



Experimental study of bound magnons and spin cluster resonances in one-dimensional $S=1/2$, Ising-Heisenberg ferromagnets
by Kathirgamathamby Ravindran

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

Montana State University

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Abstract:

Differential magnetic susceptibility of one-dimensional $S=1/2$, ferromagnetic compounds, $[(CH_3)_3NH]FeCl_3 \cdot 2H_2O$ (FeTAC), $(CH_3)_4NCuCl_3$ (TMCuC), and $CuCl_2C_2H_6SO$ ($CuCl_2 \cdot DMSO$) are presented. The data are analyzed using the Johnson and Bonner theory to look for expected bound magnon effects. It is found that in FeTAC (Ising) and TMCuC (Heisenberg) the low temperature susceptibility is almost entirely represented by bound state excitations and that the usual spin wave excitations fail to represent the data. Analysis on $CuCl_2 \cdot DMSO$ shows that owing to the strong interchain exchange significant deviation from a 1-D system occurs below 13K so that the bound magnon effect cannot be clearly identified. It is found that Takahashi's, and Schlottmann's recent low temperature expansions for the isotropic Heisenberg ferromagnet fit the zero field data of TMCuC. Numerical results of finite chain calculations of 12-spin, and 14-spin for the isotropic Heisenberg ferromagnet are discussed.

The low temperature EPR measurements along the easy axis of the Ising system FeTAC above the ordering temperature 3.1 K are presented. The expected paramagnetic resonance signal corresponding to the g -value = 7.5 as well as a broad signal of 2-fold spin cluster (bound magnon) resonance are observed below the equivalent intrachain exchange temperature. This is the first observation of spin cluster resonance above T_c . Forbidden resonances from the excited doublets are also reported, and the possibility of observing higher order spin cluster resonances are discussed.

EXPERIMENTAL STUDY OF BOUND MAGNONS AND SPIN CLUSTER
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FERROMAGNETS

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APPROVAL

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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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to my mother and late father

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ABSTRACT

Differential magnetic susceptibility of one-dimensional $S=1/2$, ferromagnetic compounds, $[(CH_3)_3NH]FeCl_3 \cdot 2H_2O$ (FeTAC), $(CH_3)_4NCuCl_3$ (TMCuC), and $CuCl_2 \cdot C_2H_6SO$ ($CuCl_2 \cdot DMSO$) are presented. The data are analyzed using the Johnson and Bonner theory to look for expected bound magnon effects. It is found that in FeTAC (Ising) and TMCuC (Heisenberg) the low temperature susceptibility is almost entirely represented by bound state excitations and that the usual spin wave excitations fail to represent the data. Analysis on $CuCl_2 \cdot DMSO$ shows that owing to the strong interchain exchange significant deviation from a 1-D system occurs below 13K so that the bound magnon effect cannot be clearly identified. It is found that Takahashi's, and Schlottmann's recent low temperature expansions for the isotropic Heisenberg ferromagnet fit the zero field data of TMCuC. Numerical results of finite chain calculations of 12-spin, and 14-spin for the isotropic Heisenberg ferromagnet are discussed.

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CHAPTER 1

INTRODUCTION

The study of thermodynamic properties of magnetic materials has been an excellent way of characterizing them and has lead to a fundamental understanding of their behavior. In recent years a considerable amount of interest has been focussed on trying to understand one-dimensional magnetic systems. It has been shown that there is no long range ordering in one-dimensional magnets except possibly at $T=0$.^[1] Because of the absence of long range ordering the mean field and standard linear spin wave type calculations, which explain three-dimensional magnetic systems, are inadequate for explaining the thermodynamics of the one dimensional case. From the theoretical point of view, these systems are among the simplest non-trivial many-body systems, displaying a large variety of unexpected features resulting from the strong fluctuations.^[2] Mikeska demonstrated that an easy plane chain of classical spins ($S > 1/2$) in a magnetic field can be mapped to a sine-Gordon (SG) equation.^[3] Apart from linear excitations (magnons) this equation has nonlinear solutions called kink solitons.^[4] Theoretical development and experimental verification of the existence of soliton excitations in quasi-one dimensional systems are rather extensive. In particular, the results of neutron-scattering studies on CsNiF_3 ($S=1$)^[5] and $(\text{CD}_3)_4\text{NMnCl}_3$ (TMMC, $S=5/2$)^[6], nuclear-spin-lattice relaxation and heat capacity measurements on CsNiF_3 ^[7,8], and TMMC^[9,10] are interpreted in terms of the SG model.

On the other hand, in a ferromagnetic Ising-Heisenberg quantum chain ($S=1/2$), the excitation spectrum contains non-linear excitations called bound magnons (BM). These bound magnons resulting from the Ising-like anisotropy were predicted by the pioneer

Hans Bethe.^[11] A number of theoretical studies following Bethe's Ansatz reveal that even a small amount of anisotropy may have a drastic influence on the thermodynamics.^[12,13] In particular, the work of Johnson and Bonner predicts that under certain experimental conditions thermodynamic properties are almost entirely represented by bound magnons.^[13] Despite the theoretical activity, the experimental evidence on these quantum systems is scarce. Besides the earlier experimental study by Haines and Drumheller^[14] on CHAC (1-D, $S=1/2$ Heisenberg ferromagnet), we are aware of only one other experimental investigation done, also on CHAC, $(C_6H_{11}NH_3)CuCl_3$,^[15] by Hoogerbeets *et al.*, in which they used ESR to measure energies of the first seven BM levels.

In an Ising system, the elementary excitations are localized spin clusters, where an n -fold spin cluster (bound magnon) is defined as having n adjacent spins which are reversed with respect to other spins. Experimentally, bound magnons in $S=1/2$, quasi 1-D Ising systems were first observed by Torrance and Tinkam^[16] using far-infrared absorption in the effective $S=1/2$, 1-D Ising ferromagnet $CoCl_2 \cdot 2H_2O$. Other studies using infrared absorption and ESR to measure the energy levels have since been done in $CoBr_2 \cdot 2H_2O$ ($S=1/2$, 1-D ferromagnet)^[17] and $RbFeCl_3 \cdot 2H_2O$ ^[18]. However, to our knowledge no experimental study has been done to investigate the possible effect of bound magnons on the thermodynamic properties of Ising chains. Most of the experimental studies focussed on antiferromagnets and mostly on their static properties, whereas the ferromagnets have received little attention and thus their dynamics are not understood.

The purpose of this thesis is to investigate experimentally the importance of bound magnons in the presently available one-dimensional $S=1/2$, ferromagnetic systems, FeTAC (Ising like), TMCuC (nearly isotropic Heisenberg), and $CuCl_2 \cdot DMSO$ (also

nearly isotropic Heisenberg). Differential susceptibilities of these compounds have been measured at low temperatures in zero and higher magnetic fields. The data has been analyzed using the Johnson and Bonner theory and also using other expressions such as that of Takahashi and Yamada and of Schlottman in the case of isotropic Heisenberg system at zero field.

Quasi-one-dimensional magnetic materials also have the interesting feature that due to the weak interchain interaction they order at temperatures significantly below the equivalent temperature of the intrachain exchange energy. Consequently, they develop strong short range spin correlations in their "paramagnetic" phase, and exhibit significant spin cluster fluctuations above T_c and below the equivalent exchange energy temperature. In an Ising system spins have discrete symmetry, *i.e.*, a spin either points up or down. Therefore it is possible to stimulate spin cluster flip resonances in this "paramagnetic" phase. Our low temperature EPR results and the observation of spin cluster resonances are discussed in Chapter 4.

One Dimensional Magnetism. Basic Models

A one-dimensional (1-D) magnet is an idealized system in which the spins lie on a chain and interact only with spins on the same chain. However, it is difficult to find such an ideal system for experimental study. In general, linear chain systems that have been synthesized so far do show weak interchain (3D) interaction (quasi one-dimensional). Nevertheless, if the interchain interaction (J') is very small compared to the intrachain interaction (J), (for example, $|J'/J| \sim 10^{-3} - 10^{-4}$) the system can be well-described by a one-dimensional model. In quasi one-dimensional systems, this weak interchain interaction leads to long-range ordering at low temperatures and thus there will be a

dimensionality crossover from one to three. However, well above the ordering temperature the long range effect is small and can be neglected and the system can be treated as one-dimensional. Figure 1 illustrates the area of interest.

Next we look at the exchange Hamiltonian which describes the one-dimensional magnetic systems. For a simple case of two interacting spins (dimer) the exchange Hamiltonian is given by:

$$H = -2JS_1 \cdot S_2$$

where J is the exchange constant, which is positive for ferromagnetic exchange and negative for antiferromagnetic exchange.

It is widely accepted that for a system of N interacting spins the isotropic exchange Hamiltonian would have the form:

$$H = -2 \sum_{\substack{i,j \\ i \neq j}} J_{ij} S_i \cdot S_j$$

Considering only the nearest neighbor interaction, a one dimensional anisotropic magnetic system can be represented by

$$H = -2 \sum_{i=1}^N \{J_x S_i^x S_{i+1}^x + J_y S_i^y S_{i+1}^y + J_z S_i^z S_{i+1}^z\}$$

The values of J_x, J_y , and J_z define the nature of the exchange coupling. When $J_x = J_y = J_z = J$, the coupling is isotropic in spin space and this case is known as the isotropic Heisenberg model. The extreme situation when $J_x = J_y = 0$ and $J_z \neq 0$ defines the Ising model. Similarly, the case when $J_z = 0$ and $J_x = J_y \neq 0$, leads to an other extreme, referred to as the XY model. The later two cases are anisotropic systems showing easy axis and easy plane anisotropy respectively.

In order to complete the spin Hamiltonian and account for the effect of an applied

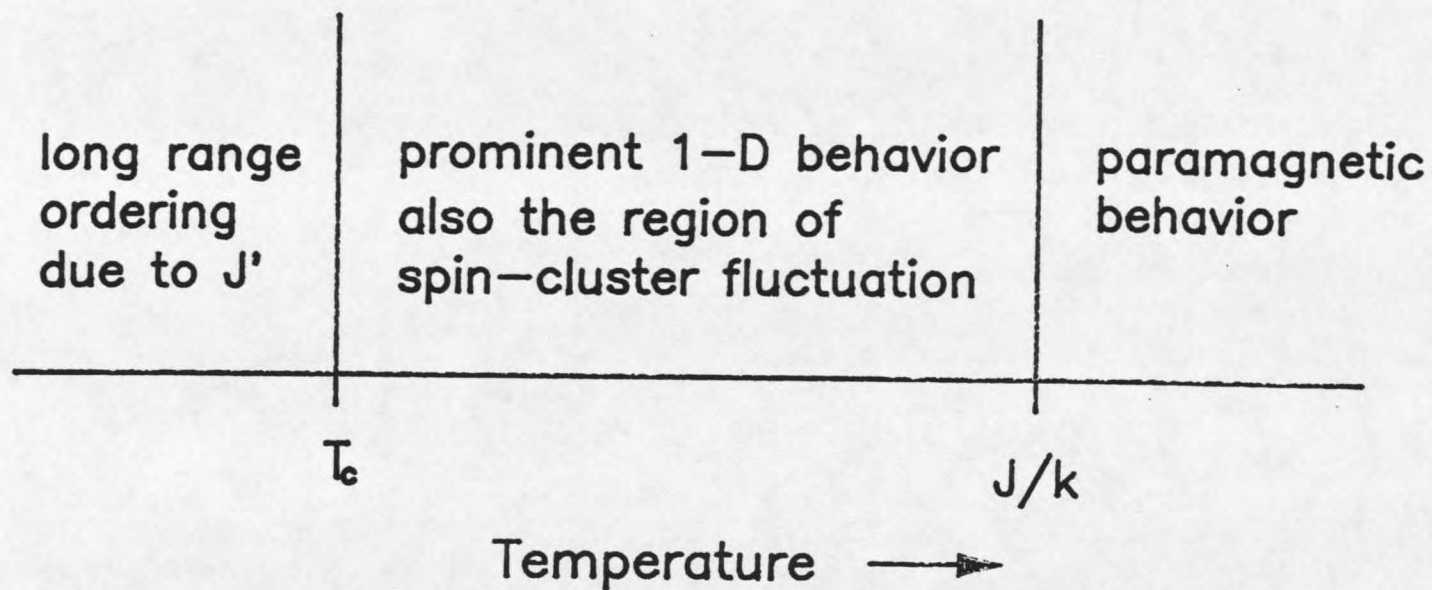


Figure 1. Behavior of a quasi one-dimensional magnetic system.

magnetic field and possible anisotropy (for orthorhombic crystal field) we add the following terms:

$$\text{Zeeman term: } -g\mu\vec{H} \cdot \vec{S}_i$$

$$\text{Single ion anisotropy term (axial): } D\left[(S^z)^2 - \left(\frac{1}{3}\right)S(S+1)\right]$$

$$\text{Single ion anisotropy term (rhombic): } E(S_x^2 - S_y^2)$$

where the single ion term accounts for the anisotropy arising from the axial crystalline electric field and the rhombic term is from the anisotropy in the plane. D and E are the measure of these anisotropies. For $S=1/2$ systems (example Cu^{2+}) the single ion term vanishes.

Other Hamiltonians have been used for mathematical convenience but they all give the same results. Among them Johnson and Bonner used the following form:

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

where γ is the anisotropy parameter and can vary from $\gamma=1$ (isotropic Heisenberg) to $\gamma=0$ (Ising).

For experimental purposes, measurements on powders are often sufficient for isotropic or weakly anisotropic materials whereas in the limiting cases (Ising or XY) magnetic measurements along the crystal axes are usually necessary to identify the nature of the anisotropy and to allow comparison with theory.

One-Spin Reversals, Dispersion Relation, Spin Waves

Spin wave theory was first introduced by Bloch in 1930.^[19] Let us imagine a Heisenberg ferromagnet in its ground state ($T=0$). At each lattice site assume there is a localized spin with a spin quantum number S and z -component S^z . In the ground state,

all the spins are completely aligned parallel to each other in a preferred direction. Each spin in this state has the maximum allowable value $S^z = S$.

A possible ground state is:

$$|\uparrow\uparrow\uparrow \dots \uparrow\uparrow\rangle.$$

but, infact for the isotropic Heisenberg system the ground state is $(N+1)$ fold degenerate.

As the temperature increases, the system will be excited to a higher energy state. The theory of Bloch showed that at low enough temperatures these excited states can be represented by spin waves (like elastic waves in solids) and as linear combinations of spin waves. In these excited states a spin wave may be described as a sinusoidal disturbance of the spin system with amplitude at each site proportional to $S - S_z$. The applications of this to a $S=1/2$ system will be shown below.

