Bound magnon dominance of the magnetic susceptibility of the one-dimensional Heisenberg spin one-half ferromagnet cyclohexylammonium trichlorocuprate(II)

by Donald Noble Haines

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Montana State University

Abstract:
This study is an experimental investigation of the differential magnetic susceptibility of the spin one-half, one-dimensional, Ising-Heisenberg ferromagnet (S=l/2,1d,HIF). Recent theoretical work predicts the existence of magnon bound states in this model system, and that these bound spin wave states dominate its thermodynamic properties. Further, the theories indicate that classical linearized spin wave theory fails completely in such systems, and may also be intrinsically incorrect in certain higher dimensional systems. The purpose of this research is to confirm the existence of bound magnons in the S=l/2,ld,HIF for the nearly Heisenberg case, and demonstrate the dominance of the bound states over the spin wave states in determining thermodynamic behavior.

A preliminary numerical study was performed to determine the ranges of magnetic field and temperature at which bound magnons might be expected to make a significant contribution to the magnetic susceptibility and specific heat of the S=l/2,ld,HIF. It was found that bound magnons dominate at low and high fields, and spin waves dominate at intermediate fields. For anisotropies less than 2% bound magnons dominate the low temperature regime for all fields.

To test the theoretical predictions cyclohexylammonium trichloro-cuprate(II) (CHAC) was chosen as a model S=l/2,ld,HIF compound for experimental study. The differential susceptibility of a powder sample of CHAC was measured as a function of temperature in fields of 0, 1, 2, and 3T. The temperature range for these studies was 4.2K to 40K. Susceptibility measurements were performed using an ac mutual inductance bridge which employs a SQUID (Superconducting Quantum Interference Device) as a null detector. The design, calibration, and operation of this instrument are described.

Data from the experiments compare favorably with the theoretical predictions, confirming the existence of bound magnons in the nearly Heisenberg S=1/2,1d,HIF. Further, the experimental results clearly show that bound magnons are the dominant excitation determining the susceptibility for all fields and temperatures studied. Spin wave theory cannot describe the data for any values of the adjustable parameters.

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Donald Noble Haines

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

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CHAPTER ONE

INTRODUCTION

In recent years there has been substantial interest in the quantum and nonlinear characteristics of one dimensional (1d) magnetic systems [1]. In particular, special attention has been given to various cases of the 1d, Ising-Heisenberg-XY model. These studies indicate that classical linearized spin wave theory is not uniformly valid in these systems, and that nonlinear excitations and quantum effects play a significant role [2-4]. Although much of this research has dealt with soliton models and their experimental realizations [5-9], significant progress has also been made in numerical and analytical studies of the low temperature excitation spectrum and dynamics [10-14]. However, complete and rigorous solutions are available only for a few special cases of the general model. Consequently, even though appropriate quasi-1d magnetic compounds are available, detailed experimental studies of their quantum aspects, especially of the low lying excitations (commonly referred to as bound spin waves or bound magnons) are scarce. Far infrared absorption has been used by Torrance [15] and Bosch [16] to show that these excitations exist in the ferromagnetic Ising chain compounds $CoCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2(pyr)$. Also, Nijhof [17] has interpreted the low temperature ESR spectrum of the anisotropic linear chain antiferromagnet $RbCoCl_3 \cdot 2H_2O$ in terms of magnon bound states.

There exists only one experimental study of bound magnons in the ferromagnetic spin one-half (S=1/2) Heisenberg chain: Hoogerbeets [18] has measured the first seven bound state energies in $(C_6H_{11}NH_3)CuCl_3$ (CHAC) using low temperature ESR. This thesis presents experimental confirmation of the existence of bound magnons in this important case, and of their dominance over spin waves in determining thermodynamic behavior [19].

To present these results in more detail it is first necessary to introduce concepts which are fundamental to the study of 1d magnetic systems. The remainder of this chapter is devoted to a discussion of these ideas.

One-Dimensional Magnetism

A one dimensional (1d) magnet is an idealized system in which the spins lie on a line and interact only with spins on the same line.

Although study of 1d systems instead of the physical 3d case may seem unreasonable, there is justification for this choice. Quite simply, the mathematics entailed by a theoretical treatment of the magnetic properties of a 3d system are intractable, and an exact solution has not been found even in the simplest case. Further, although a variety of approximate calculations--mean field theory, spin wave theory, high temperature series expansions, and a number of others--have often been successful in describing experimental data, they invariably neglect or obscure the nonlinear and quantum aspects inherent in magnetism, and therefore provide only a vague understanding of these phenomena. Consequently, a great deal of theoretical

attention has been given to the mathematically simpler lower dimensional systems.

Unfortunately, calculations are only slightly less difficult in 2d, and only the simplest model has been solved exactly. However, in 1d, even though theoretical difficulties are still substantial, several exact results, and a number of approximate analytical calculations have appeared [1-4,10-14]. These studies show that even though they do not display critical behavior except at zero temperature, nonlinear and quantum effects are more prominent in 1d magnets than in their 3d counterparts. Indeed, it now appears that some of the basic assumptions typically made in studies of higher dimensional systems may be incorrect [2-4].

These theoretical results have generated interest in experimental studies of 1d magnets. For experimental purposes, a magnetic insulator is said to be 1d if its structure consists of widely separated chains of spins, with the chains weakly bonded together so that the interactions between spins within a chain are much stronger than interactions between spins which lie in different chains. Although compounds with these characteristics are rare, a number have been synthesized, some with intrachain interactions 10,000 times greater than interchain interactions [20,21].

Basic Theory

The following sections provide a review of fundamental theoretical concepts. This treatment is not intended to be complete, and presents only the ideas needed for discussion of the Johnson and

Bonner theory in the next chapter. The material presented below is for the spin one-half, 1d, Heisenberg ferromagnet (abbreviated S=1/2,1d,HF) in zero field. An analysis of the ground state, calculations of the energy spectra for one spin reversal (one magnon solution--the spin wave states) and two spin reversals (two magnon solution), which contains not only the spin wave states but also a bound magnon state, are given. The discussion of the one magnon solution and of spin waves follows that of Keffer [23], and the two magnon solution can be found in Mattis [22] and in Keffer [24].

