v_k are chosen to bring the Hamiltonian into diagonal decoupled form. The Hamiltonian then takes the form

$$\mathcal{H}^{(2)} = \sum_k (\hbar\omega_\alpha \alpha_k^+ \alpha_k + \hbar\omega_\beta \beta_k^+ \beta_k) \tag{27}$$

which is the desired result.

4.3 The ferrimagnon dispersion relation

The normal-mode energies in Equation 27 are given by

$$\hbar\omega_\alpha = \mu_{BB} u_k^2 - (\mu_{AB} + \mu_{BA}) u_k v_k + \mu_{AA} v_k^2$$

$$\hbar\omega_\beta = \mu_{BB} v_k^2 - (\mu_{AB} + \mu_{BA}) v_k u_k + \mu_{AA} u_k^2 \tag{28}$$

$$= \hbar\omega_\alpha - (\mu_{BB} - \mu_{AA})$$

The transformation coefficients are determined from the equations of motion of the magnon operators α_k , β_k , a_k , b_k, i.e.,

$$i\frac{d\alpha_k}{dt} = [\alpha_k, \mathcal{H}_k] = \omega_\alpha \alpha_k \tag{29}$$

and since, from Equation 26, $u_k^2 - v_k^2 = 1$, we obtain the equation

$$\begin{pmatrix} \mu_{BB} - \omega & -\mu_{BA} \\ \mu_{AB} & -\mu_{AA} - \omega \end{pmatrix} \begin{pmatrix} u_k \\ v_k \end{pmatrix} = 0 \tag{30}$$

and the coefficients may be defined by the relations

$$u_k = \{1 - (v_k/u_k)^2\}^{-\frac{1}{2}} \quad , \quad v_k = (v_k/u_k)\{1 - (v_k/u_k)^2\}^{-\frac{1}{2}}$$

To obtain the dispersion relation (Equation 29) in terms of recognizable quantities we must substitute for the μ's from Equations 21 and 24. First we consider the ratio of the transformation coefficients.

$$(v_k/u_k) = \frac{\mu_{BB} - \omega}{\mu_{BA}} \simeq \frac{\hat{z}(N_A/N_B)^{\frac{1}{2}} (S_A/S_B)^{\frac{1}{2}}}{\frac{1}{2}\{Z_B(N_B/N_A)^{\frac{1}{2}} \gamma_k^B + Z_A(N_A/N_B)^{\frac{1}{2}} \gamma_k^A\}} = \eta(S_A/S_B)^{\frac{1}{2}}$$

This equation is used to define a parameter η which, since it depends on N_A, N_B, Z_A, Z_B, describes the nonequivalence of the two sublattices. For small k, $\eta \simeq (N_A/N_B)^{\frac{1}{2}}$. Then, we find that

$$u_k^2 = \frac{S_B}{S_B - \eta^2 S_A} \quad , \quad u_k v_k = \frac{\eta(S_A S_B)^{\frac{1}{2}}}{S_B - \eta^2 S_A} \quad , \quad v_k^2 = \frac{\eta^2 S_A}{S_B - \eta^2 S_A} \quad (31)$$

To put the α-mode dispersion relation in a more understandable form we rewrite it as

$$\hbar\omega_\alpha = - \mu_{AA} + (\mu_{AA} + \mu_{BB})u_k^2 - (\mu_{AB} + \mu_{BA})u_k v_k$$

Now, from Equations 21 and 24,

$$\hbar\omega_\alpha^o = - \mu_{AA}^o + (\mu_{AA}^o + \mu_{BB}^o)u_k^2 - (\mu_{AB}^o + \mu_{BA}^o)u_k v_k$$

$$\qquad\qquad (32)$$

$$= g\mu_B H + Z'JS_{eff} \{\eta^2(N_B/N_A) - 1\}$$

with $\quad Z' = (N_B/N_A)^{\frac{1}{2}} \hat{z} \quad , \quad S_{eff} = \frac{N_A}{N_B}\left(\frac{S_A S_B}{S_A - \eta^2 S_B} \right)$

For small k, $\eta^2 \simeq (N_A/N_B)(1 + \frac{1}{3} a_{nn}^2 k^2)$, for a cubic lattice, where a_{nn} is the nearest neighbor distance. In this approximation the dispersion relation assumes the familiar ferromagnetic form given by