Using Pauli spin matrices an isotropic Heisenberg 1-D system can be described by the Hamiltonian:

$$H' = -\frac{1}{2}J \sum_{ij} \left(\frac{1}{2} \sigma_i^+ \sigma_j^- + \frac{1}{2} \sigma_i^- \sigma_j^+ + \sigma_i^z \sigma_j^z \right)$$

where

$$\sigma_i^\pm = \sigma_i^x \pm i\sigma_i^y,$$

$$\sigma_i^z \alpha_i = +\alpha_i, \quad \sigma_i^z \beta_i = -\beta_i$$

where α_i 's and β_i 's represent the wave functions:

$$\alpha_i = |\uparrow\rangle_i,$$

$$\beta_i = |\downarrow\rangle_i.$$

The ground state is (for N spins):

$$\psi_0 = \alpha_1 \alpha_2 \dots \alpha_N.$$

This is the state at $T=0$; it represents the maximum alignment of spins or saturation magnetization. As temperature increases, the system will be excited out of the ground state. The next state may be thought of as one in which a single spin is reversed, however the function

$$\phi_j = \alpha_1 \alpha_2 \dots \alpha_{j-1} \beta_j \alpha_{j+1} \dots \alpha_N$$

does not diagonalize the Hamiltonian. An eigenfunction ψ_k may be formed by taking a linear combination containing a reversal at a different lattice site:

$$\psi_k = \sum_j C_j^k \cdot \phi_j$$

Substituting this function into the Schrodinger equation $H' \psi_k = E \psi_k$ and equating the coefficient of C_j^k we get^[20]:

$$\left[E + \frac{1}{2}(N-4)J \right] C_j^k + J [C_{j+1}^k + C_{j-1}^k] = 0 \quad (1.1)$$

This equation has solutions of the form,

$$C_j^k = N^{-1/2} e^{ikja} \quad (1.2)$$

where 'a' is the distance between the spins. This solution represents the wave nature of the excited states (spin waves), i.e., the excited state is equivalent to a spin wave of wave number k. Here the allowed values for k can be determined with the assumption of periodic boundary conditions that require $C_j^k = C_{j+N}^k$: $(Nka)/(2\pi) = 0, \pm 1, \pm 2, \dots \pm N/2$. Further substituting (1.2) into (1.1) gives the dispersion relation:

$$E + \frac{1}{2}(N-4)J + 2J \cos ka = 0$$

$$\text{or } E - E_0 = 2J(1 - \cos ka),$$

where $E_0 = -NJ/2$ is the ground state energy level.

Each of these wave-like quantum states is called a magnon. The magnon energy for small k is given by

$$E_k = \hbar\omega_k \approx (\text{const}) \cdot J a^2 k^2$$

As temperature is increased more spin waves are excited. Bloch assumed that the interaction between the spin waves may be neglected and any number of spin waves of a given k can be excited. However this assumption is not accurate.

Actually, spin waves have a repulsive or attractive interaction. For $S=1/2$, the repulsion results from the fact that there cannot be more than one spin deviation on a given atom. Thus if two spin deviations approach the same lattice site, they will be scattered because of this interaction. The attractive part comes from the fact that the energy of a configuration in which two spin deviations are located on nearest neighbors (bound magnon), is lower than that of a configuration in which the two spin deviations are further apart. In a one dimensional system this can lead to bound spin complexes. This was first pointed out by Bethe.^[11]

Two Magnon States and Bound Magnons

As the temperature increases more spins are flipped from the ground state configuration. While the dispersion relation obtained above is true for a single $n=1$ spin flip, the question arises whether the spin wave picture is valid for $n \geq 2$ (where n labels the number of single spins). Bloch argued that at low temperatures, the presence of a second spin wave cannot seriously modify the derivation of the dispersion law for a second spin wave, and similarly on up to n spin waves, provided n is much smaller than

the number N of spins in the sample. Further, Bloch assumed that the eigen function should be very nearly a linear superposition of non interacting spin waves.

Following this picture, the wave function for two spin reversals is:

$$\psi_K = \sum_{l>m} C_{lm}^K \phi_{lm}$$

where, $\phi_{lm} = \alpha_1 \alpha_2 \dots \beta_l \dots \beta_m \dots \alpha_n$

where $K = k + k'$ and K is the total momentum (which is a good quantum number).

Substituting the above into the $H\psi_K = E_K\psi_K$ equation we obtain

$$\begin{aligned} (E - E^0 - 2g\mu H_0 - 4J) C_{lm}^K + J(C_{l,m-1}^K + C_{l,m+1}^K + C_{l+1,m}^K + C_{l-1,m}^K) \\ = 0 \quad \text{if } l, m \text{ not neighbors} \\ = J[C_{ll}^K + C_{mm}^K - C_{lm}^K - C_{ml}^K] \quad \text{if } l, m \text{ are neighbors} \end{aligned} \quad (1.3)$$

If l, m are not neighbors, a possible solution is

$$C_{lm}^K = e^{iKR} \cos pr$$

with $r = (l + m)a/2$; $R = (l - m)a$.

This implies that

$$(E - E_0) = E_K(p) = 2g\mu H + 4J(1 - (\cos Ka/2) \cos pa)]$$

with,

$$K = k + k', \quad p = (k - k')/2$$

This can be rewritten as

$$E_K(p) = 2g\mu H_0 + 2J(1 - \cos ka) + 2J(1 - \cos k'a)$$

which represents the sum of the energies of two "non-interacting" spin waves of momentum k and k' , where k and k' determined by

$k = \frac{2\pi m + \psi}{Na}$, $k' = \frac{2\pi m' - \psi}{Na}$ where m and m' are integers $< N$, and $|m - m'| \geq 2$ and ψ determined by:

$$2 \cot \frac{\psi}{2} = \cot \frac{ka}{2} - \cot \frac{k'a}{2}.$$

If the neighboring spins are reversed, then the non zero term in equation (1.3) would account for bound states. The energy levels for such a bound state can be shown to be:

$$(E - E^0)_{\text{bound}} = 2g\mu H + J(1 - \cos Ka)$$

The derivation of this expression is more complicated and lengthy than for linear spin waves, so we refer the reader to Mattis.^[21]

In the limit $ka = \pm\pi$, the magnon and BM energies become:

$$E - E^0 = 2g\mu H + 4J$$

$$(E - E^0)_{\text{bound}} = 2g\mu H + 2J.$$

Note the bound state energy is $2J$ below the two spin wave continuum and is shown as the solid line in Figure 2. The existence of the lower lying bound magnon states caught the attention of theorists. There has been considerable interest in trying to understand the 2-magnon bound state and possible higher order bound magnons. Exact bound magnon energy levels have been calculated by Bethe^[11], Wortis^[22], Hanus^[23], Majumdar^[24], and Reklis and Drumheller^[25]. Bethe's solution for an isotropic chain is:

$$E_n(k) = \frac{2J}{n} (1 - \cos ka) + ng\mu H.$$

where n represents the bound spin reversals of n spins. Bethe's work further provides a formalism which involves the bound spin complexes. Although his formalism is complicated and difficult to interpret physically, it serves as a powerful technique to obtain analytical expressions for thermodynamic properties.

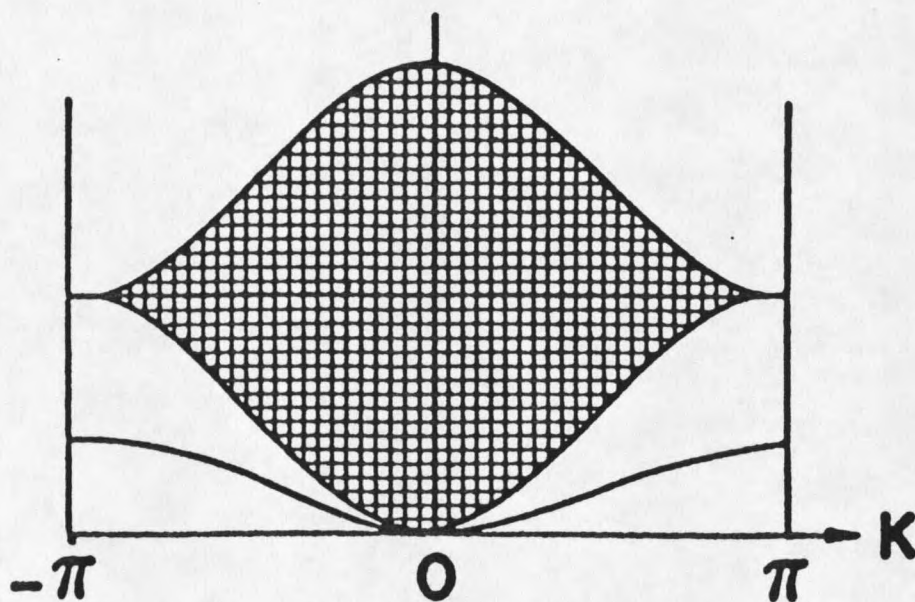


Figure 2. Energy of 2-magnon states in a linear chain. Shading indicates continuum, single line represents bound state.

CHAPTER 2

A SHORT REVIEW OF THE THEORIES

One-dimensional magnetic systems are the simplest systems but still present difficult theoretical problems. Finite chain calculations and high temperature series expansions may be used to understand the thermodynamic properties of these systems at higher temperatures. But the low temperature properties were not clearly understood because of the lack of exact expressions. The difficulty in finding exact solutions gave rise to the application and development of new techniques for solving nonlinear differential equations. Mikeska^[3] demonstrated that an easy plane chain of spins ($S > 1/2$) in a magnetic field is equivalent to a sine-Gordon system, which possesses soliton solutions. However, this continuum approximation is not applicable in the quantum limit $S=1/2$. It has been found that Bethe's ansatz formalism is an excellent way to approach this problem, although, due to its complexity, it took several years to develop to a stage where it could be used to derive thermodynamic properties. In particular the work of Gaudin^[26] and Takahashi^[27] are relevant in this respect. Gaudin was able to express the free energy as an elliptic integral containing an energy function whose form is determined by an infinite set of coupled, nonlinear, integral equations. Extending Gaudin's work, Johnson and Bonner^[13] obtained an analytical expression for the low temperature thermodynamic properties of Ising-Heisenberg linear ferromagnetic systems. On the other hand, Takahashi *et al.*, and Schlottmann tried to solve the coupled equations numerically. In this section we review the relevant expressions for the low temperature susceptibility (and specific heat in some cases) of $S=1/2$, isotropic-Heisenberg,

Ising-Heisenberg, and Ising linear ferromagnetic systems.

S=1/2, 1-D, Ising-Heisenberg Ferromagnet

Johnson and Bonner Analytical Expression

Johnson and Bonner (JB) used the Hamiltonian:

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

where $0 \leq \gamma < 1$ is the anisotropy parameter, ($\gamma = 0$ for Ising $\gamma = 1$ for Heisenberg). They analytically solved Gaudin's expression for the free energy, which is an infinite set of coupled nonlinear equations, and obtained expressions for the thermodynamic properties at the low temperature limit. For the susceptibility they obtained

$$\chi = T_0^2 \exp[-(\Delta^2 - 1)^{1/2}/T_0] \left[4 \left\{ \frac{H_0^2}{4} + T_0^2 \exp(-(\Delta^2 - 1)^{1/2}/T_0) \right\}^{3/2} \right]^{-1} \quad (2.1)$$

$$+ (2\pi T_0)^{-1/2} \exp(-(\Delta + H_0 - 1)/T_0)$$

and for the specific heat:

$$C_H = (\Delta^2 - 1) \exp[-(\Delta^2 - 1)^{1/2}/T_0] \left\{ \frac{H_0^2}{2} + T_0^2 \exp[-(\Delta^2 - 1)^{1/2}/T_0] \right\} \quad (2.2)$$

$$\times \left(4T_0 \left\{ \frac{H_0^2}{4} + T_0^2 \exp(-(\Delta^2 - 1)^{1/2}/T_0) \right\}^{3/2} \right)^{-1}$$

$$+ (2\pi T_0^3)^{-1/2} (\Delta + H_0 - 1)^2 \exp[-(\Delta + H_0 - 1)/T_0]$$

which are valid for $\Delta = 1/\gamma > 1$ and $T_0 \ll 1$. T_0 and H_0 are defined as $T_0 = (k_B T)/2\gamma J$ and $H_0 = (g\mu H)/2\gamma J$. The first term in each of the above expressions is the contribution from the bound magnon (BM) type excitations and the second term is the contribution from the linear spin wave (SW) type excitations. These expressions provide one way to

investigate the effect of bound magnons and spin waves on the low temperature thermodynamic properties of 1-D magnetic systems.

The above expressions, obtained from the free energy formalism given by Gaudin, are exact at least at the low temperature limit. The approximation methods involved are complicated and long. However, JB showed that their expressions for the susceptibility and specific heat can be obtained from a simplified physical argument.^[28] In JB notation, the zero-temperature dispersion curves for the $S=1/2$, 1-D, Ising-Heisenberg ferromagnet are given by

$$E_n(P) = nH_o + \sinh \phi (\cosh n\phi - \cos P) / \sinh n\phi$$

where $\cosh \phi = \Delta = 1/\gamma$, $n=1,2,\dots$ and P is just a number that satisfies $0 \leq P \leq 2\pi$. The P 's are distributed uniformly between 0 and 2π and for a given n , obey a Fermi-like exclusion principle. The $n=1$ excitations and a linear combination of the $n=1$ excitations are spin waves and higher- n excitations are bound states of spin waves. The energies of the first excited states are $E_1(q) = H_o + \Delta - \cos q$. There are N such states with $q = 2\pi m/N$, $0 \leq m < N$. When these states and their degeneracies are used to form a partition function, and the thermodynamic functions are calculated, it gives an expression which is exactly the same as the spin wave term in the above expressions. Accordingly the thermodynamic functions obtained from using the high n -bound states, after making low-temperature approximation, give the bound magnon term in the above expression.

Since we are interested in the susceptibility measurements and the comparison with JB theory, the expression for χ is plotted in Figures 3(a)-3(c) to demonstrate the behavior of the susceptibility as a function of field, temperature and the anisotropy parameter γ . Recall the expressions given by Johnson and Bonner are unitless. Looking at these expressions at the high temperature limit at zero field and comparing with the Curie-law one can find the unit conversion factor to be $N_A g^2 \mu^2 / 2\gamma J$. All these theoretical curves

shown are the JB susceptibility expression multiplied by this conversion factor.

Figure 3(a) shows χ vs T in fields of 0, 1, 1.5, and 2 Tesla. The solid lines are drawn for the parameter $J/k = 45\text{K}$, $g=2.1$, and $\gamma = 0.95$ (5% anisotropy) and represent the total contribution of both SW and BM. The behavior of χ is distinctive, showing a broad maximum at higher field. Also the maxima at higher fields occur at relatively higher temperatures. These maxima are not related to any ordering phenomena, but rather are due to the freezing out of dynamic modes. Figure 3(b) shows the temperature dependence of the SW, BM, and total contribution separately at $H=1$ Tesla. It is clear that the maxima are almost entirely due to the BM contribution to the susceptibility. The SW term gives very little contribution and can be almost neglected. Figure 3(c) shows χ vs T for different anisotropy parameters γ . Note that the location of the maxima is sensitive to γ . A further description of the JB expressions and a summary of calculations based on these expressions can be found in Donald N. Haines's Ph.D. thesis (1987).

In the Ising limit the Johnson and Bonner expression for the susceptibility exactly follow the Ising expression given by Fisher (see the section below). However, the Johnson and Bonner theory is not valid at the exact isotropic Heisenberg limit. The only available expressions for $S=1/2$, isotropic Heisenberg systems are of Takahashi and Yamada^[29], and of Schlottmann^[30]. They approached this limit numerically and used the Hamiltonian:

$$H = -J \sum_i \left[S_i^x S_{i+1}^x + S_i^y S_{i+1}^y - \frac{1}{4} \right] - 2H \sum_i S_i^z$$

Compared to the JB Hamiltonian, there is a factor of 2 in the Zeeman term and J is used for the coupling constant instead of the usual $2J$. Therefore, care must be used when comparing this expression with other expressions for the susceptibility. It turns out that we need to multiply the expression for the susceptibility by a conversion factor $N_A g^2 \mu^2 / 4$.