The Hamiltonian for the S=1/2,1d,HF in zero field is

$$H = -2J \sum_{i=1}^{N} \underline{S}_i \cdot \underline{S}_{i+1} ,$$

where $J>0$ is the exchange energy, N is the number of spins in the chain, and $\underline{S}_i$ is the spin operator in units of $\hbar$ at site i. Only interactions between nearest neighbors in the chain are considered. Periodic boundary conditions, $\underline{S}_{N+1} = \underline{S}_1$, will be applied. Since the ground state and the zero temperature excited states are degenerate in the absence of a magnetic field, it will be assumed that an effective field which removes this degeneracy exists, but this field will not be included in the calculation of the energy levels. Also, it is assumed that the field is in the z-direction so that the preferred spin orientation is along the z-axis.

To proceed further it is necessary to introduce and define the relevant angular momentum operators. Basic elements of the quantum theory of angular momentum are discussed by Mattis [22]. The spin

operator at site i is

$$\underline{S}_i = S_i^x \hat{x} + S_i^y \hat{y} + S_i^z \hat{z} ,$$

where the components S_i^λ satisfy the usual commutation relations $[S_i^\mu, S_i^\nu] = i\varepsilon_{\mu\nu\sigma} S_i^\sigma$. Spin states at site i are given in terms of the spinors α_i (spin up) and β_i (spin down), which have z components

$$S_i^z \alpha_i = (1/2)\alpha_i , \text{ and } S_i^z \beta_i = (-1/2)\beta_i .$$

Spinors α_i and β_i are normalized and orthogonal to each other:

$$\langle \alpha_i | \alpha_i \rangle = \langle \beta_i | \beta_i \rangle = 1 , \quad \langle \alpha_i | \beta_i \rangle = 0 .$$

Operators $S_i^\pm = S_i^x \pm S_i^y$ are the raising and lowering operators for spinors α_i and β_i :

$$S_i^+ \alpha_i = 0 , \quad S_i^+ \beta_i = \alpha_i ;$$
$$S_i^- \alpha_i = \beta_i , \quad S_i^- \beta_i = 0 .$$

The total spin at i is given by $S_i^2 \alpha_i = (3/4)\alpha_i$, $S_i^2 \beta_i = (3/4)\beta_i$. Operators for the spin at site i leave spinors at other sites unaffected; e.g., $S_i^+ \alpha_j = \alpha_j$. Also, inner products can only be formed between spins on the same site, so that for product wave functions such as $\Omega_{mn} = \alpha_m \beta_n$ the inner product of Ω_{mn} and Ω_{nm} is

$$\langle \Omega_{mn} | \Omega_{nm} \rangle = \langle \alpha_m | \beta_m \rangle \langle \alpha_n | \beta_n \rangle = 0 .$$

For what follows it is convenient to write the Hamiltonian in terms of the raising and lowering operators $S_i^\pm$:

$$H = -2J \sum_{i=1}^{N} [(1/2)S_i^+S_{i+1}^- + (1/2)S_i^-S_{i+1}^+ + S_i^zS_{i+1}^z] . \qquad (1)$$

Although analysis of the ground state and first two excited states cannot provide a complete understanding of the spin system, these results illustrate important basic concepts. We begin with a discussion of the ground state.

Ground State

At zero temperature all spins in the chain point in the same direction, which is defined to be the z-direction. This means that all of the spins have the same quantum number for their z-component of angular momentum, m=+1/2. This ground state can be expressed as the product wave function

$$\psi_o = \alpha_1\alpha_2\alpha_3 \cdots \alpha_N . \qquad (2)$$

This is an eigenfunction of Hamiltonian (1):

$$H\psi_o = -2J \sum_{i=1}^{N} [0 + 0 + (1/2)(1/2)\psi_o] = -2J(N/4)\psi_o .$$

So, the ground state energy is

$$E_o = -(1/2)NJ . \qquad (3)$$

Since the interaction energy between two spins with S=1/2 is just $-2J(\underline{S}_1 \cdot \underline{S}_2) = -2J(1/2)^2$, and there are N spins interacting, this is the expected result.

The squared magnitude of the z-component of spin at site j is given by

$$(S_j^z)^2\psi_o = (1/4)\psi_o \ ,$$

and its total magnitude squared by

$$S_j^2\psi_o = (3/4)\psi_o \ .$$

Clearly, part of the total angular momentum is carried by the x and y-components of spin. ψ_o is not an eigenfunction of S_j^x and S_j^y, and the expectation values of these operators is zero. However, the squared magnitude of the transverse component $(S_j^\perp)^2 = (S_j^x)^2 + (S_j^y)^2$ is an eigenfunction

$$(S_j^\perp)^2\psi_o = (1/2)\psi_o \ .$$

Thus, the spins must precess about the z axis. The transverse spin correlation function

$$\langle \underline{S}_j^\perp \cdot \underline{S}_k^\perp \rangle = \langle S_j^x S_k^x + S_j^y S_k^y \rangle \ , \quad j \neq k \ ,$$

is zero for all sites j and k. Since the correlation function is proportional to the average of the cosine of the phase angle between spins j and k, the precession must therefore be random. This is consistent with the zero average values found for the x and y-components of spin j.

The precession gives rise to a zero point correction in the ground state energy. Each spin has magnitude $[S(S+1)]^{1/2} = \sqrt{3/4}$. If the spins were completely aligned, as if they were classical angular

momentum vectors, the energy would be $E_o' = (-2J)(3/4)N = -(3/2)NJ$. So, the zero point energy resulting from quantum mechanical uncertainty is $E_o - E_o' = NJ$.