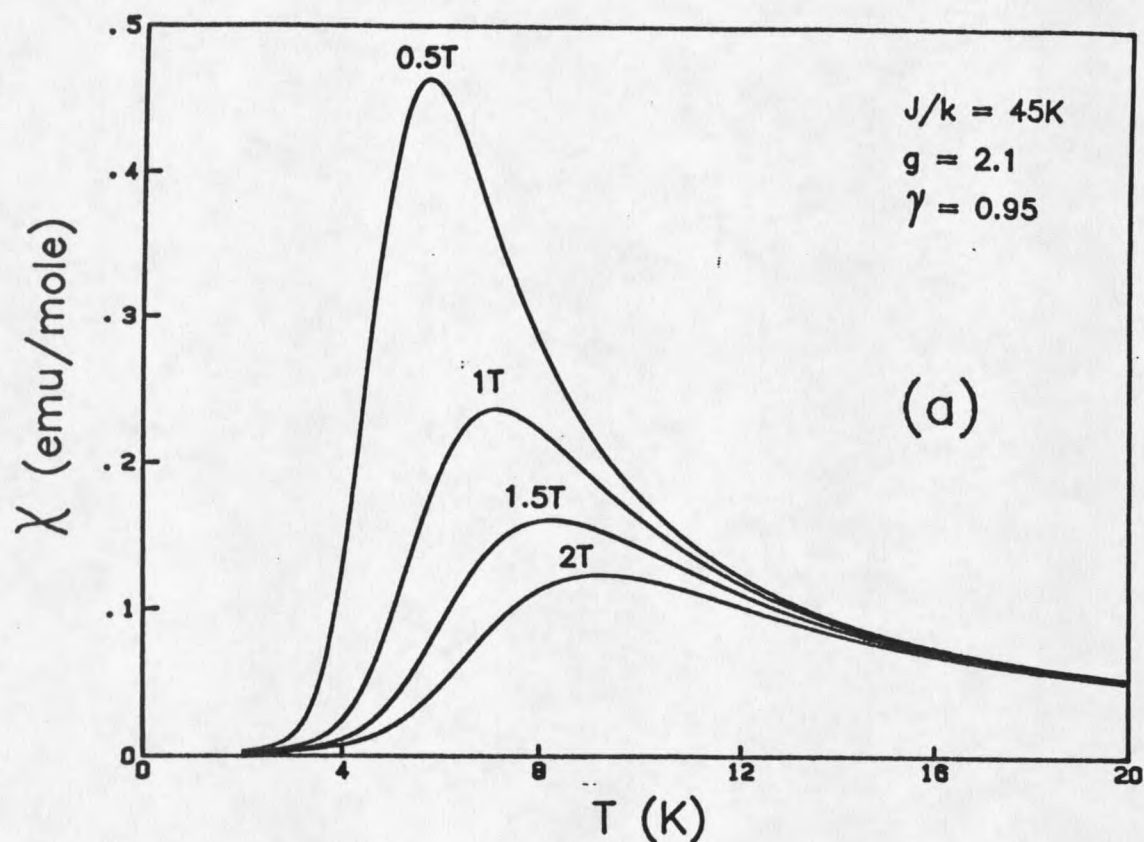


Figure 3. Johnson and Bonner susceptibility as a function of temperature for $J/k=45K$, $g=2.1$:

- (a). at different magnetic fields for $\gamma = 0.95$. The solid lines represent the total (SW+BM) contribution to the susceptibility.
- (b). at 1 Tesla for $\gamma = 0.95$. The contributions from spin waves (SW), bound magnons (BM), and total (SW+BM) are drawn separately.
- (c). for different values of γ at 1 Tesla.

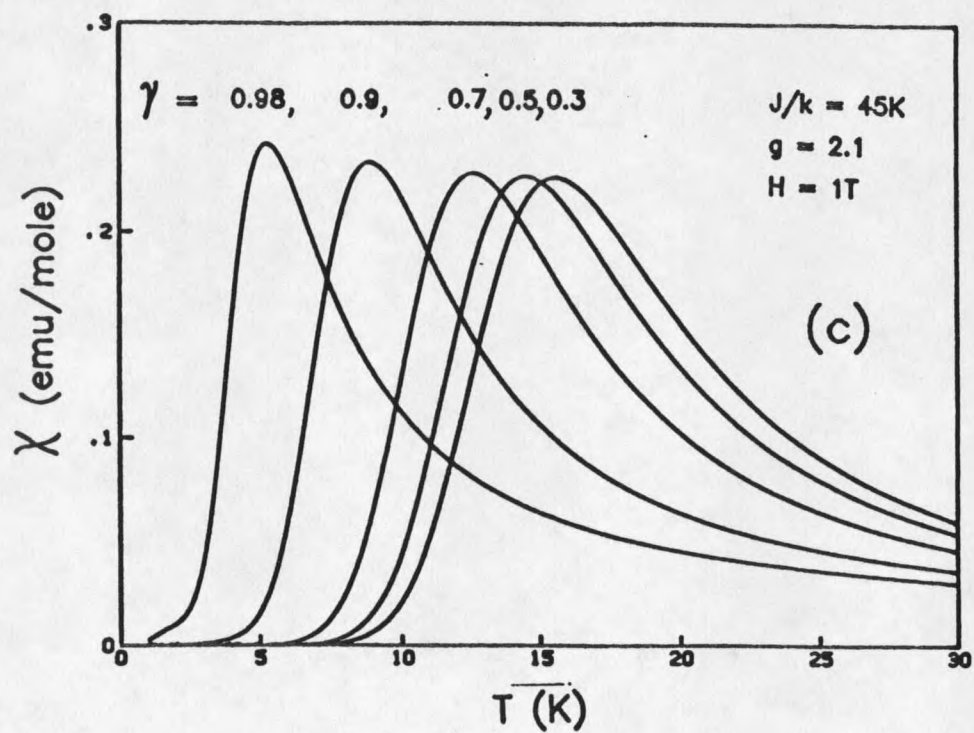
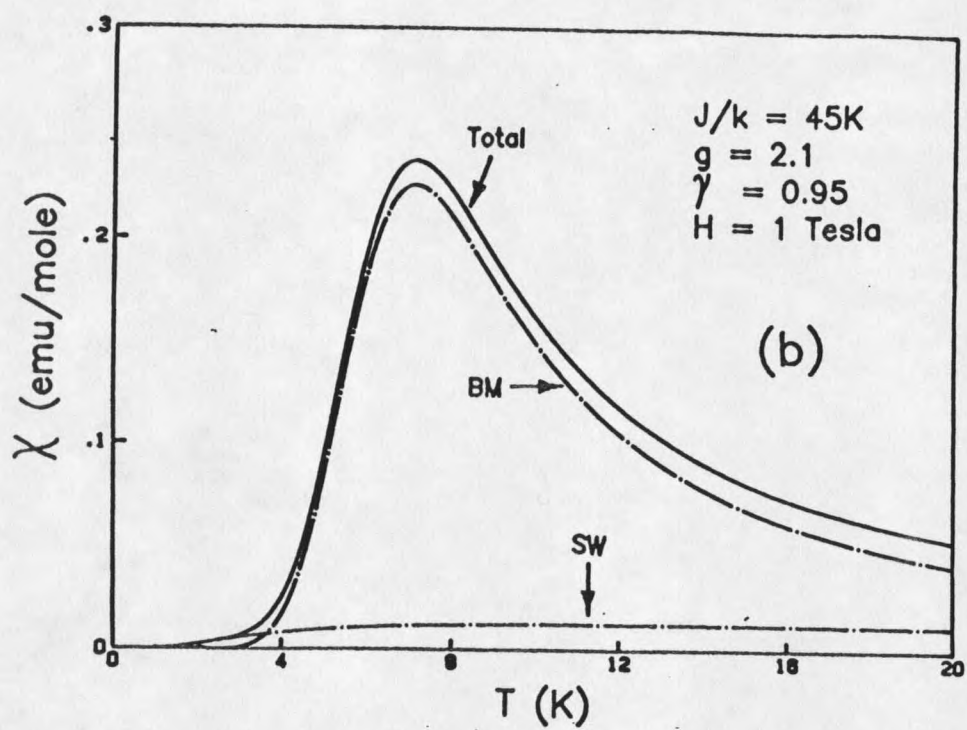


Figure 3 continued

S=1/2, 1-D, Isotropic Heisenberg Ferromagnet

Takahashi-Yamada Zero Field Expression

Following Takahashi's earlier work^[27], Takahashi and Yamada obtained expressions for free energy, f , and susceptibility, χ , by numerically solving the thermodynamic Bethe-Ansatz integral equations of the planar XXZ model and extrapolating the anisotropy to zero.^[29] Their results are:

$$f = |J| \left\{ -1.042 \left(\frac{T}{|J|} \right)^{3/2} + 1.00 \left(\frac{T}{|J|} \right)^2 - 0.9 \left(\frac{T}{|J|} \right)^{5/2} + O \left(\frac{T}{|J|} \right)^3 \right\} \quad (2.3)$$

$$\chi = |J|^{-1} \left\{ 0.1667 \left(\frac{|J|}{T} \right)^2 + 0.581 \left(\frac{|J|}{T} \right)^{3/2} + 0.68 \left(\frac{|J|}{T} \right) + O \left(\frac{|J|}{T} \right)^{1/2} \right\} \quad (2.4)$$

These are valid for $0 \leq T/J \leq 1.00$ and zero field. Here the first term of the free energy expression coincides with the spin wave calculations.^[19,31] The first term of the susceptibility expression diverges as $\frac{1}{T^2}$ at $T=0$ similar to the behavior of Fisher's solution for classical ($S > 1/2$) Heisenberg ferromagnet.^[32] It would be interesting to extend their work to finite magnetic fields, but it would not be trivial.

Schlottmann's Zero Field expression

Schlottmann on the other hand, truncated the infinite set of coupled nonlinear integral equations so that only a finite set of coupled nonlinear equations are solved.^[30]

For the zero field susceptibility near $T = 0$, he obtained:

$$\chi = 0.84 \frac{|J|}{T^2} \left[\frac{1}{\ln \left(\frac{|J|}{T} \right)} + \frac{\ln \ln \left(\frac{|J|}{T} \right)}{\ln^2 \left(\frac{|J|}{T} \right)} \right] \quad (2.5)$$

This shows that χ diverges as $J/(T^2 \ln(J/T))$, whereas Takahashi and Yamada's expression for χ diverges as J/T^2 . Schlottmann further solved the integral equations analytically and obtained the same results. However, Takahashi questioned the approximation that Schlottmann made in his extrapolation method and for this reason he did not believe that this derivation is exact. Figure 4 shows Takahashi's comparison of his expression (solid line) with Schlottmann's expansion (dashed line) and the numerical results (crosses) of the Bethe-Ansatz integral equations from Ref. [29]. It appears that Takahashi's formula coincides accurately with numerical results of the Bethe-Ansatz integral equation. Nevertheless, Lee and Schlottmann^[33] extended the Schlottmann results for very large magnetic fields, resulting in expressions for magnetization and specific heat as a function of (H/T) which are given as

$$M = 2 \left[\frac{1}{2} - \frac{6}{\pi} \left[\frac{T}{|J|} \right]^{1/2} \exp\left(\frac{-3H}{T}\right) + \dots \right] \quad (2.6)$$

$$C_H = \frac{3}{\pi} \left[\frac{T}{|J|} \right]^{1/2} \exp\left[\frac{-3H}{T}\right] \times \left[6 \left[\frac{H}{T} \right]^2 + 2 \left[\frac{H}{T} \right] + \frac{1}{2} \right] + \dots \quad (2.7)$$

These are valid for $T \ll H \ll |J|$. Again the results are not particularly useful since, for example, for a field of 5 Tesla the temperature needs to be $T \ll 3.35\text{K}$ for the very large exchange $J/k = 45\text{K}$. As far as we know, no further attempts have been made to solve the integral equations to obtain expressions for thermodynamical properties at finite fields and low temperatures at the isotropic limit.

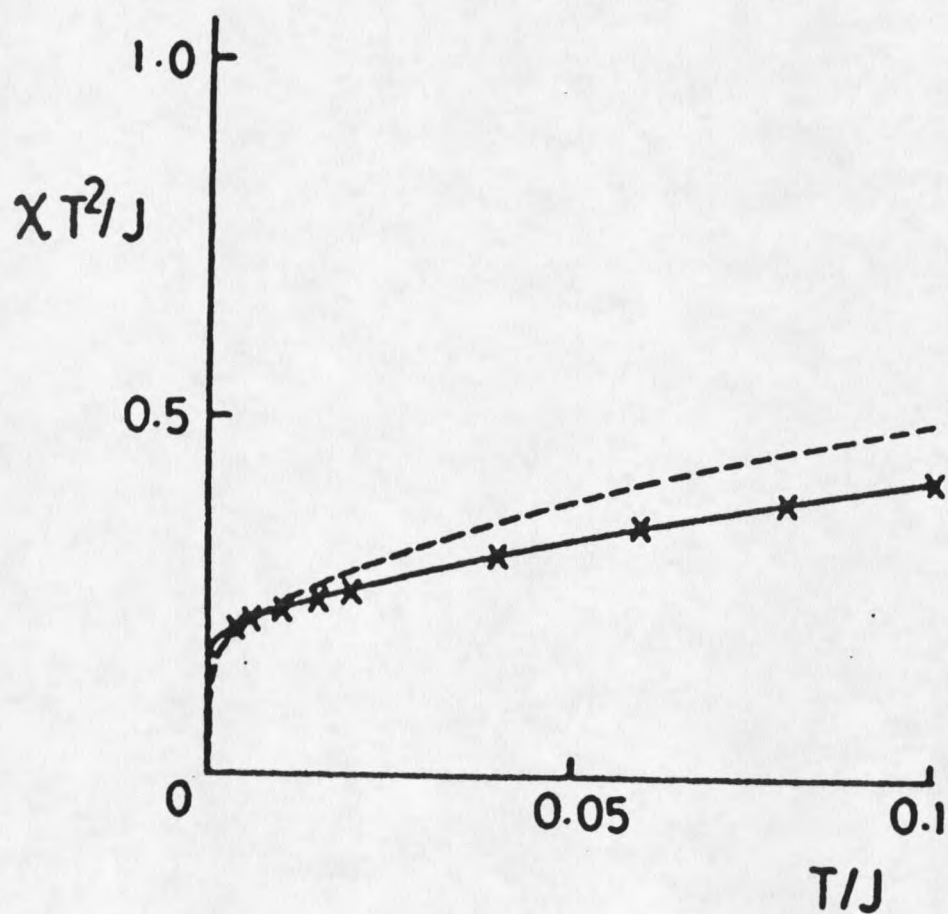


Figure 4. $\chi T^2 J^{-1}$ vs $T J^{-1}$ for the $S=1/2$, isotropic Heisenberg linear chain. Solid line is Takahashi's expression, dashed line is Schlottmann's expression, and crosses are results of Bethe-Ansatz integral equations.^[29]

S=1/2, 1-D. Ising Ferromagnet

Fisher's Exact Expression

In a S=1/2 Ising ferromagnetic system, the exchange coupling is very anisotropic and the spins have a discrete symmetry, *i.e.*, the spins can be either pointing up or down with respect to an "easy" axis. The Hamiltonian is given by:

$$H = -2J \sum_i S_i^z S_{i+1}^z - \sum_i g \mu H S_i^z$$

Exact solutions are known for both parallel (H is parallel to the easy axis) and perpendicular (H is perpendicular to the easy axis) susceptibility for this model. The model was first studied by Ising^[34] who evaluated only $\chi_{parallel}$. Fisher^[35] and Katsura^[36] independently arrived at an expression for $\chi_{perpendicular}$.

$$\chi_{parallel} = \frac{N_A g^2 \mu^2}{4k} \frac{1}{T} \exp\left(\frac{J}{kT}\right) \quad (2.8)$$

$$\chi_{perpendicular} = \frac{N_A g^2 \mu^2}{4k} \frac{1}{(J/k)} \left\{ \tanh\left(\frac{J}{2kT}\right) + \left| \frac{J}{2kT} \right| \operatorname{sech}^2\left(\frac{J}{2kT}\right) \right\} \quad (2.9)$$

The Johnson and Bonner expression for the BM term given in equation (2.1) agrees with the above expression for $\chi_{parallel}$ in the Ising limit.

Spin Cluster Excitation and Spin Cluster Resonance

The elementary magnetic excitations in an Ising system are not collective spin waves as in a Heisenberg system, but localized spin reversals called spin clusters or bound magnon states as discussed earlier. An m-fold spin cluster is defined as a cluster of m neighboring spins which are reversed with respect to their direction in the ground state.