One Spin Reversed

As the temperature is raised from T=0 the spin system will be excited out of the ground state into low energy excited states. The first excited state is one in which a single spin is reversed from its ground state direction. This is called the one magnon state. A one spin reversed state, with the jth spin reversed, is given by

$$\phi_j = S_j^- \psi_o = \alpha_1\alpha_2\alpha_{j-1}\beta_j\alpha_{j+1}\cdots\alpha_N . \tag{4}$$

This state, however, is not an eigenfunction. Operating on ϕ_j with Hamiltonian (1) yields

$$\begin{aligned} H\phi_j = HS_j^-\psi_o &= -2J \sum_{i=1}^{N} [(1/2)S_i^+S_{i+1}^- \\ &\quad + (1/2)S_i^-S_{i+1}^+ + S_i^zS_{i+1}^z]S_j^-\psi_o \\ &= -2J \sum_{i=1}^{N} [(1/2)(S_i^+S_j^-)S_{i+1}^-\delta_{j,i} \\ &\quad + (1/2)S_i^-(S_{i+1}^+S_j^-)\delta_{j,i+1} + S_i^zS_{i+1}^zS_j^-]\psi_o \\ &= -2J[(1/2)\phi_{j+1} + (1/2)\phi_{j-1} \\ &\quad + (1/4)\phi_j(j-2) - 2(1/4)\phi_j + (1/4)\phi_j(N-j)] \\ &= -2J[(1/2)\phi_{j+1} + (1/2)\phi_{j-1} + (1/4)(N-4)\phi_j] . \end{aligned} \tag{5}$$

In order to diagonalize H, form a linear superposition of the product wave functions ϕ_j:

$$\psi_1 = \sum_{i=1}^{N} c_j \phi_j \, .$$

Normalization requires that

$$\langle \psi_1^* | \psi_1 \rangle = \sum_{i=1}^{N} |c_j|^2 = 1 \, .$$

Since all sites are equivalent, the modulus of the amplitude for each reversed spin site should be independent of j. Then c_j can be expressed in polar form:

$$c_j = c\exp(i\theta_j) \, ,$$

where c is the magnitude of c_j and θ_j is the phase. The normalization condition gives $c = N^{-1/2}$, so ψ_1 can be written as

$$\psi_1 = (N^{-1/2}) \sum_{j=1}^{N} e^{i\theta_j} \phi_j \, . \qquad (6)$$

To find the energy of ψ_1 use the Schroedinger equation $H\psi_1 = E_1\psi_1$ and take the inner product with ϕ_i:

$$E_1 = \langle \phi_i | H\psi_1 \rangle = \langle \phi_i | \sum_{j=1}^{N} c_j H\phi_j \rangle$$

$$= \langle \phi_i | \sum_{j=1}^{N} c_j \{-2J[(1/2)\phi_{j+1} + (1/2)\phi_{j-1} + (1/4)(N-4)\phi_j]\} \rangle \, ,$$

$$E_1 = -J[c_{i-1} + c_{i+1} + (1/2)(N-4)c_i] ,$$

where expression (5) for $H\phi_j$ has been used. This can be written as

$$\varepsilon_1 c_n + J(c_{n-1} + c_{n+1}) = 0 , \tag{7}$$

where $\varepsilon_1 = (E_1 - E_o) - 2J$. Expressing c_n in polar form gives

$$\exp[i(\theta_{n+1} - \theta_n)] + \exp[-i(\theta_n - \theta_{n-1})] = -\varepsilon_1/J . \tag{8}$$

Equating the imaginary parts of equation (8) yields

$$\sin(\theta_{n+1} - \theta_n) - \sin(\theta_n - \theta_{n-1}) = 0 ,$$

which is satisfied for $\theta_n = (1/2)(\theta_{n+1} + \theta_{n-1})$, indicating that the phase at site n is intermediate between the phase at site n+1 and the phase at site n−1. One possible solution is $\theta_n = \kappa n$, κ=constant. For n=N the periodic boundary conditions require that $\theta_{N+1} = \theta_1$, so κ is restricted to the values

$$\kappa = 2m\pi/N , \quad m=\text{integer} . \tag{9}$$

Equating the real parts of equation (8) with $\theta_n = \kappa n$ results in a relationship between the energy and κ:

$$E_1 - E_o = 2J(1 - \cos\kappa) = 4J\sin^2(\kappa/2) . \tag{10}$$

This is periodic with half-period π, so κ can be restricted to be between $-\pi$ and π without loss of generality, thereby limiting the range of m to $|m| \leq N/2$. If κ is expressed in units of the lattice spacing a, the familiar reciprocal lattice formalism is obtained.

The solution thus is a linear combination of the one spin reversed product wave functions (4),

$$\psi_1^k = (N^{-1/2}) \sum_{j=1}^{N} e^{i(ka)j} \phi_j \ , \tag{11}$$

with energy given by equation (10) with $\kappa=ka$,

$$E_1 - E_o = 2J(1 - \cos ka) \ , \tag{12}$$

$$k = 2m\pi/aN \ , \quad m = 0,\pm1,\pm2,\ldots,\pm N/2 \ .$$

To interpret this solution it is necessary to calculate the values of the various spin components. The total z-component of spin for the whole chain reflects the net loss of one unit of angular momentum caused by flipping a single spin in the ground state:

$$S_{tot}^z \psi_1 = \sum_{i=1}^{N} S_i^z \sum_{j=1}^{N} c_j \phi_j = [(N/2) - 1]\psi_1 \ .$$

The operator S_i^z acting on ψ_1 gives

$$S_i^z \psi_1 = S_i^z \sum_{j=1}^{N} c_j \phi_j = (1/2)\psi_1 - c_i \phi_i \ ,$$

so the expectation value of the z-component of spin at site i is just

$$\langle \psi_1^* | S_i^z | \psi_1 \rangle = (1/2) - |c_i|^2 = (1/2) - (1/N) \ ,$$

indicating that on the average the loss of one unit of angular momentum from the ground state configuration is shared equally by all N spins.

As was found for the ground state, the squared magnitude of the z-component of spin at site i is given by

$$(S_i^z)^2\psi_1 = (1/4)\psi_1 ,$$

and its total magnitude squared by

$$S_i^2\psi_1 = (3/4)\psi_1 .$$

Again, part of the total angular momentum must be carried by the x and y-components of spin. S_j^x and S_j^y operating on ψ_1 give

$$S_j^x\psi_1 = (1/2)(S_j^+ + S_j^-)\sum_{n=1}^{N} c_n\phi_n$$

$$= (1/2)c_j\psi_o + (1/2)\sum_{n=1}^{N} c_n\phi_{jn} ,$$

and

$$S_j^y\psi_1 = (1/2i)(S_j^+ - S_j^-)\sum_{n=1}^{N} c_n\phi_n$$

$$= (1/2i)c_j\psi_o - (1/2i)\sum_{n=1}^{N} c_n\phi_{jn} ,$$

where ϕ_{jn} is the product wave function (4) with a second spin reversed ($\phi_{nn} = 0$). As in the ground state the expectation values of S_j^x and S_j^y are zero, and ψ_1 is not an eigenfunction. But ψ_1 is an eigenfunction of the squared magnitude of the transverse component and has an eigenvalue equal to one-half:

$$(S_j^{\perp})^2\psi_o = (1/2)\psi_1 \quad .$$

Again, the spins must precess about the z axis. In the ground state the precession was random: the spins were in a state of maximum (quantum mechanical) alignment so that their relative orientations had no effect on the energy. However, in the first excited state the spins are not aligned, and the phase of the precession, which determines the orientation of neighboring spins, will therefore also determine the energy. The transverse spin correlation operator for sites j and n is

$$\begin{aligned} S_j^{\perp} \cdot S_n^{\perp} &= S_j^x S_n^x + S_j^y S_n^y \\ &= (1/4)(S_j^+ + S_j^-)(S_n^+ + S_n^-) - (1/4)(S_j^+ - S_j^-)(S_n^+ - S_n^-) \\ &= (1/2)(S_j^+ S_n^- + S_j^- S_n^+) \ . \end{aligned}$$

Operating on ψ_1 with $S_j^{\perp} \cdot S_n^{\perp}$ gives

$$(S_j^{\perp} \cdot S_n^{\perp})\psi_1 = (1/2)(c_j\phi_n + c_n\phi_j) \ ,$$

which yields the transverse spin correlation function

$$\left\langle \underline{S}_j^{\perp} \cdot \underline{S}_n^{\perp} \right\rangle = (1/N)\cos[ka(j - n)] \ .$$

Since the correlation function is the expectation value of $|S^{\perp}|^2\cos\Phi$ where Φ is the angle between $S_j^{\perp}$ and $S_n^{\perp}$, the transverse component has magnitude $N^{-1/2}$, and the angle between adjacent spins is ka.

To summarize, in the single spin reversed state the spins precess about the z-axis with constant phase. The first excited state has one unit of z-component of angular momentum less than the ground state,

and this difference is on the average divided equally among all the spins in the chain. Each spin therefore has a transverse component with magnitude 1/N, and rotates with frequency $E_2/\hbar$. The difference in phase angle between adjacent spins is ka. Thus, the amplitude of the y-component varies sinusoidally in space and time:

$$\langle S_j^y(r,t)\rangle = (1/N)\exp[i(kaj - \omega t)] .$$

Because of this plane wave form the one spin reversed solutions are called spin waves. By analogy with phonons the quantized excitations with energy $E_2 = \hbar\omega$ are called magnons, and the one spin reversed solutions are one magnon states.

The analysis of spin systems in terms of spin waves was first developed by Bloch [25]. He extended the analysis given above by assuming that all of the higher energy excitations (multiple spin reversals) could be approximately described by combinations of the ψ_1^k, and that the number of spin waves excited was small compared to N, so that interaction between magnons could be neglected. Under these assumptions Bose-Einstein statistics apply, and Bloch used them to derive the $T^{3/2}$ law for the magnetization of a ferromagnet as a function of temperature:

$$M(T) = M(0)\left[1 - (T/T_c)^{3/2}\right] ,$$

where T_c is the critical temperature at which ferromagnetic ordering occurs.

Although the above analysis is exact, spin wave (SW) theory is not limited to systems where the one spin reversed solution is the

exact lowest excited state. Virtually any spin Hamiltonian can be analyzed in terms of SWs. Because the spin operators can be written in terms of spin raising and lowering operators, as in Hamiltonian (1), an analogy can be drawn between the harmonic oscillator creation-annihilation operators used in the analysis of elastic solids and the spin operators used in the study of magnetic phenomena. If the Hamiltonian is expanded in terms of the analogous spin creation-annihilation operators, and anharmonic terms are neglected, the resulting energies are proportional to $(ka)^2$, which is just the one spin reversed solution for small k. A similar procedure can be successfully applied to other systems besides the S=1/2,1d,HF.

Although SW theory has been applied to a wide variety of systems, there are circumstances in which its validity is questionable. These shortcomings of SW theory are discussed in the following sections. The first question which must be dealt with in this context is whether or not the higher excited states can be represented in terms of the single spin reversed solutions. This question was first examined by Bethe [26], who studied the multiple reversed spins problem and discovered the existence of bound spin wave states. In order to provide a simple introduction to the bound magnon (BM) states, a discussion of the two spins reversed state is given below.

Two Spins Reversed

A two spins reversed wave function is obtained by flipping two spins out of the ground state

$$\phi_{jm} = S_j^- S_m^- \psi_o = \alpha_1\alpha_2\alpha_{j-1}\beta_j\alpha_{j+1} \cdots \alpha_{m-1}\beta_m\alpha_{m+1} \cdots \alpha_N . \qquad (13)$$