Such a reversed spin cluster is short range and appears randomly in crystals and has a character different from usual spin waves.^[17,18] It should be pointed out that the spin-cluster state cannot be an eigenstate if the system consists of Heisenberg spins because terms such as $JS_i^+S_j^-$ in the Heisenberg spin Hamiltonian act to mix the localized spin-cluster state with other states. In the Ising spin system however, the state of the localized spin cluster is an eigenstate because there are no transverse components of spins.

In the presence of a magnetic field, the total energy E_m necessary to create (excite) an m-fold cluster is given by:

$$E_m - E_0 = 2J + mg\mu H$$

where the external field H is along the easy axis and E_0 is the ground state energy level. Note that the first term $2J$, is independent of the cluster length. This energy E_m is much less than m times the energy $E_1 (= 2J + g\mu H)$ required to create a single spin excitation. For example, the energy required to flip two non-adjacent spins is equal to $2E_1 = 4J + 2g\mu H$, while a 2-fold spin cluster requires energy $E_2 = 2J + 2g\mu H$, which is energy $2J$ lower than $2E_1$. Figure 5 describes the energy levels for an Ising system for small magnetic fields.

Recall the behavior of a quasi-one-dimensional system illustrated in Figure 1. Although no long range ordering is possible in an ideal one-dimensional system, a quasi-one-dimensional system can order at a finite temperature due to the small interchain interaction. Spin cluster resonances have been observed in Ising systems in the temperature region below T_c where spins are correlated over an infinite range. The next two paragraphs review the results. However, we are interested in the region above T_c where spins are only coupled to their nearest neighbors and the one-dimensional behavior is very clear. We point out that a different kind of spin-cluster resonance can be observed

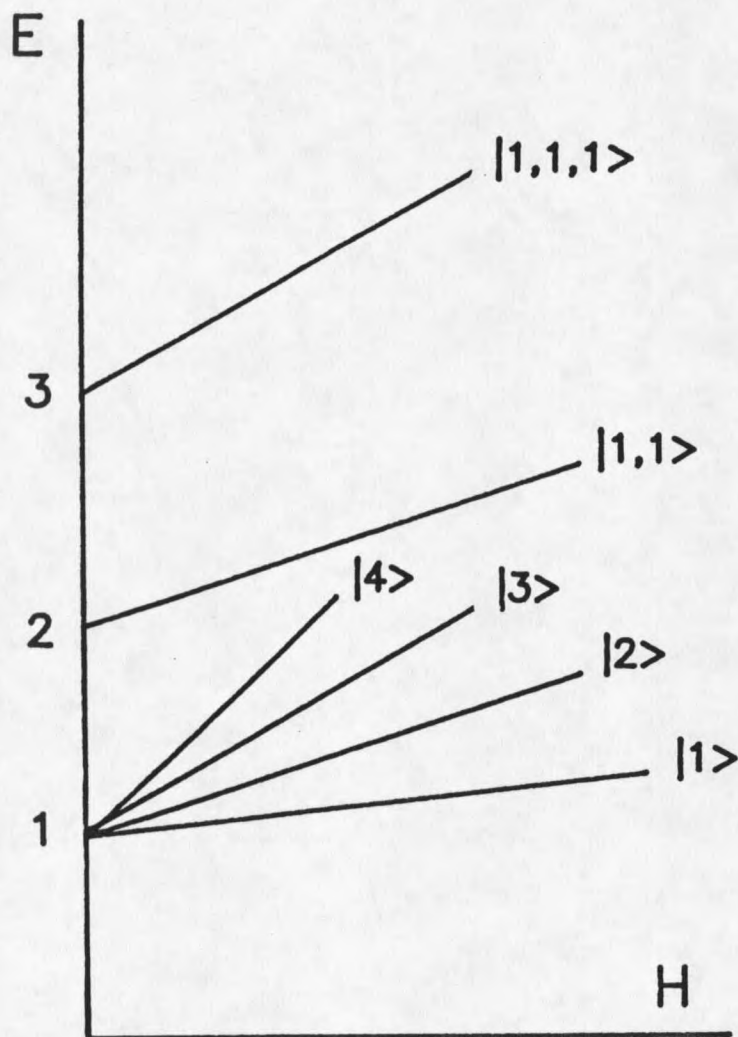


Figure 5. The Ising spectrum for n -fold ($|1\rangle$, $|2\rangle$, ...) spin clusters. $|1,1\rangle$, $|1,1,1\rangle$ represent two and three one-fold clusters.

in this region.

At zero field all clusters ($m \geq 2$) have the same energy independent of m . The applied field splits the degeneracy. Unlike spin waves, these energy levels are discrete and are only separated by the difference in the Zeeman energy. The energy required to create a spin cluster is of the order of the intrachain coupling $2J$, whereas the energy needed to change the length of such a cluster is determined by the Zeeman energy. Therefore it is possible to have transitions between spin clusters $|m\rangle \rightarrow |m+l\rangle$ called spin cluster resonance (SCR) which can be observed in the microwave region. A simple spin cluster resonance which involves a transition of $|m\rangle \rightarrow |m\pm 1\rangle$ is illustrated in Figure 6.

The first direct observation of spin cluster states was reported by Torrance and Tinkham^[16] using far-infrared absorption in the effective $S=1/2$, quasi 1-D, Ising ferromagnet $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. They observed absorption lines corresponding to the g -values of about 7, 14, 21, 28 and 35 as compared to the g value of 7 for the single magnon. This was a direct indication for two-, three-, four-, and five-magnon states. Recently, van Vlimmeren *et al.*,^[18] have observed SCR in the pseudo- one-dimensional canted Ising antiferromagnet $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$. They reported that they observed SCR in the microwave region corresponding to the transition between clusters of up to 9 spins ($|m\rangle \rightarrow |m+9\rangle$). Although this compound is an antiferromagnet, because the spins are canted in the chain with respect to each other a net ferromagnetic array results along the chain axis. All of these SCR and spin cluster states were observed in the one dimensional Ising systems but below the long range ordering temperatures. The interchain interaction was therefore taken into account in the calculations. For this reason the results must be interpreted cautiously.

Next we introduce a different kind of spin-cluster resonance which may be observed

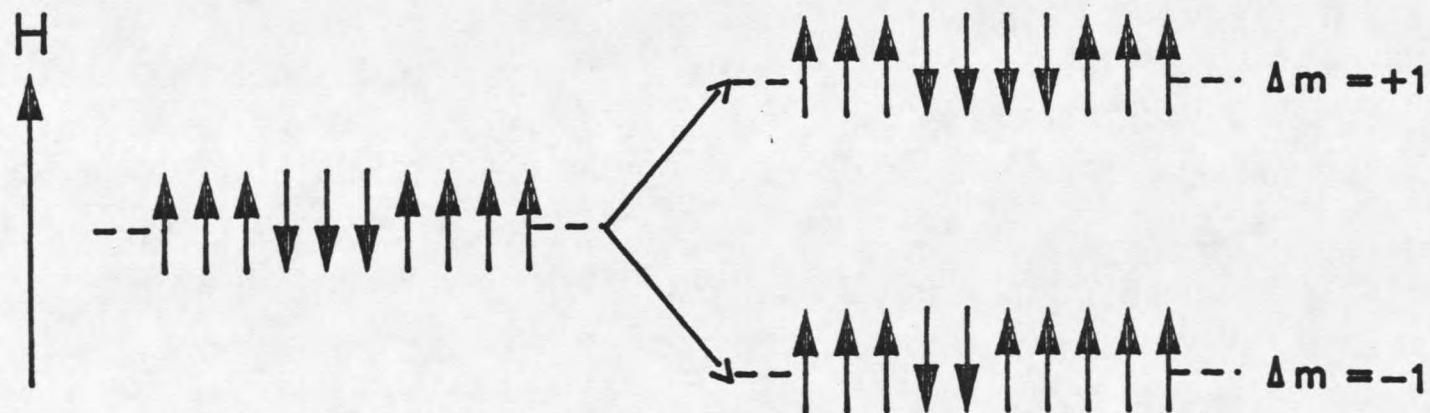
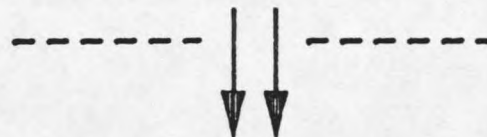


Figure 6. Spin configuration in an Ising system for spin-cluster resonance which involves a transition of $|m\rangle \rightarrow |m \pm 1\rangle$.

in quasi-one-dimensional Ising ferromagnetic systems in the temperature region above the long range ordering temperature but below the equivalent intrachain exchange temperature ($T_c < T < J/k$), *i.e.*, in the region where spin cluster fluctuations exist and the one dimensional behavior is dominant (see Figure 1). Spin clusters of different sizes may momentarily stay coupled to form clusters of different sizes in this region. The members of the spin clusters may keep switching partners on a rapid time scale. For example, at a given point in the chain there might be a 2-fold spin cluster for which the cluster size has changed at a later time (including of course the case of the cluster disappearing). If, however, the spin clusters stay coupled long enough (with respect to the EPR microwave frequency), then paramagnetic resonances which are involved in flipping of clusters of different sizes (1,2,3,...) may possibly be observed in this temperature region (see Figure 7). In an EPR experiment the microwave frequency is usually kept fixed and the magnetic field is swept to look for resonance signals. A resonance peak will appear when the condition $h\nu = g\mu H$ is satisfied where ν is the microwave frequency. Spin clusters of 2,3,.. can be considered as effective spin 1/2 with corresponding effective g -values of $2g, 3g, \dots$. Therefore, for a fixed frequency, resonance signals for spin clusters of 2,3,.. may be seen at magnetic fields of $H/2, H/3, \dots$, where H is the field corresponding to the resonance of a single spin cluster. However, the appearance and the sharpness of such a resonance signal will depend on several factors such as spin-spin relaxation time, spin-cluster relaxation times, microwave frequency (time scale), exchange interaction between the spins and the temperature. Our experimental results on FeTAC (Ising system) do indeed show evidence for the cluster resonance corresponding to 1, 2, and possibly higher number of spins. Much higher order spin cluster resonances are too broad to be seen. Further discussion is given in *Chapter 4*.



(a)

(b)

Figure 7. Paramagnetic resonances which are involved in the flipping of clusters of 1-, and 2-spin.

CHAPTER 3

EXPERIMENTS

Introduction

The experimental techniques used in this thesis work are dc magnetization, ac susceptibility and the EPR spectrum. The main work has been measurement of the low temperature ac susceptibility at different magnetic fields in order to investigate the bound magnon effects by comparing the data with the Johnson and Bonner theory. In addition, dc magnetization measurements have been performed to verify certain reported values of exchange (J/k) and g -tensor values (g). First we give a short description of dc and ac susceptibility measurements.

In the dc magnetization measurements the total magnetization of the sample is measured as a function of applied magnetic field at constant or different temperatures. The static magnetization measurements were made using a Vibrating Sample Magnetometer (VSM, see below). Although in a VSM the magnetized sample is vibrated between pickup coils, the magnetic moment of the sample does not change with time so that the static magnetic measurement is performed. The static susceptibility, $\chi_{st}(=M/H)$, therefore can be determined simply by dividing the measured magnetization M by the applied field H . Such an approach can only be useful if $M \propto H$, or at least the relation between these quantities is uniquely defined. However, in tackling unknown magnetic systems, this assumption is not always justified.

In an ac measurement this problem can be avoided because the quantity measured

is $\chi_{ac} = dM/dH$, *i.e.* the slope of the M vs H curve (see Figure 8(a)). A small ac signal, dH , perturbs the system and allows dM/dH to be measured. Because it is the slope which is measured, the ac susceptibility is sometimes referred to as differential susceptibility. In this measurement the moment of the sample is actually changing in response to the small applied ac field, permitting the dynamics of the magnetic system to be studied. Ac susceptibility measurements were performed using an ac-SQUID susceptometer (see below). One of the major advantages of ac susceptibility measurements is that zero field or low field measurements may be performed even at very low ac field amplitude (depending on the sensitivity of the system - a SQUID system is the very best for this), whereas with an VSM a substantial field is necessary in order to make measurements. The actual physics of that which is happening in an ac measurement is far more complicated than for dc measurements. χ_{ac} will reflect the slope of the dc magnetization curve, for example, only when the operating frequencies are much lower than the time scale of any relaxation process which might occur.

Additional physics, which is not available in a dc measurement, can be obtained from an ac measurement. Since the actual response of the sample to an applied ac field is measured, the magneto-dynamics can be studied through the complex susceptibility ($\chi' + i\chi''$). The real component χ' represents the component of the susceptibility which is in phase with the applied ac field, while χ'' represents the component of the susceptibility which is out of phase. χ'' is related to the energy losses which occur within the sample or, in other words, the energy absorbed by the sample from the ac field.

In ac or dc susceptibility measurement, the magnetic properties measured are the macroscopic average of the moments of all the spins in the system. However, in EPR measurements, the situation is different (Figure 8(b)). The spins can be set at resonance between energy levels which satisfy certain resonance conditions so the details of the

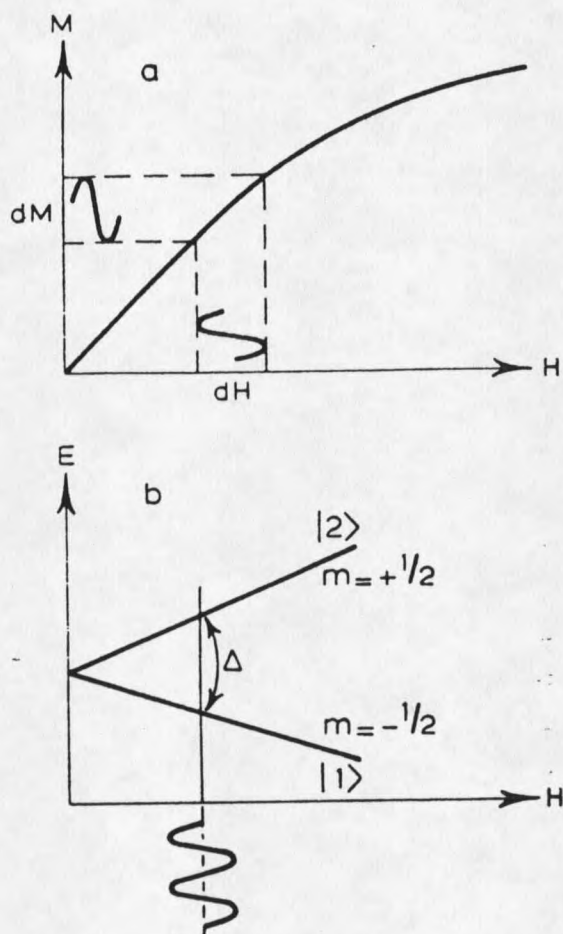


Figure 8. (a). M vs H curve illustrating differential susceptibility measurement. (b). Energy level splitting of a two-level system and the microwave perturbation which sets up the EPR resonance is illustrated.

energy levels can be studied. In an Ising system (which is included in this thesis) the energy levels corresponding to bound magnons are discrete and only separated by the Zeeman energy. Therefore, one should be able to observe the resonance peaks due to the transition between the bound magnon energy levels.

In the rest of this chapter the VSM, ac-SQUID susceptometer, and EPR spectrometer are briefly described. Because the VSM and EPR apparatuses are commercially made and the technical details and experimental procedures are well described in the instruction manual, we refer to these manuals for further details. The ac-SQUID susceptometer that we used to perform measurements was designed and built by Dr. Donald N. Haines, so for details of that apparatus we refer to his Ph.D. thesis.^[37] However, the special techniques that we used to adjust the residual field to zero, and the expression derived to correct for the demagnetization effect, are described in detail.