Note that the same spin cannot be reversed twice, $\phi_{jj} = 0$, and that $\phi_{jm} = \phi_{mj}$. This state, however, is not an eigenfunction. Operating on ϕ_{jm} with Hamiltonian (1)

$$H\phi_{jm} = HS_j^- S_m^- \psi_o = -2J \sum_{i=1}^{N} [(1/2)S_i^+ S_{i+1}^- + (1/2)S_i^- S_{i+1}^+ + S_i^z S_{i+1}^z] S_j^- S_m^- \psi_o ,$$

gives three terms. From the one spin reversed analysis it is apparent that the first term in the Hamiltonian shifts the reversed spins one position to the right, yielding $\phi_{j+1,m} + \phi_{j,m+1}$. If the reversed spins are adjacent, $m = j \pm 1$, one of these terms is zero. Similarly, the second term in the Hamiltonian shifts the reversed spins one position to the left, resulting in $\phi_{j-1,m} + \phi_{j,m-1}$. Again, if the reversed spins are adjacent one of these terms is zero. The third term is, by inspection,

$$\{N(1/2)^2 - 2[2(1/2)^2] - 2[2(1/2)^2]\}\phi_{jm} = (1/4)(N-8)\phi_{jm}$$

if the reversed spins are not adjacent, or

$$\{N(1/2)^2 - 2[2(1/2)^2]\}\phi_{jm} = (1/4)(N-4)\phi_{jm}$$

if the reversed spins are adjacent. So $H\phi_{jm}$ is given by

$$H\phi_{jm} = -J(\phi_{j+1,m} + \phi_{j,m+1} + \phi_{j-1,m} + \phi_{j,m-1}) - (J/2)(N - 8 + 4\delta_{j\pm1,m})\phi_{jm} .$$

Since $H\phi_{jm}$, consists of a combination of ϕ_{jm} and other states with only two spins flipped, it is reasonable to try a solution which is a linear superposition of the ϕ_{jm}:

$$\psi_2 = \sum_{j=1}^{N} \sum_{m=1}^{N} f_{jm}\phi_{jm} , \tag{14}$$

where $f_{jm} = f_{mj}$, $f_{jj} = 0$.

The energy of ψ_2 can be found by taking the inner product of both sides of the Schroedinger equation $H\psi_2 = E_2\psi_2$ with ϕ_{qr}. Since the ϕ_{jm} are orthonormal,

$$\langle\phi_{qr}|\phi_{in}\rangle = \delta_{qi}\delta_{rn} + \delta_{qn}\delta_{ri} ,$$

the inner product of ϕ_{qr} and $H\psi_2$ is just

$$\langle\phi_{qr}|H\psi_2\rangle = -2J[f_{q+1,r} + f_{q-1,r} + f_{q,r+1} + f_{q,r-1}] - J[N - 8 + 2(\delta_{q\pm1,r} + \delta_{r\pm1,q})]f_{qr} .$$

And, the inner product of ϕ_{qr} and $E_2\psi_2$ is

$$E_2\langle\phi_{qr}|\psi_2\rangle = 2E_2 f_{qr} .$$

Finally, the equation governing the amplitudes f_{qr} is

$$\varepsilon_2 f_{qr} + J(f_{q+1,r} + f_{q-1,r} + f_{q,r+1} + f_{q,r-1}) = -J(\delta_{q\pm1,r} + \delta_{r\pm1,q})f_{qr} , \tag{15}$$

where $\varepsilon_2 = (E_2 - E_o) - 4J$.

If the reversed spins are not nearest neighbors, the right hand side of equation (15) is zero. In this case the analogy to equation

(7) which gives the amplitudes c_j for the one spin reversed solution is clear. Separating the q and r dependence of the amplitudes, $f_{qr} = \lambda_q \mu_r$, gives

$$[(1/2)\varepsilon_2 \mu_r + J(\mu_{r-1} + \mu_{r+1})]\lambda_q + [(1/2)\varepsilon_2 \lambda_q + J(\lambda_{q-1} + \lambda_{q+1})]\mu_r = 0 .$$

Obviously, this equation is satisfied if λ_q and μ_r are chosen to be the plane wave solution found in the one spin reversed analysis. This is physically reasonable. Since only neighboring spins interact, if two non-neighboring spins are flipped, the system should behave as if there were two non-interacting SWs present. The plane wave solutions for λ_q and μ_r are

$$\lambda_q = (N^{-1/2})\exp(ik_1 aq), \quad \text{and} \quad \mu_r = (N^{-1/2})\exp(ik_2 ar) , \qquad (16)$$

where k_1 and k_2 are the momenta (wavenumbers) of the two plane waves. As with the single spin flipped solution the periodic boundary conditions are satisfied for only the values of $\kappa = k_n a$ given in equation (9). For f_{qr} to be symmetric only the symmetric part of $\lambda_q \mu_r$ can be retained

$$f_{qr} = (1/2N)(\lambda_q \mu_r + \lambda_r \mu_q) . \qquad (17)$$

Substituting the solution of equations (16) and (17) into the non-adjacent reversed spin form of equation (15) yields the energy:

$$E_2 - E_o = 2J(1 - \cos k_1 a) + 2J(1 - \cos k_2 a) , \qquad (18)$$

which is the energy of two plane waves with wavenumbers k_1 and k_2.

The energy can be conveniently expressed in terms of the total momentum $K = k_1 + k_2$ and the relative momentum $p = (1/2)(k_2 - k_1)$:

$$E_2 - E_o = 4J[1 - \cos(Ka/2)\cos(pa)] \ . \qquad (19)$$

For a given K this is periodic with half-period $pa = \pi$, so only $|p| \leq \pi$ need be considered. Similarly, $|K| \leq \pi$. Likewise, the amplitudes f_{qr} can be written in terms of K, p, the center of mass coordinate $R_{qr} = (a/2)(q + r)$, and the relative separation of the flipped spins $r_{qr} = a(q - r)$:

$$f_{qr} = (1/N)\exp(iKR_{qr})\cos pr_{qr} \ . \qquad (20)$$

It now remains to solve equation (15) for the f_{qr} and the energy when the reversed spins are nearest neighbors. Since the total momentum K is a constant of the motion the resulting states can be classified in terms of K. One constructs a solution which employs the f^K_{qr} found for the non-adjacent flipped spin problem, using $\cos pr_{qr}$ as a set of basis functions. Summing over all of the allowed values of $p = (n\pi/aN)$, $n = 0, \pm1, \pm2, \ldots, \pm N$, gives

$$f_{qr} = (1/N)\exp(iKR_{qr}) \sum_{n=-N}^{N} f_n \exp[i(\pi/aN)r_{qr}n] \ ,$$

where the f_n are to be determined. Substituting this expansion into equation (15) for the amplitudes f_{qr}, multiplying by $\exp[-i(\pi/aN)r_{qr}m]$ and summing over q and r (using the orthogonality of the exponentials to evaluate the sums) leads to an integral equation which can be solved, after some effort, for the f_n and the energy E_2. This

derivation is tedious, and provides little physical insight, so only the final results will be presented. Details are given by Mattis [22].

As might have been expected from analysis of the non-adjacent reversed spins problem, the SW spectrum of the single spin flipped problem is recovered, but is now expanded into a continuum because of the added degree of freedom provided by the possible choices of k_1 and k_2 for a given total momentum $K = k_1 + k_2$. The energy (correct to O(1/N)) is given by equations (18) and (19). From equation (19) the upper bound of the continuum (for cospa = -1) is

$$E_2 - E_o = 4J[1 + \cos(Ka/2)] ,$$

and the lower bound (for cospa = +1) is

$$E_2 - E_o = 4J[1 - \cos(Ka/2)] .$$

Because of the interaction between reversed spins, a bound state appears. It has energy

$$E_2^b - E_o = J\sin^2(Ka/2) ,$$

which lies below the lower bound of the continuum energy. Physically, it is reasonable that a single (bound) state with energy lower than the SW continuum should exist in the spectrum of the two reversed spins state. If the system is considered to be a chain of classical spins with perfect spin alignment, and two non-adjacent spins are flipped, each of those spins becomes antialigned with its two nearest neighbors. The resulting energy increase due to the exchange

interaction is 16J. Each of these spin reversals is free to move along the chain with no constraints on its momentum, and the resulting energy spectrum for a given total momentum is a continuum. However, if the two reversed spins are adjacent each spin becomes antialigned with only one of its nearest neighbors, resulting in an energy increase of only 8J. Since these spins are bound together their momenta are constrained to one-half of the total momentum and there is only a single energy state for each momentum.

Clearly, the presence of a BM in the excitation spectrum casts doubt on the validity of SW theory. The BM cannot be accounted for by a superposition of the simple one reversed spin solutions described above. Further, as the number of flipped spins increases more BMs appear. Despite this apparent theoretical failing, SW theory has been quite successful in describing a wide variety of experimental data. This paradox points out the need for a careful study of the limitations of SW theory.

Limitations of Spin Wave Theory

Since the introduction of SW theory by Bloch [25], and the subsequent prediction of BMs by Bethe [26], there have been a number of attempts to understand how the existence of BMs affects the validity of the assumptions made in SW theory.

Spin wave theory is successful in many 3d experimental systems because the BMs exist only at large K values. Wortis [27] and Hanus [28] have studied the two spins reversed problem in 2d and 3d. In 2d there is at least one bound state below the continuum for all K, and a

second bound state may exist for some values of K. In 3d a single bound state exists for sufficiently large K, and as K increases a second and even a third bound state appears. However, all of the bound states in 3d occur only in a restricted range of K near the zone boundary. There is a broad range of low energy K values for which there are no bound states. Thus, even though the linearization procedure used in the SW approximation may not be valid in 1d and 2d, its use appears to be justified in 3d. Some caution must be exercised though: introduction of anisotropy, as in the Ising-Heisenberg ferromagnet, pushes the BM momentum existence threshold towards smaller values of K, and BMs can exist for all K if the anisotropy is sufficiently large [27]. Even in this case, Reklis [29] has shown that for sufficiently small K values (low temperatures) SW theory should be valid.

Even though the effects of BMs are negligible in some 3d systems the linearization procedures used in SW theory still are cause for concern. Careful analysis of the low order nonlinear corrections to the theory provide insight into SW interactions. Studies have been done by Dyson [30], Boyd [31], and Hepp [32]. Other than the possible effects of BMs Dyson identifies two basic flaws in SW theory. First, the SW states which describe situations with multiple reversed spins do not form an orthogonal set. This gives rise to what Dyson calls a kinematical interaction between SWs. Each SW reduces the total z-component of angular momentum by one unit, so that if 2NS magnons are excited the sample magnetization is completely reversed. Clearly, only a finite number of SWs can be supported, so they must interact in

some way to account for the finite value of NS. Further, in order to keep SWs from accumulating at a single spin site the kinematical interaction must be repulsive. Excitation of too many magnons causes spin reduction, destruction of the ordered ground state assumed to exist in SW theory, and can cause the theory to fail. Second, the SW states do not diagonalize the Hamiltonian. Dyson identifies the associated energy correction, which shifts the energy downwards, as being due to an attractive dynamical interaction between magnons. This is the same interaction which leads to the formation of the BMs but the approximate nonlinear corrections to SW theory do not predict formation of a BM. Indeed, Dyson's calculation predicts a very small energy shift at low temperature. But at higher temperatures, where the density of magnons is increased and spin reduction becomes a problem, the dynamical interaction could seriously affect the applicability of SW theory. In 1d, recent calculations by Müller [3,4] indicate that the failure of SW theory is not due to spin reduction, as was previously thought, but is due to other factors (perhaps the dynamical interaction) relating to neglect of the anharmonic terms. If this is the case, the reliability of SW theory is suspect even in the ordered state of 3d magnets.

In summary, there are three problems associated with linearized SW theory. First, the existence of BMs cannot be accounted for in a linear theory. Second, spin reduction may cause energy shifts associated with the kinematical interaction. Third, the dynamical interaction between magnons may induce further shifts in energy. All of these difficulties are introduced because anharmonic terms are not

included in the linearized SW Hamiltonian. Obviously, because of their common origin, these effects complement each other, and it is very difficult to tell which is dominant. Consequently, it is also very difficult to decide on a set of criteria for the validity of SW theory.