Magnetization Measurements

The VSM basically contains a pickup coil to measure the change in magnetic flux due to the presence of a magnetized sample. The sample in question is mounted at the lower end of the sample rod which is usually situated inside the detection or pick-up coil. A mechanical assembly vibrates this sample rod so that an ac current is induced into the pickup coil. This induced signal is proportional to the magnetic moment of the sample and when it is properly calibrated with a nickel standard, yields the value of the magnetic moment. The temperature is varied using a helium flow-thru valve and a heater, and it is measured via a calibrated carbon-glass resistor by measuring the resistance. The magnetic field from 0 $\rightarrow$ 5000 Oe can easily be obtained by controlling the current in the electromagnet (EG&G PAR model 155).

Ac Susceptibility Measurements

A block diagram of the measurement system for the ac susceptometer is shown in Figure 9. Briefly, its operation is as follows: changes in the sample (S) magnetization in turn change the flux through the flux transformer (FT), which consists of a closed loop of superconducting wire and has a sample coil (inductance L_s) and two compensation coils (each of inductance L_c) wound as part of the loop. These flux changes are detected by the SQUID sensor. The SQUID and the 330X controller act together as a flux to voltage converter/amplifier, and produce a voltage V_{sq} which is directly proportional to the flux change sensed by the SQUID. This voltage is measured by the lock-in amplifier and it is directly proportional to the susceptibility when properly calibrated. The susceptibility of an unknown sample can be measured directly. The in-phase and out-of-phase (quadrature) signals are separated in the lock-in amplifier. Current for the ac excitation field I_{ex} , generated by solenoid L_p , is provided by the RBU bridge oscillator. The oscillator voltage also provides a reference signal V_{ref} for the lockin. The excitation frequency is limited to four values: 16, 32, 80 and 160 Hz. The apparatus seems to perform best at 80 Hz.

This system is also equipped with a superconducting magnet such that the desired field between 0 and 8 Tesla can be obtained by setting a proper current through the superconducting magnet. A calibration chart of the field at the center of the magnet (and also at different points inside) as a function of the current is provided in the manual. Although in principle one can obtain fields between 0 and 8 Tesla, in practice it is difficult to make measurements in the presence of magnetic fields because the SQUID detector is so sensitive (output voltage = $20 \text{ mV}/\phi_0$, where ϕ_0 is the flux quantum: $\phi_0 = 2.07 \times 10^{-7} \text{ G cm}^2$) and the maximum amplitude for the reversed locked loop operation is limited

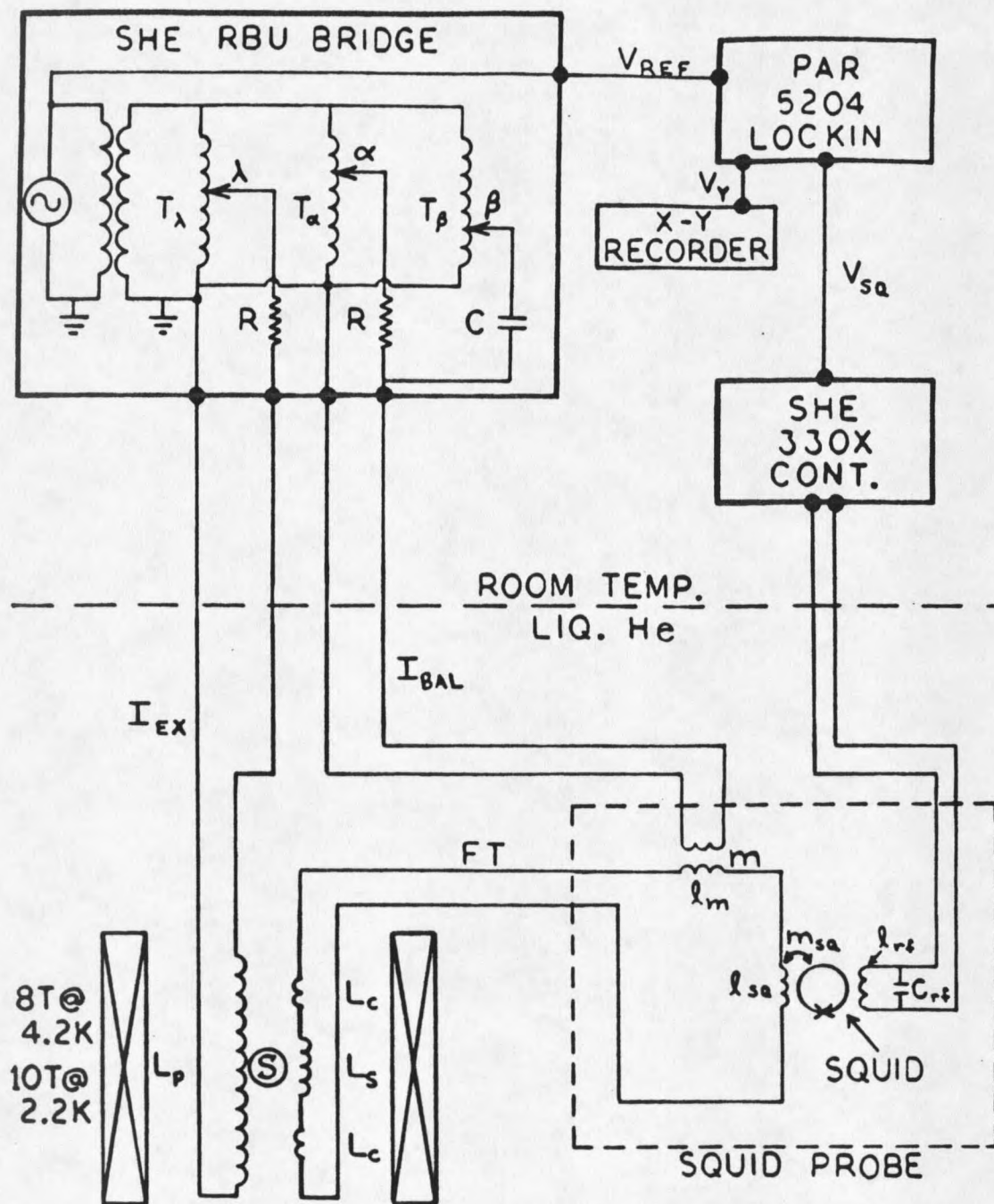


Figure 9. Susceptibility measurement system.

(see manual) by the slow rate of feedback amplifiers ($3 \times 10^{-5} \phi_0/\text{sec}$). However, the performance has been improved with a use of an active filter (80 Hz) which is designed to filter any large fluctuation coming from the 330X controller output.

Zero Field Adjustment Using Pb Sphere

The residual field is a general problem in superconducting (SC) magnets. Most of the time, when the magnet current is brought to zero after measurements have been made there tends to be a small amount ($\sim 10\text{-}20$ Oe) of residual field in the SC magnet. For certain experimental purposes measurement at this small field is sufficient and may be approximated as zero field data. However, it is often necessary to adjust the field more nearly to zero. The general procedure to do this is to simply apply a small amount of current in the forward/reverse direction to cancel the residual field. This can be achieved if the field near the sample can be measured. Unfortunately, our system is not built with any cryogenic Hall probe to measure the field. However, the field inside can be adjusted to near zero by using a separate superconducting sample such as a small lead sphere and monitoring the magnetization (Meissner effect) value.

The idea is simple. A type I superconducting sample will expel the external magnetic field due to the Meissner effect. A typical M vs H diagram for a type I superconductor is shown in Figure 10(a). Note that M decreases linearly with H and reaches $M = 0$ when $H = 0$. Also the state above T_c is paramagnetic so at zero field $M=0$. Therefore, by monitoring the magnetization of a type I superconductor the magnet current may be adjusted to minimize M . A type II superconductor (Figure 10(b)) can also be used for this technique. We were able to adjust the field to near zero (± 1 Oe) by using a sample of Pb-sphere (type I, $T_c = 7.18\text{K}$) and using a Keithley constant current source (Model 227) to adjust the current through the magnet.

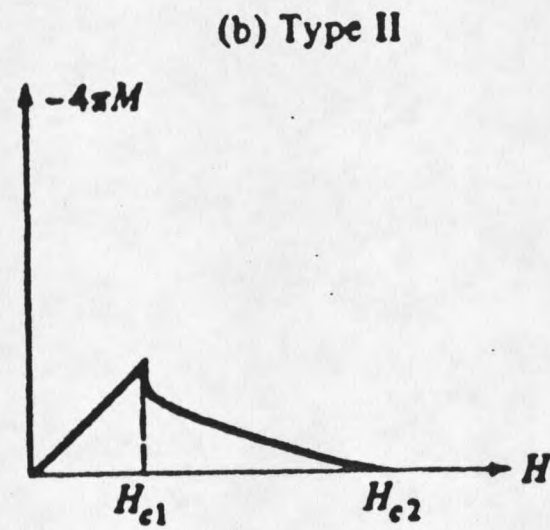
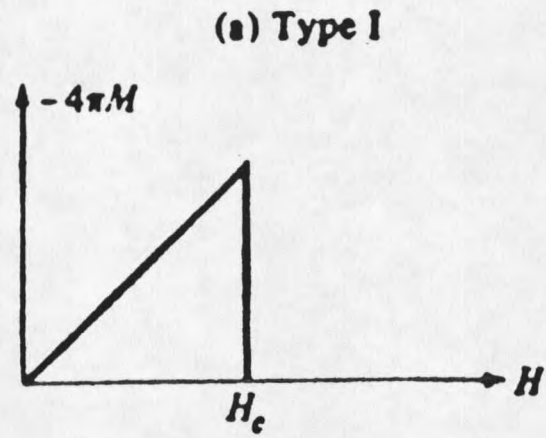


Figure 10. Typical M vs H diagram for a (a). Type I superconductor (b). Type II superconductor.

Demagnetizing Effect

Much of the work in this thesis required correction for the demagnetizing effect. Although a general expression to correct the measured susceptibility for the demagnetizing effect can be found in the literature (for example see Morrish^[38]), no explicit expression is given for the case in which the quadrature signal is non-zero ($\chi'' \neq 0$). Since this calculation has not appeared elsewhere we include the details and present the proper expression to be used for the correction of both χ' and χ'' . We also show that our expression reduces to the standard expression for $\chi' \gg \chi''$.

The demagnetizing correction is a correction to the applied field, owing to the fact that the field H' inside a sample is different from the applied field H_a :

In a static field:

$$H' = H_a - \frac{D}{V}M$$

where M is the magnetization of the sample, D is the demagnetizing factor and V is the volume of the sample.

The static (or dc) susceptibility ($= \frac{M}{H}$) is;

$$\begin{aligned} \chi_{\text{measured}} &= \frac{M}{H_a} \\ \chi_{\text{corrected}} &= \frac{M}{H'} = \frac{M}{H_a - \frac{D}{V}M} = \frac{\chi_{\text{mea}}}{1 - \frac{D}{V}\chi_{\text{mea}}} \end{aligned} \quad (3.1)$$

In an alternating field:

$$dH = h_a = h \cos \omega t$$

where, h is the amplitude of the ac magnetic field and ω is the frequency. Suppose the change in magnetization, dM , (due to this field) lags the field by a phase ϕ then

$$\begin{aligned} dM &= m \cos(\omega t - \phi) \\ &= (m \cos \phi) \cos \omega t + (m \sin \phi) \sin \omega t \end{aligned}$$

where m is the amplitude of dM . The real (in phase) and imaginary (out of phase) ac susceptibility ($= \frac{dM}{dH}$) is:

$$\begin{aligned} \chi_{\text{real}} &= \chi' = \frac{m \cos \phi}{h} \\ \chi_{\text{imaginary}} &= \chi'' = \frac{m \sin \phi}{h} \end{aligned}$$

Now consider the demagnetizing effect

$$\begin{aligned} h' &= h_a - D \frac{m}{V} \\ &= h \cos \omega t - \frac{D}{V} (m \cos \phi \cos \omega t + m \sin \phi \sin \omega t) \\ &= \left(h - \frac{D}{V} m \cos \phi \right) \cos \omega t - \left(\frac{D}{V} m \sin \phi \right) \sin \omega t \\ h' &= |h'| \cos(\omega t + \alpha) \end{aligned}$$

where, $|h'| = \sqrt{a^2 + b^2}$, $a = h - \frac{D}{V} m \cos(\phi)$, $b = \frac{D}{V} m \sin(\phi)$, and $\alpha = \tan^{-1}\left(\frac{b}{a}\right)$.

but the applied field is $h_a = h \cos \omega t$. This means the field inside the sample (effective field) leads the applied field by a phase " α ".

$$\begin{aligned} \chi'_{\text{correct}} &= \frac{m \cos(\alpha + \phi)}{|h'|} \\ \chi''_{\text{correct}} &= \frac{m \sin(\alpha + \phi)}{|h'|} \end{aligned}$$

but

$$\chi'_{\text{mea}} = \chi_{\text{real}} = \frac{m \cos \phi}{h}$$

$$\chi''_{\text{mea}} = \chi_{\text{ima}} = \frac{m \sin \phi}{h}$$

Therefore we have

$$\begin{aligned} \chi'_{\text{corr}} &= \frac{m \cos \alpha \cos \phi - m \sin \alpha \sin \phi}{\sqrt{a^2 + b^2}} \\ &= \frac{(m \cos \phi) \frac{a}{\sqrt{a^2 + b^2}} - (m \sin \phi) \frac{b}{\sqrt{a^2 + b^2}}}{\sqrt{a^2 + b^2}} \\ &= \frac{(m \cos \phi) \left(h - \frac{D}{V} m \cos \phi \right) - (m \sin \phi) \left(\frac{D}{V} m \sin \phi \right)}{\left(\left(h - \frac{D}{V} m \cos \phi \right)^2 + \left(\frac{D}{V} m \sin \phi \right)^2 \right)} \\ \chi'_{\text{corr}} &= \frac{\chi'_{\text{mea}} \left(1 - \frac{D}{V} \chi'_{\text{mea}} \right) - \chi''_{\text{mea}} \frac{D}{V} \chi''_{\text{mea}}}{\left(1 - \frac{D}{V} \chi'_{\text{mea}} \right)^2 + \left(\frac{D}{V} \chi''_{\text{mea}} \right)^2} \quad (3.2) \\ &= \frac{\chi'_{\text{mea}} - \frac{D}{V} ((\chi'_{\text{mea}})^2 + (\chi''_{\text{mea}})^2)}{\left(1 - \frac{D}{V} \chi'_{\text{mea}} \right)^2 + \left(\frac{D}{V} \chi''_{\text{mea}} \right)^2} \end{aligned}$$

$$\begin{aligned} \chi''_{\text{corr}} &= \frac{m \sin \alpha \cos \phi + m \cos \alpha \sin \phi}{\sqrt{a^2 + b^2}} \\ &= \frac{(m \cos \phi) \left(\frac{D}{V} m \sin \phi \right) + (m \sin \phi) \left(h - \frac{D}{V} m \cos \phi \right)}{\left[\left(h - \frac{D}{V} m \cos \phi \right)^2 + \left(\frac{D}{V} m \sin \phi \right)^2 \right]} \\ \chi''_{\text{corr}} &= \frac{\chi'_{\text{mea}} \frac{D}{V} \chi''_{\text{mea}} + \chi''_{\text{mea}} \left(1 - \frac{D}{V} \chi'_{\text{mea}} \right)}{\left(1 - \frac{D}{V} \chi'_{\text{mea}} \right)^2 + \left(\frac{D}{V} \chi''_{\text{mea}} \right)^2} \quad (3.3) \end{aligned}$$

which will further reduce to

$$\chi''_{\text{corr}} = \frac{\chi''_{\text{mea}}}{\left(1 - \frac{D}{V} \chi'_{\text{mea}} \right)^2 + \left(\frac{D}{V} \chi''_{\text{mea}} \right)^2}$$

Suppose that χ'' is small $\chi' \gg \chi''$ (e.g., paramagnet) then the expression (3.2) becomes

$$\chi'_{\text{corr}} = \frac{\chi'_{\text{mea}}}{\left(1 - \frac{D}{V} \chi'_{\text{mea}}\right)} \quad (3.4)$$

which has the same form as for the static susceptibility given in expression (3.1).