This thesis presents experimental confirmation of the existence of BMs in the S=1/2,1d,HF, and gives experimental evidence of their importance in determining the magnetic susceptibility of a quantum spin chain. Further, the relative importance of BMs and SWs in the S=1/2,1d,HF has been numerically studied by comparing the sizes of their magnetic susceptibilities and specific heats at various applied field strengths. In order to interpret the experimental results and perform the numerical studies, the Johnson and Bonner theory [12] for the thermodynamics of the S=1/2,1d,HIF was used. This theory is reviewed in Chapter Two. Chapter Three presents the results of the numerical studies. Chapter Four consists of two parts, a description of the experimental apparatus, and a discussion of the model S=1/2,1d,HIF compound used in the experiments. The data is presented and analyzed in Chapter Five. A conclusion, along with a discussion of possible extensions of this work, is given in Chapter Six.

CHAPTER TWO

A REVIEW OF THE JOHNSON AND BONNER THEORY

The last chapter introduced the basic concepts of bound magnons and spin waves. These simple calculations, however, do not provide a complete description of the spin system. Only the ground, one magnon and two magnon states were discussed. In order to understand the excitation spectrum, and the relative importance of spin waves and bound magnons in determining the behavior of the system, the higher energy multi-magnon states must be considered. Unfortunately, the mathematical complexity involved in calculating the energies of these states makes such an approach impractical. Solutions are available in some cases [33,34], but are mathematically complex and difficult to interpret, and/or are incomplete in some respect.

In addition to these difficulties, knowledge of the m-magnon energy spectrum is not sufficient. It is the combined spectrum of all magnon excitations which determines the properties of the system. Also, it is not enough simply to know the energy levels. As pointed out by Johnson and Bonner [12], it is not only the low lying energy levels of the excitation spectrum which are important to the characteristic behavior of a quantum spin system, but also the degeneracies of those levels. It is important to verify the existence of bound magnons, but it is perhaps more important to determine their impact on the behavior of the spin system. This requires a thorough study of

thermodynamic properties as a function of temperature, magnetic field, and any other relevant parameters.

Since the thermodynamics depends only on the free energy of the system, much of the mathematical complexity of calculating magnon energy levels can be circumvented by directly substituting the transcendental equations for these energies into the free energy. This has been done by Gaudin [35]. The result is still complicated, but leads more directly to the thermodynamic functions. Johnson and Bonner have extended the formalism presented by Gaudin to develop a complete, analytic theory for the excitation spectrum and low temperature thermodynamics of the spin one-half, 1d, Ising-Heisenberg ferromagnet (S=1/2,1d,HIF).

Johnson and Bonner Theory

The remainder of this chapter deals with the theory of the S=1/2,1d,HIF. A brief review of analytic results for this model is given by Johnson [11]. The Hamiltonian is given by

$$H = -2J \sum_i [S_i^z S_{i+1}^z - (1/4) + \gamma(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y)] - g\mu_B H_p \sum_i S_i^z$$

where the S's are 1/2 the respective Pauli matrices, H_p is the applied (physical) magnetic field, J is the exchange energy, and γ is the anisotropy parameter. The allowed anisotropy range is $0 \leq \gamma < 1$, with $\gamma = 1$ corresponding to the Heisenberg model and $\gamma = 0$ to the Ising model.

The low temperature excitation spectrum and thermodynamics of the S=1/2,1d,HIF model have been calculated by Johnson and Bonner (JB) [12]. Using Gaudin's free energy formalism [35], they derive the low temperature free energy, susceptibility and specific heat. The susceptibility and specific heat are

$$\chi = T_o^2 e^{-(\Delta^2-1)^{1/2}/T_o}\left[4(H_o^2/4 + T_o^2 e^{-(\Delta^2-1)^{1/2}/T_o})^{3/2}\right]^{-1} \quad (1)$$

$$+ (2\pi T_o)^{-1/2}\, e^{-(\Delta+H_o-1)/T_o}$$

and,

$$C_H = (2\pi T_o^3)^{-1/2}(\Delta + H_o - 1)^2 e^{-(\Delta + H_o - 1)/T_o} \quad (2)$$

$$+ (\Delta^2 - 1)e^{-(\Delta^2 - 1)^{1/2}/T_o}\left[H_o^2/2 + T_o^2 e^{-(\Delta^2 - 1)^{1/2}/T_o}\right]$$

$$x\left[4T_o\{H_o^2/2 + T_o^2 e^{-(\Delta^2 - 1)^{1/2}/T_o}\}^{3/2}\right]$$

In these expressions the dimensionless field and temperature (H_o,T_o) are given in terms of the physical field and temperature (H_p,T_p), the exchange energy J, and the anisotropy parameter $\Delta = 1/\gamma$: $H_o = (g\mu_B H_p)/(2\gamma J)$, $T_o = (kT_p)/(2\gamma J)$. Although these forms are low temperature approximations ($T_o << 1$), the approximations are introduced only in the final step of the derivation. The analytical approach used by JB appears to be exact [12].

The free energy formalism is exact, but provides little physical insight into the fundamental excitations involved. A simplified,

physical argument which gives the same results is possible [12]. The T=0 elementary excitations for the S=1/2,1d,HIF are given by

$$E_n(P) = nH_o + \{[\cosh(n\Phi)-\cos(P)]\sinh\Phi\}/\sinh(n\Phi) \quad ,$$

where $\Delta = 1/\gamma = \cosh\Phi$, $n = 1,2,3,\ldots$, and $0 \leq P \leq 2\pi$. The P's are uniformly distributed between 0 and 2π and, for a given n, obey a Fermi-like exclusion principle. The n=1 excitations and linear combinations of them are free magnons (spin waves). When the E_1 and their degeneracies are used to form a partition function, and the thermodynamic functions calculated, the results are (after appropriate low temperature approximations are made) just the second terms in χ and C_H. The higher n excitations are bound magnons (bound states of spin waves). For large n the E_n become independent of P, and are just the energies of a 1d Ising model with exchange constant $J = \sinh\Phi$. Accordingly, the thermodynamics of these excitations are just those of the Ising model, which, after making the low temperature approximations, give the first terms in χ and C_H. The susceptibility, equation (1), and specific heat, equation (2), are thus the sum of two different types of thermodynamic behavior which result from two distinctly different types of excitations: the n=1 spin wave (SW) excitations, which lead to the second terms of equations (1) and (2); and, the high-n, Ising-like bound magnon (BM) excitations, which produce the first terms of equations (1) and (2).