EPR Measurements

Electron paramagnetic resonance (EPR), [known also as electron spin resonance (ESR)] is a kind of spectroscopy in which, as usually performed, the sample is placed in an appropriate magnetic field (typically, a few thousand Gauss) and is irradiated with microwaves (typically 9 GHz) in order to satisfy the resonance equation $h\nu = g\mu H$. By sweeping the applied magnetic field a pattern of energy absorption is detected reflecting the magnetic properties of electrons in the sample. These properties reveal considerable information about the microscopic structure and dynamics of the sample. The technique has the advantages of being nondestructive and sensitive and has contributed significantly to our knowledge of magnetic systems.

In EPR we are concerned with transitions between energy levels which are only separated by Zeeman splitting. For example, consider the case for $S=1/2$. In zero magnetic field the energy levels are two fold degenerate ($m = \pm 1/2$). An applied field will split the degeneracy and the energy levels will diverge linearly with H , with slopes $\pm \frac{1}{2}g\mu H$ (see Figure 8(b)). Transition between these energy levels is allowed when the resonance condition is satisfied:

$$h\nu = g\mu H$$

where ν is the microwave frequency. For a general spin S , transitions are allowed for $\Delta m = \pm 1$ and $h\nu = g\mu H$.

The experimental results presented in this thesis were performed using a Varian EPR spectrometer. This was built with an Oxford flow-through cryostat. The microwave frequency is near 9.2 GHz and can be fine tuned for resonance. The details of the experimental procedure can be found in the instruction manual.

CHAPTER 4

RESULTS AND ANALYSIS

This chapter is divided into three sections. In the first section, the experimental data on the compound FeTAC is presented. In the second and third sections, the results of compounds TMCuC and $\text{CuCl}_2 \cdot \text{DMSO}$ are presented, respectively. A short description of these quasi 1-D, ferromagnetic systems is given in the following table.

Table 1. Quasi one-dimensional ferromagnetic systems.

Compound	$[(\text{CH}_3)_3\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ (FeTAC)	$(\text{CH}_3)_4\text{N CuCl}_3$ (TMCuC)	$\text{CuCl}_2 \cdot \text{C}_2\text{H}_5\text{SO}$ ($\text{CuCl}_2 \cdot \text{DMSO}$)
Type	Ising	Heisenberg	Heisenberg
Magnetic Ion	Fe^{2+}	Cu^{2+}	Cu^{2+}
Spin	$S = 2$ effective $S = 1/2$ at low T	$S = 1/2$	$S = 1/2$
$\frac{J}{k}(\text{K})$	17.5	35 - 45	45
$\left(\frac{J'}{J}\right)$	-2×10^{-3}	-10^{-4}	-3.6×10^{-2}
$T_c(\text{K})$	3.1	1.25	5.0

FeTAC - an Effective $S=1/2$, 1-D, Ising Ferromagnet

In this section we present the low temperature magnetization, susceptibility and EPR measurements on the compound $[(\text{CH}_3)_3\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ (FeTAC). This compound was chosen for this study because it is the best quasi-1-D, spin-1/2 Ising ferromagnet available at this time. The samples were provided by Professor C. P. Landee of Clark University, Worcester, Massachusetts.

The structural and magnetic properties of FeTAC have been recently studied by Greeney et al. and found to consist of bichloride-bridged Fe^{2+} ions extending along the b-axis of the orthorhombic unit cell.^[39] These chains are linked into a 2-D network through hydrogen bonding in the c direction with the resulting planes well isolated in the third direction (a-axis) by the organic molecules. Figure 11 shows the projection of the chains on the bc plane. The coupling along the chains is the strongest interaction ($J_b = 17.5$ K) making this compound a good approximation to an ideal one dimensional ferromagnet. Owing to the weak interchain interaction ($J_c = -0.04$ K) a transition to an antiferromagnetic state was observed near 3.1 K with the easy axis along the b-direction (needle axis). The phase diagram is metamagnetic with a $T=0$ critical field of 90 Oe. Recent specific heat measurements at zero field and the analysis of the data indicates that this transition is due to a state of 2-D long range order.^[40] Although the b-axis is the effective easy axis the local anisotropy fields are alternatively canted with components along both c and a axes.

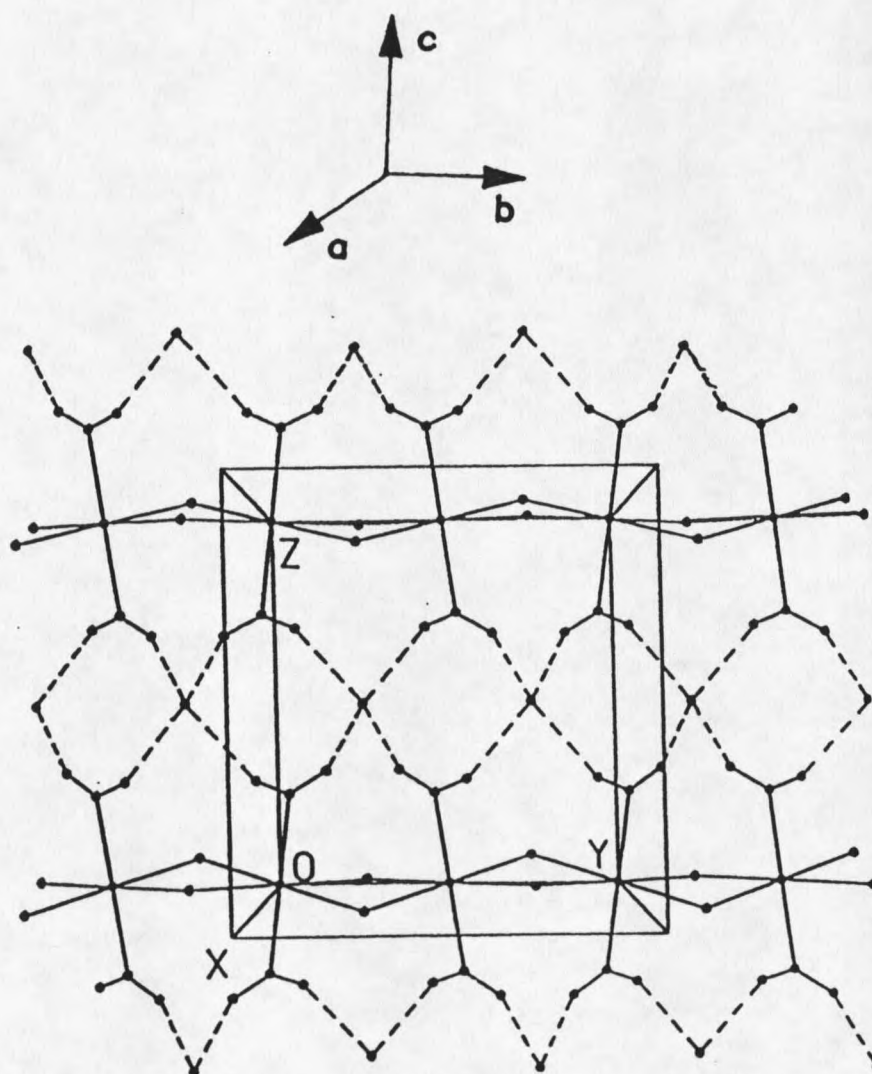


Figure 11. Adjacent chains are shown projected onto the bc plane. Dotted lines indicate interchain hydrogen bonding between water molecules and interchain free chloride ions. All iron atoms lie in a plane. All other atoms lie slightly above or below this plane.^[39]

Effective $S=1/2$ Behavior at Low Temperature

In FeTAC, Fe^{2+} ions belong to the $3D^5$ ($L=2, S=2$) state. However the ground state will split in a crystal field giving an orbital singlet with five fold ($S=2$) degeneracy as the lowest in energy level. The combined action of a crystal of orthorhombic symmetry and spin-orbit interaction splits this remaining degeneracy resulting in a single ion energy level scheme with a pseudo-doublet ground state.^[41] The splitting of the spin quintet of a single ion is represented by the Hamiltonian

$$H = -DS_z^2 + E(S_x^2 - S_y^2) - g\mu HS_z$$

where magnetic field is applied along the z-axis. Note that besides the Zeeman term, two crystalline electric field terms are added. These represent respectively the axial and rhombic crystal field splitting. In FeTAC, the axial field is very strong: $D \gg E$ and $D > 0$.

For $E=0$, the states and the energy levels are

$$|\pm 2\rangle; \quad E_{\pm 2} = -4D \pm 2g\mu H$$

$$|\pm 1\rangle; \quad E_{\pm 1} = -D \pm g\mu H$$

$$|0\rangle; \quad E_0 = 0$$

This results in a ground state doublet (± 2) at zero field. The next excited state is above the ground state by an energy of $3D$ as shown in Figure 12. Therefore at low enough

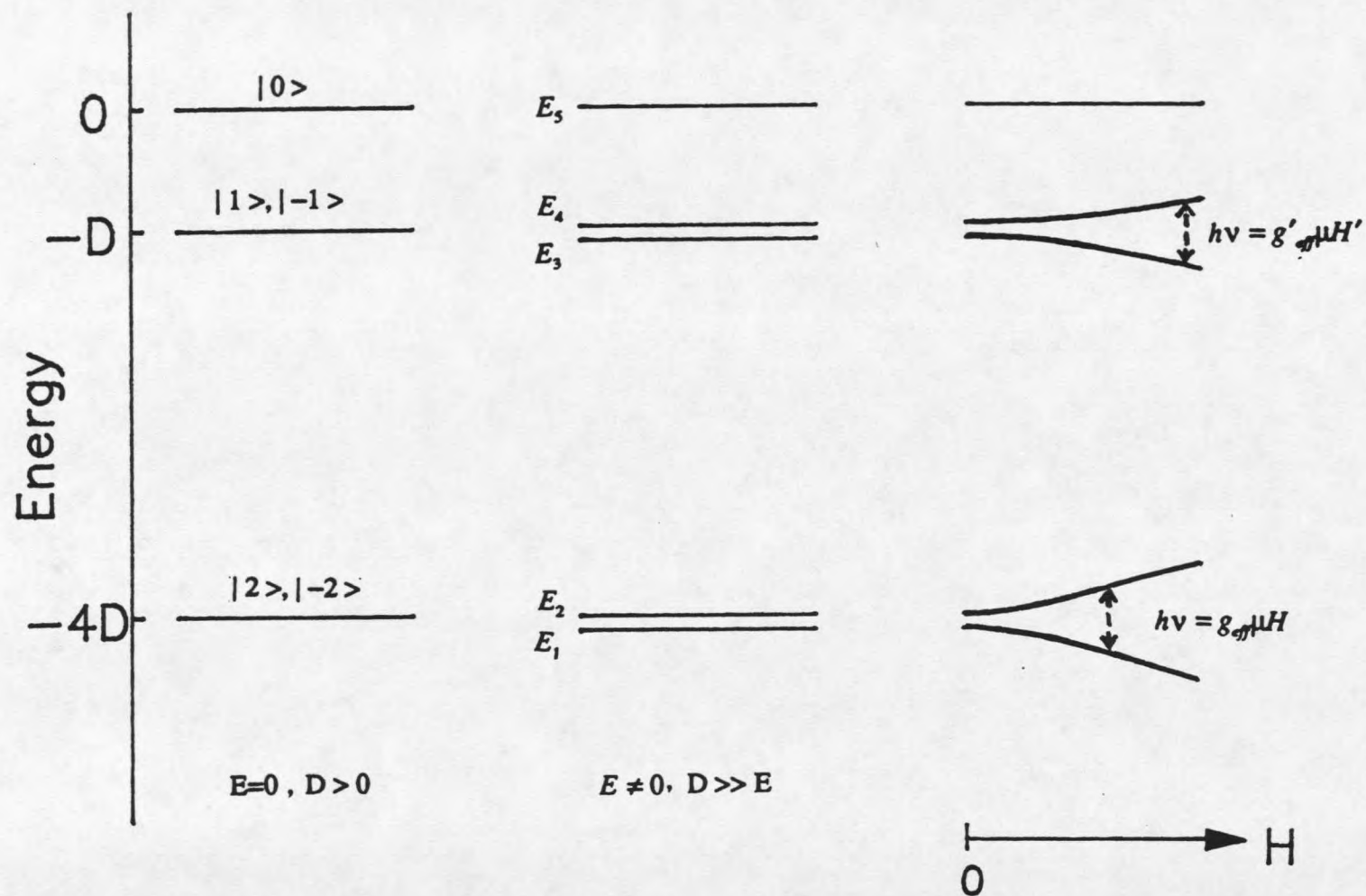


Figure 12. Energy level splitting of Fe^{2+} in FeTAC for $D > 0$, $D \gg E$.

temperatures ($T \ll 3D/k$) only this lowest doublet will be populated so that this system can be treated as an effective $S=1/2$ with an effective g value $g_{\text{eff}} = 4g$ where g is approximately equal to 2.

If $E \neq 0$, the rhombic term further splits the doublet and results in a small increase in the effective g -value.^[41] In order to obtain the energy level it is necessary to diagonalize the Hamiltonian. For simplicity consider the case $H=0$, then the Hamiltonian becomes:

$$H = -DS_z^2 + E(S_x^2 - S_y^2) = -DS_z^2 + \frac{E}{2}(S_+^2 + S_-^2)$$

Using $S_{\pm} |l, m\rangle = \sqrt{l(l+1) - m(m \pm 1)} |l, m \pm 1\rangle$, in the basis of $\{|2\rangle, |0\rangle, |-2\rangle, |1\rangle, |-1\rangle\}$, the following matrix obtains:

$$\begin{pmatrix} -4D & \sqrt{6}E & 0 & 0 & 0 \\ \sqrt{6}E & 0 & \sqrt{6}E & 0 & 0 \\ 0 & \sqrt{6}E & -4D & 0 & 0 \\ 0 & 0 & 0 & -D & 3E \\ 0 & 0 & 0 & 3E & -D \end{pmatrix}$$

Diagonalization yields the following eigenfunctions and energy levels (see Figure 12).

$$|\psi_1\rangle = \{|2\rangle, |-2\rangle\} \quad E_1 = -2D - 2D\sqrt{1 + 3\left(\frac{E}{D}\right)^2}$$

$$|\psi_2\rangle = \{|2\rangle, |0\rangle, |-2\rangle\} \quad E_2 = -4D$$

$$|\psi_3\rangle = \{|1\rangle, |-1\rangle\} \quad E_3 = -D - 3E$$

$$|\psi_4\rangle = \{|1\rangle, |-1\rangle\} \quad E_4 = -D + 3E$$

$$|\psi_5\rangle = \{|0\rangle, |2\rangle, |-2\rangle\} \quad E_5 = -2D + 2D\sqrt{1 + 3\left(\frac{E}{D}\right)^2}$$

In either case ($E=0$ or $E \neq 0$), it is clear that the lowest energy level is a (pseudo) doublet so that at temperatures well below $3D$ ($T \ll 3D/k$) the magnetic behavior can be explained by an effective $S=1/2$ model with an effective g -value. Greeney *et al.*,^[39] as well as our own susceptibility and magnetization measurements, which we describe below, confirm this behavior.