Figures 1, 2, and 3 show susceptibility vs. temperature. The solid curves are for the JB model with $J/k = 70K$, $\gamma = 0.99$, and $g = 2.15$. The dashed curve is for a simple paramagnet with field

dependence included. Figure 1 gives χ vs. T in fields of 3, 6, and 9T. The behavior of the JB susceptibility is distinctive, showing pronounced high temperature maxima. These maxima are not related to any ordering phenomena, but rather are due to the freezing out of dynamic modes (spin waves and bound magnons). Referring to Figure 2, which shows the T dependence of the total, SW, and BM susceptibilities at H = 4T, it is clear that the maxima are almost entirely due to the BM contribution to the susceptibility. Figure 3 shows χ vs. H at the temperatures 4, 5, and 6K. Here the deviations from paramagnetic behavior are even more pronounced. The large values of zero field susceptibility, and the rapid decrease in χ as T and H are increased are due to the behavior of the BM term.

Specific heat is shown in Figures 4, 5, and 6. Solid lines are from the JB theory for J/k = 70K, γ = 0.99, and g = 2.15. The dashed line is the field dependent Schottky specific heat of a paramagnet. As with the susceptibility, the behavior of the Johnson and Bonner curves is distinctive, and can be attributed to the influence of bound magnons. Figure 4 shows C_H vs. T for 2, 6, and 10T, and Figure 5 gives the total, BM, and SW specific heat vs. T at H = 8T. Clearly, the BM contribution determines the general shape and magnitude of C_H. Figure 6 shows C_H vs. H at T = 2, 4, 7K. Again, the large zero field values and the rapid decreases as field and temperature are increased are due to the influence of BMs.

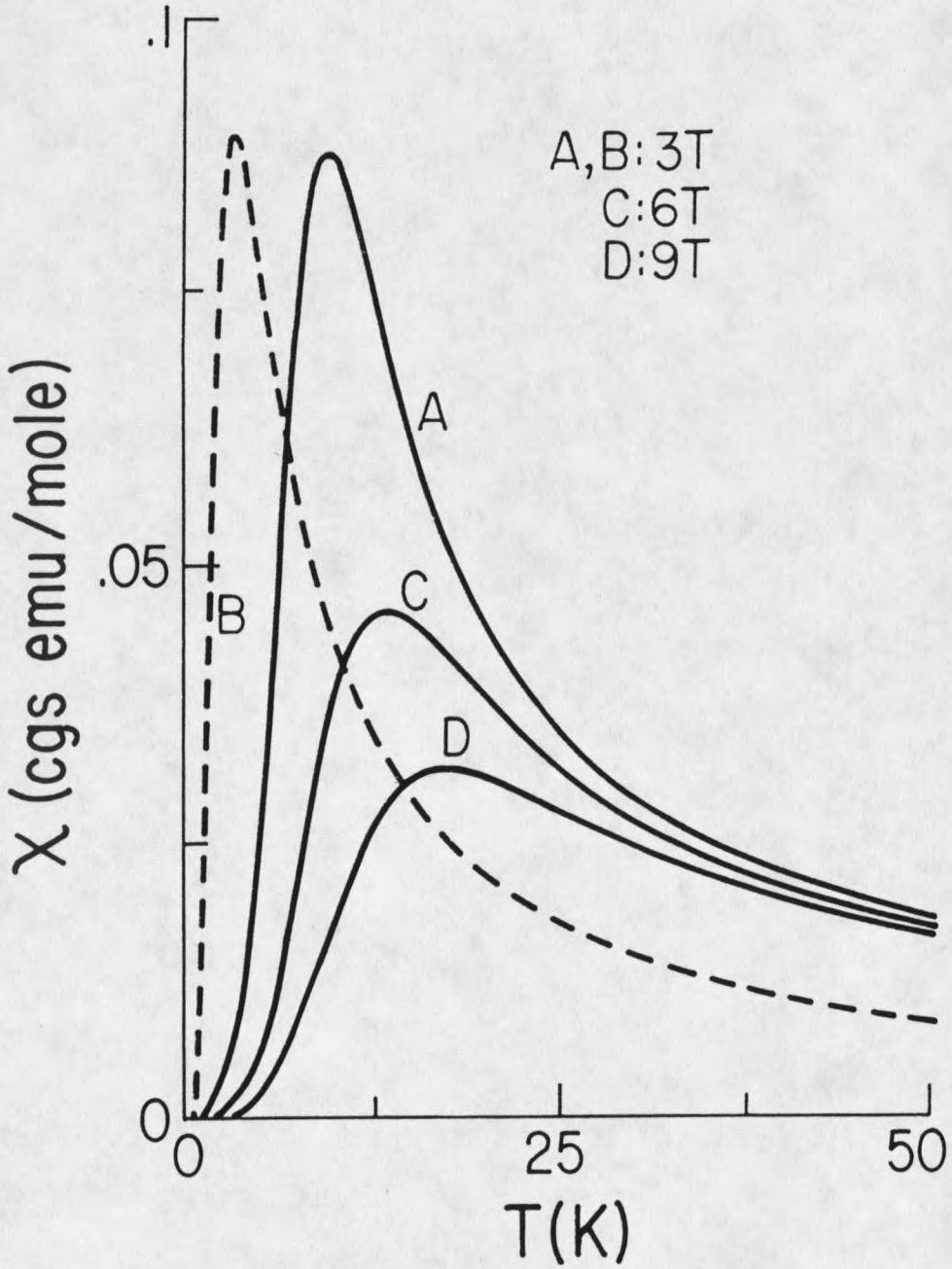

Figure 1. Susceptibility vs. temperature in fields of 3, 6, and 9T. Solid lines are the Johnson and Bonner model for J/k = 70K, γ = 0.99, g = 2.15. Dashed curve is for a simple paramagnet with field dependence included.