Magnetization Measurements

In order to verify the effective $S=1/2$ and Ising behavior and to obtain an average g value to compare with the reported value ($g=7.5$), we measured the magnetization as a function of field at different constant temperatures using the VSM. A single crystal of FeTAC weighing 1.26 mg was used in this experiment. Applied fields were corrected for the demagnetizing effect which is explained in detail in the EPR measurements (see below). Figure 13 shows the magnetization measured along the easy axis in the field region of 0 to 5000 gauss. The magnetization reaches a maximum value of 20000 emu Oe/mole. at 4.7K. These data points are found to fit very well with the $S=1/2$ Ising model. The solid lines represent the theoretical fits drawn for the same fitting parameters $g=7.5$ and $J/k=17.2K$ which are in excellent agreement with those of Greeney, *et al.*^[39] Note that no other fitting parameters are used; interchain interaction is very small a molecular

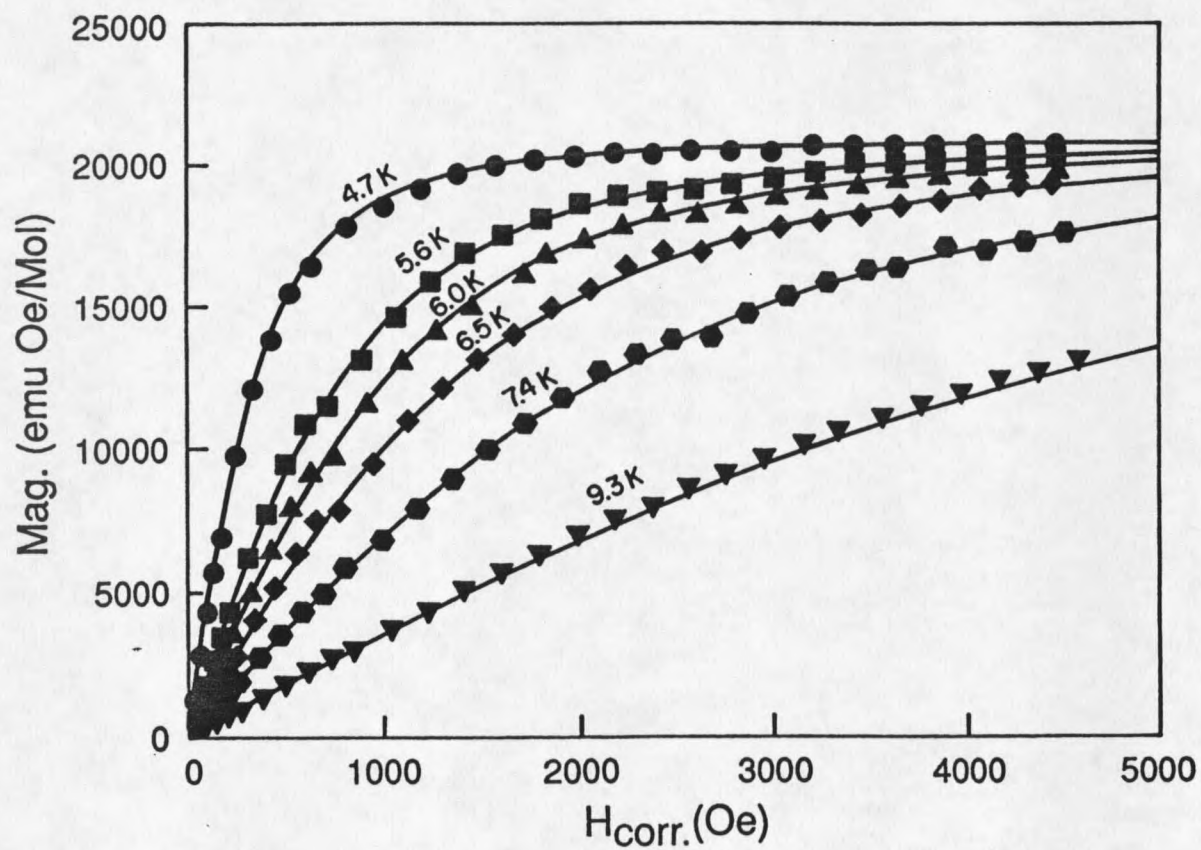


Figure 13. M vs H data for FeTAC at various temperatures measured along the b-axis (easy axis). The applied fields were corrected for demagnetizing effect.

field correction was unnecessary.

EPR Measurements

In an attempt to observe the possible spin cluster resonance and to measure the g -value, EPR measurements were carried out on the same crystal of FeTAC. The temperature was varied from room temperature to liquid helium temperature by controlling the helium flow and the heater current in an Oxford flow-thru cryostat. The long range ordering temperature is 3.1K, lower than the lowest possible temperature of our cryostat therefore, the results which we present below were all made in the paramagnetic region. The magnetic field was applied along the (easy) b -axis.

No distinct spectrum was observed until below 10K. A typical spectrum obtained at 5.5K is shown in Figure 14. This shows a very distinct strong resonance signal at $H=1050$ gauss as an indication of a regular single spin paramagnetic resonance. In addition, this spectrum indicates a very weak resonance at $H=2160$ gauss and a very broad resonance near $H=760 (\pm 50)$ gauss. The gain settings are denoted in the figure. Note that the weak signal is about 100 times smaller in intensity than the sharp one in the middle. Because the broad signal overlaps with the sharp signal the exact location of the broad signal is subject to a large uncertainty (± 50 gauss). For convenience we will label these signals as "weak", "strong" and "broad".

In order to make sure that none of these peaks originate from the sample holder or any other impurity in the system we also measured the angular dependence (anisotropy) of this system. Figure 15 shows the anisotropy measured at $5.5 \pm 0.1K$. Here θ denotes the angle between the b -axis and the external magnetic field. It is clear from the figure that these resonance peaks belong to the same family and originated from the sample. Any of the peaks not originating from the sample would have a different angular

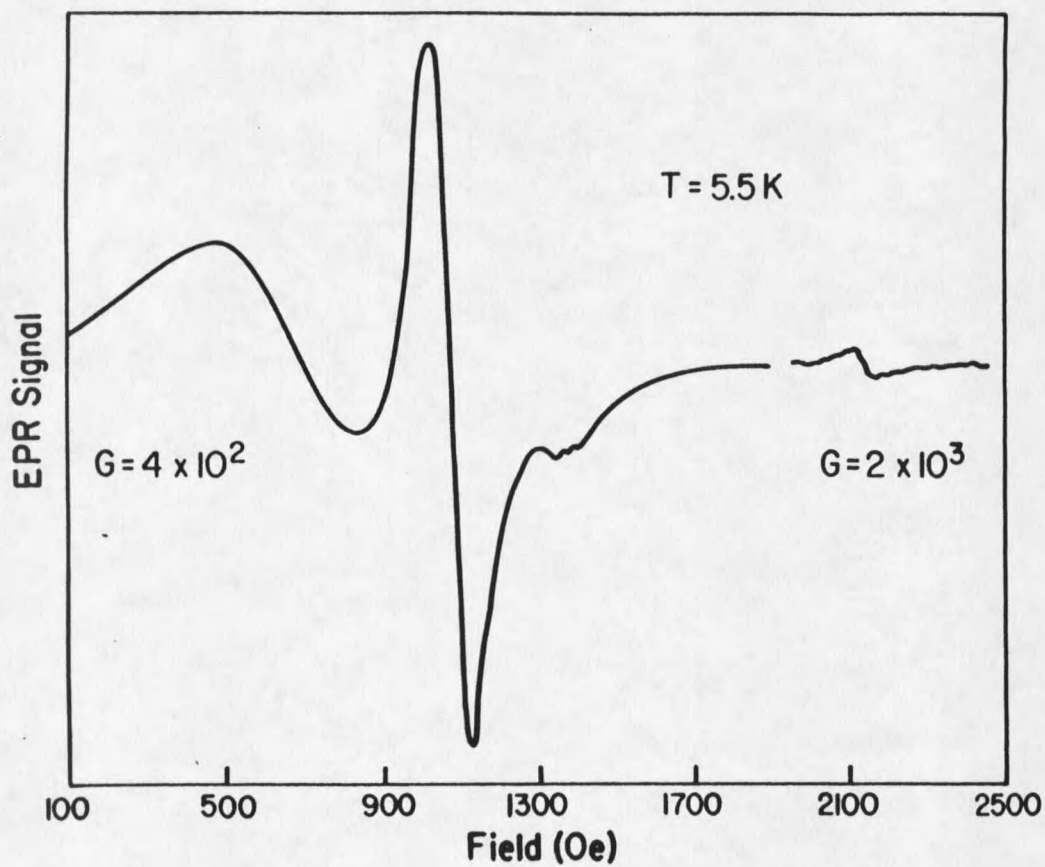


Figure 14. The EPR signal of FeTAC at $\nu = 9.24 \text{ GHz}$ and $T = 5.5 \text{ K}$ for H parallel to the easy axis. Note the resonance signals; weak (at $H = 2160 \text{ Oe}$), strong (at $H = 1050 \text{ Oe}$) and broad (near $760 \pm 50 \text{ Oe}$).

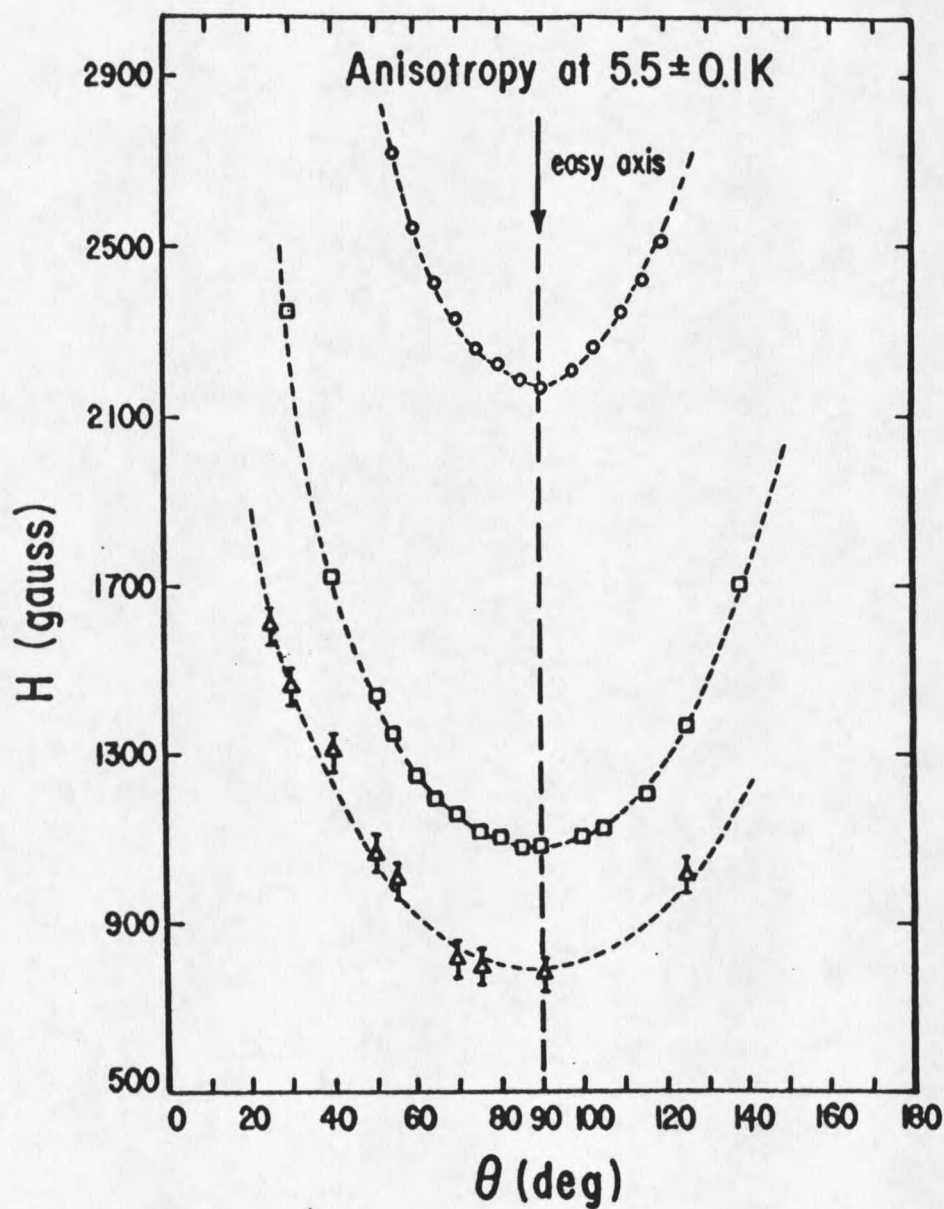


Figure 15. Angular dependency of the resonance signal at 5.5K. Here θ denotes the angle between the easy-axis and the external magnetic field. The symbols O, $\square$, and Δ denote the weak, strong and broad signals. Dotted lines are drawn to guide the eye.

dependence or none at all.

The spectrum was also studied as a function of temperature in the temperature region, $4.2\text{K} < T < 10\text{K}$. From this spectrum the peak to peak amplitudes, (A) , and the line widths, (ΔH) , are obtained and the results are plotted as a function of temperature in Figure 16. This shows that the resonance peaks are broadening as temperature increases. In fact the "broad" signal is so broad above 7K that it is difficult to identify. Correspondingly the peak to peak amplitude appears to decrease as temperature increases.

The results presented were all made above the long range ordering temperature ($T > T_c = 3.1\text{K}$) but significantly below the interchain exchange energy ($2J=35\text{K}$) temperature. This means that although we are observing the resonances in the "non-ordered" paramagnetic region ($T > T_c$) significant spin cluster fluctuations should be contributing ($T < J/k$). An n -fold spin cluster in this case can be viewed as a spin cluster of n neighboring spins which are momentarily coupled and pointing in the same direction with respect to each other. A typical paramagnetic resonance then can be pictured as a transition which involves the resonance, or spin flip, of the entire n -fold spin cluster. The ordinary single spin resonance is of course a "cluster" of a single spin. There are clusters of different sizes (orders) which exist in this region and therefore the EPR spectrum corresponding to flipping of 2,3,...fold clusters (spin-cluster-flip) should be observed.

In the Figure 14 we identify the "sharp" signal as the paramagnetic resonance or the one-fold spin flipped cluster resonance. This transition corresponds to the transition between the energy levels of E_1 and E_2 (see Figure 12) whereas the "weak" signal is interpreted as the transition between the levels E_3 and E_4 . At this temperature these energy higher levels are weakly populated; therefore the spectrum is several orders of magnitude weaker than that of the "sharp" one. The "weak" signal originates from the excited levels

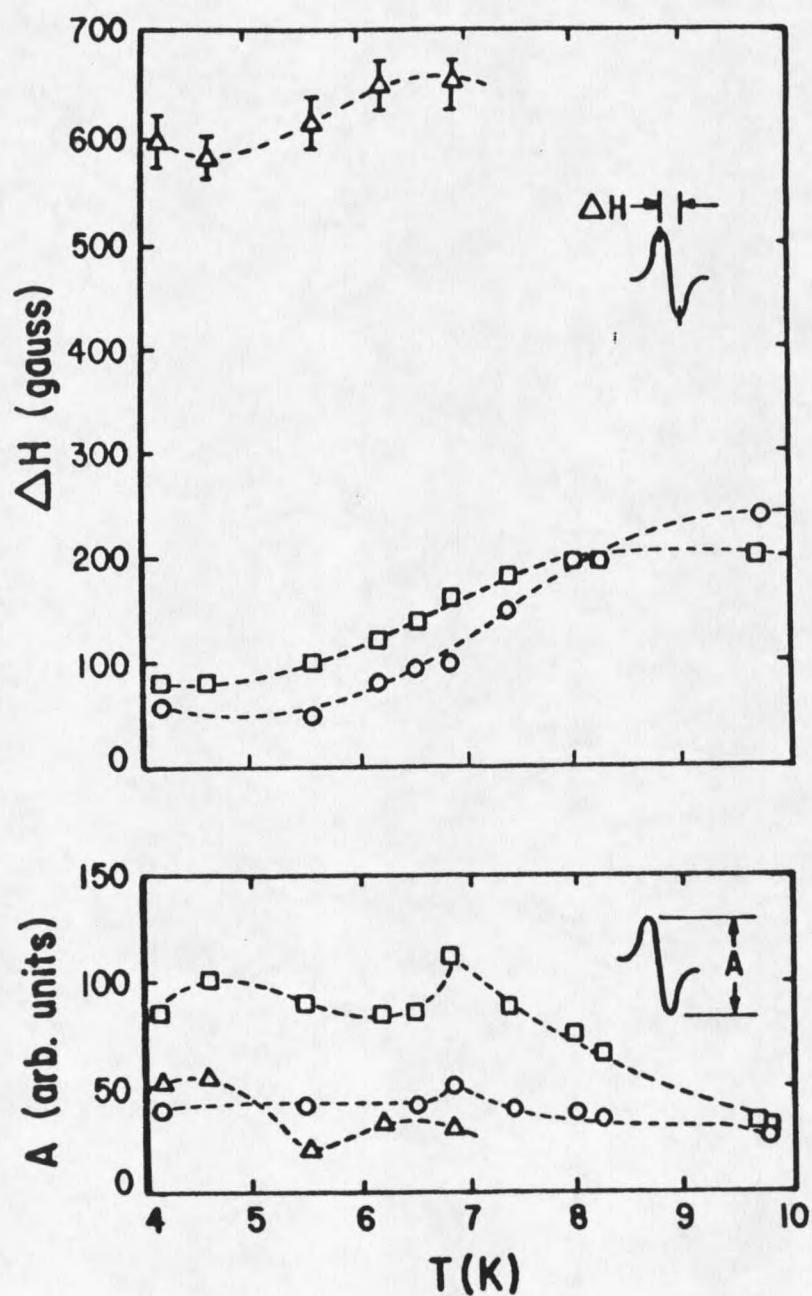


Figure 16. Linewidths (ΔH) and peak to peak amplitude (A) as a function of temperature. Same symbolic notations are used as in Figure (15). The amplitude for weak signal ($\circ$) shown in the figure are 100 times magnified to fit into the scale.

and therefore the intensity is expected to increase with temperature due to the Boltzmann population, $I \propto \exp(-3D/kT)$. From the results in Figure 16 intensities are calculated using $I = A(\Delta H)^2$. This is plotted in Figure 17 as $\ln(I)$ vs T^{-1} . Results for the "weak" signal are found to fit a straight line with the slope of $3D = 45.3K$. Note that the intensity corresponding to the "sharp" signal also increases with an increase in temperature but not linearly. This may be due to the thermal energy tending to break the large spin clusters and form more single spin clusters as temperature is raised.

The appearance of the "broad" signal is very encouraging. Because the ordinary single spin cluster resonance occurs at $H=1050$ gauss we would expect to see the 2-fold spin cluster resonance at $H/2 = 525$ gauss, and the higher order spin cluster resonances at $H/3, H/4, \dots$ etc (see the last section in Chapter 2). However, the "broad" signal appears near 760 gauss which is larger than $H/2 = 525$ gauss. One of the reasons is that the values of these magnetic fields are the measure of the external applied field and not the internal field. Because of the demagnetization effect the actual field experienced by each spin will be less than the external field (see below). Also it is possible that the "broad" signal is a superposition of 2 and higher order spin cluster resonances therefore, the exact location of the resonance signal cannot be clearly defined.

The transitions between the energy levels are determined by the selection rule $\Delta M = \pm 1$ (for the usual resonance in which the microwave perturbation is perpendicular to the applied magnetic field) and $\Delta M = 0$ (if the perturbation is parallel to the field). With these selection rules no transition would normally be allowed between the $|\pm 2\rangle$ doublet or $|\pm 1\rangle$ doublet for the case when $E = 0$. However, in the presence of E (even for very small E) the states are mixed and have a matrix element of the type $\langle \{2, -2\} | g_{eff} \mu S_z | \{2, -2, 0\} \rangle$, $\langle \{1, -1\} | g'_{eff} \mu S_z | \{1, -1\} \rangle$ so that the transitions are allowed within the

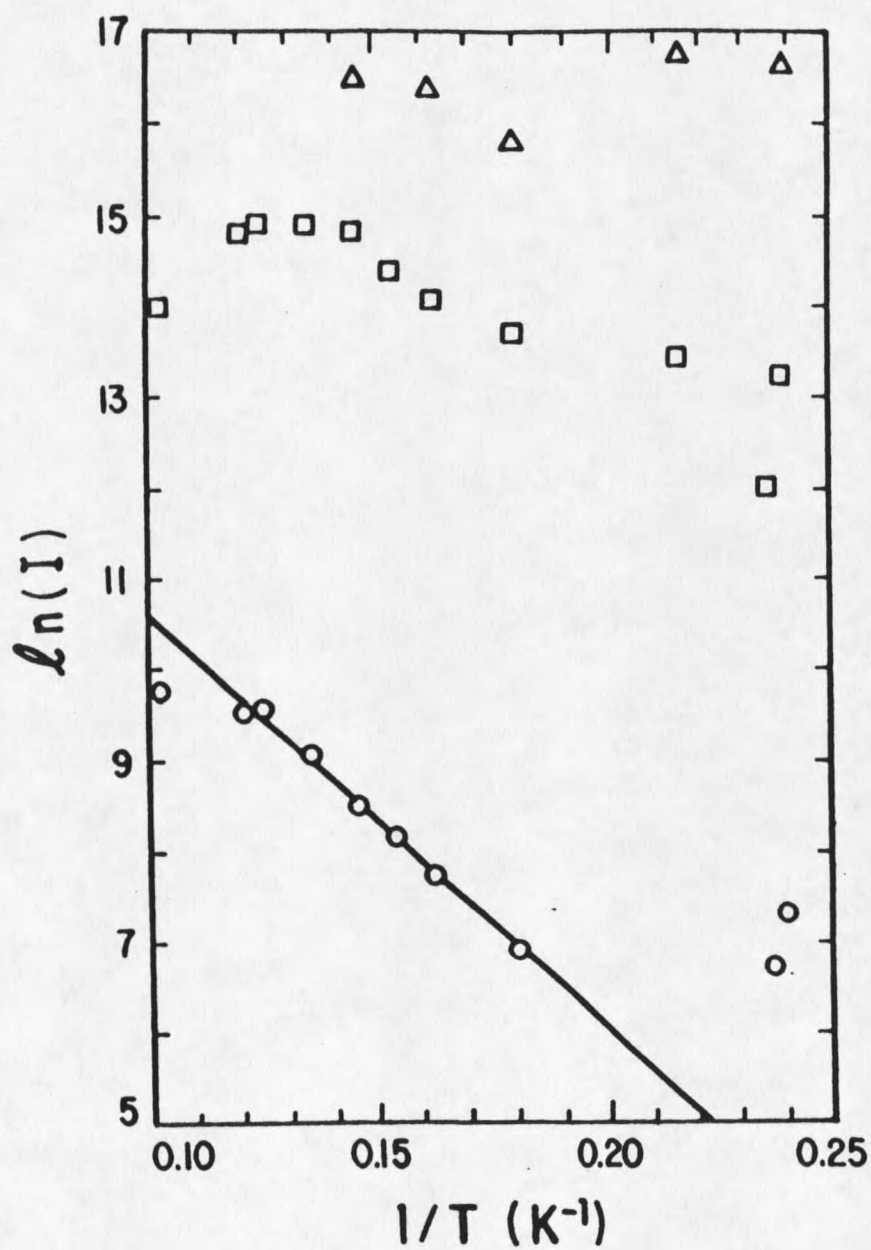


Figure 17. Intensity $I = A(\Delta H)^2$, calculated using the values from Figure (16) are plotted as $\ln(I)$ vs $1/T$. Same symbolic notations are used; (O) for broad, (□) for strong, and (Δ) for weak. Most of the points for weak signal follow a straight line with a slope of $3D=45.3\text{K}$.

energy levels (E_1, E_2) and (E_3, E_4) for the microwave field along the z-axis (see Figure 12).^[41] Neglecting the small corrections to g that arise from the admixtures of the other states, the resonance condition would yield:

$$(E_1, E_2); \quad h\nu = \{(4g\mu H)^2 + (-3E^2/D)^2\}^{1/2} = g_{\text{eff}}\mu H$$

$$(E_3, E_4); \quad h\nu = \{(2g\mu H')^2 + (6E)^2\}^{1/2} = g'_{\text{eff}}\mu H'$$

An example of such a transition has been observed by Tinkham (1956) in the ground state doublet of Fe^{2+} in ZnFe_2 which has rhombic symmetry.^[42] In our experiment the FeTAC crystal was mounted at the edge of the microwave cavity so that in practice there was enough perturbation along the z-axis to allow this normally forbidden transition.

The above resonance condition can be used to calculate the effective g -values corresponding to the resonance signals that we have observed in FeTAC. However, this expression is true for non-interacting spins. In our case, the spins are Ising-like exchange coupled to their nearest neighbors in the experimentally interesting temperature region, $T_c < T < J/k$. Also in the presence of external magnetic field, the magnetization data shows a large value for M ($M=20000$ emu Oe/mol at 4.2K above $H=2000$ Oe) at low temperatures. This means that there would be an induced internal demagnetizing field, h_d , and therefore the effective field experienced by each spin will be; $H_{\text{effective}} = H_{\text{applied}} - h_d$. Then the resonance condition can be written as $h\nu = g_{\text{eff}}\mu(H_{\text{applied}} - h_d)$. This demagnetizing field is equal to $h_d = \frac{D}{V_m}M$, where D is the demagnetizing factor, V_m is the molar volume (volume per mole) and M is the total magnetic moment per mole. The demagnetizing factor depends only on the geometry of the sample. In order to precisely calculate the demagnetizing field, the sample has to be in a special shape such as spherical or ellipsoidal. Irregular shaped samples would have non uniform internal fields. However, by carefully approximating the shape of the sample to a spheroidal shape crystal

the demagnetizing factor can be estimated.

The sample dimensions were carefully measured to be approximately $(0.64) \times (1.93) \times (0.95)$ mm³ and the demagnetizing factor (divided by the molar volume) was estimated to be $\frac{D}{V_m} = 0.016$ emu⁻¹ mol. Using the measured value for $M(H,T)$ in Figure 13), the corrections to the fields are estimated to be: $h_d(\text{weak})=283$ Oe, $h_d(\text{strong})=210$ Oe and $h_d(\text{broad})=160$ Oe for the peaks observed at 5.5K. This results in the effective g-values: $g(\text{weak})=3.4$, $g(\text{strong})=7.5$ and $g(\text{broad})=10.7$ for the peaks observed at 5.5K. Similarly the temperature dependence of these g-values are estimated and the results are plotted in Figure 18 for the temperature region of $4.2\text{K} < T < 8\text{K}$, indicates that the g-values are almost constant in this temperature region. This implies an average g-values: $g_{\text{ave}}(\text{weak})= 3.4 \pm 0.1$, $g_{\text{ave}}(\text{strong})= 7.63 \pm 0.29$, $g_{\text{ave}}(\text{broad})=(10.9 -- 12.0)$. Note that the $g_{\text{ave}}(\text{strong})$ is in good agreement with the magnetization result, 7.5. For a two-fold spin cluster resonance, the effective g-value is expected to be near 15 which is slightly larger than the average value we obtained for $g(\text{broad})$. This is because the exact location of the broad signal is not well defined or may be because the broad signal is a superposition of 2-fold, and higher-fold cluster resonances. Also, although the b-axis appears as the easy-axis, the local anisotropy fields are alternatively canted with components along both c and a axes.^[39] A detailed theoretical analysis is therefore necessary to further understand the discrepancy in the g-values. However the evidence for spin-cluster resonances is clear from the appearance of the broad signal.

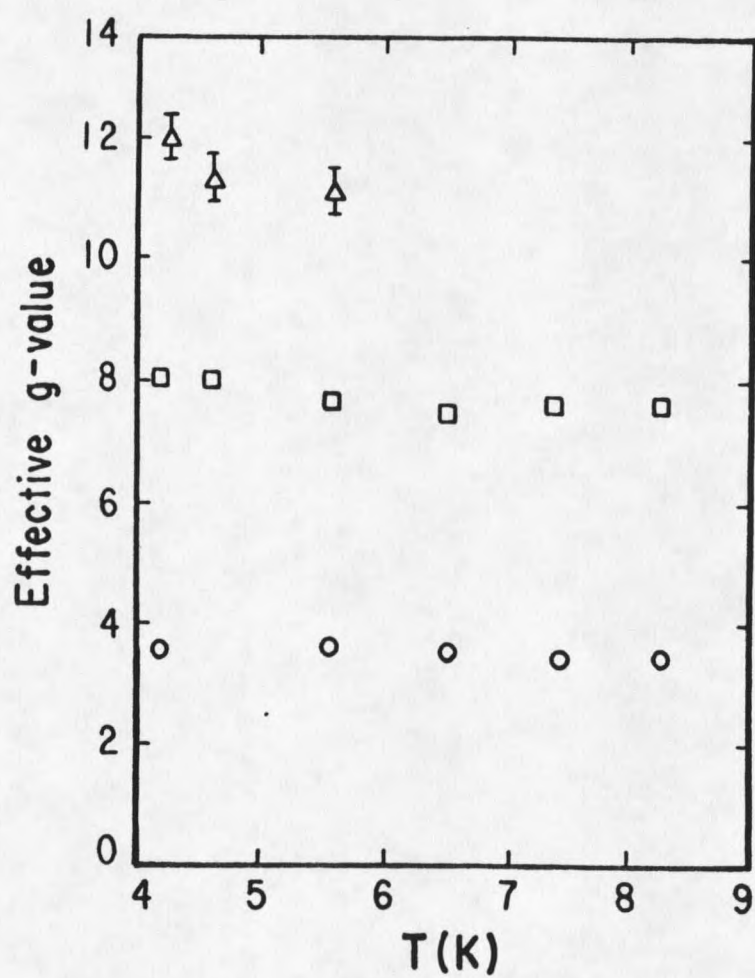


Figure 18. Effective g-values as a function of temperature. Same symbolic notations are used.

Ac Susceptibility Measurements

EPR and magnetization measurements clearly indicate the effective $S=1/2$, Ising ferromagnetic behavior of this system, FeTAC, at low temperatures and the existence of spin clusters. Although the 1-D, Ising model fits the dc-magnetization data very well it does not give any insight as to how the spin cluster dynamics affect the thermodynamics. As we mentioned in the theory (Chapter 2), the Johnson and Bonner expression for the ac susceptibility provides a way to investigate this question. In this section we present the experimental results of ac susceptibility measurements and the analysis using JB results.

A single crystal weighing 0.403 mg with the approximate dimensions $1.7 \times 0.6 \times 0.4$ mm was selected for this experiment. The sample was examined under a polarizing microscope to minimize the possibility of twinning and other imperfections. The crystal was visually oriented with its long axis(b), corresponding to the magnetic easy axis, parallel to the applied field in the SQUID susceptometer. Differential magnetic susceptibility was measured as a function of temperature in the range $4.2\text{K} < T < 20\text{K}$ in fields of 0, 500, 1000 and 1500 Oe. The amplitude and frequency of the excitation field were 6 mOe and 80 Hz. The data were corrected for demagnetization effects by assuming an approximately prolate spheroidal shape of the crystal, resulting in a demagnetizing factor $D_z = 1.3(8) \pm 0.30$. Molar volume was estimated to be $V_m = 21(4) \pm 50 \text{ cm}^3$. The data and theoretical fits of Johnson and Bonner bound magnon (spin cluster) susceptibility are plotted as χ vs T in Figure 19(a)-(b); with data points shown as open symbols and fits of the JB theory as solid lines. Relative errors in the data are less than or equal to the symbol radius. The spin wave susceptibilities are indistinguishable from the temperature axis in both figures. For example, the dashed line in Figure 19(b) shows

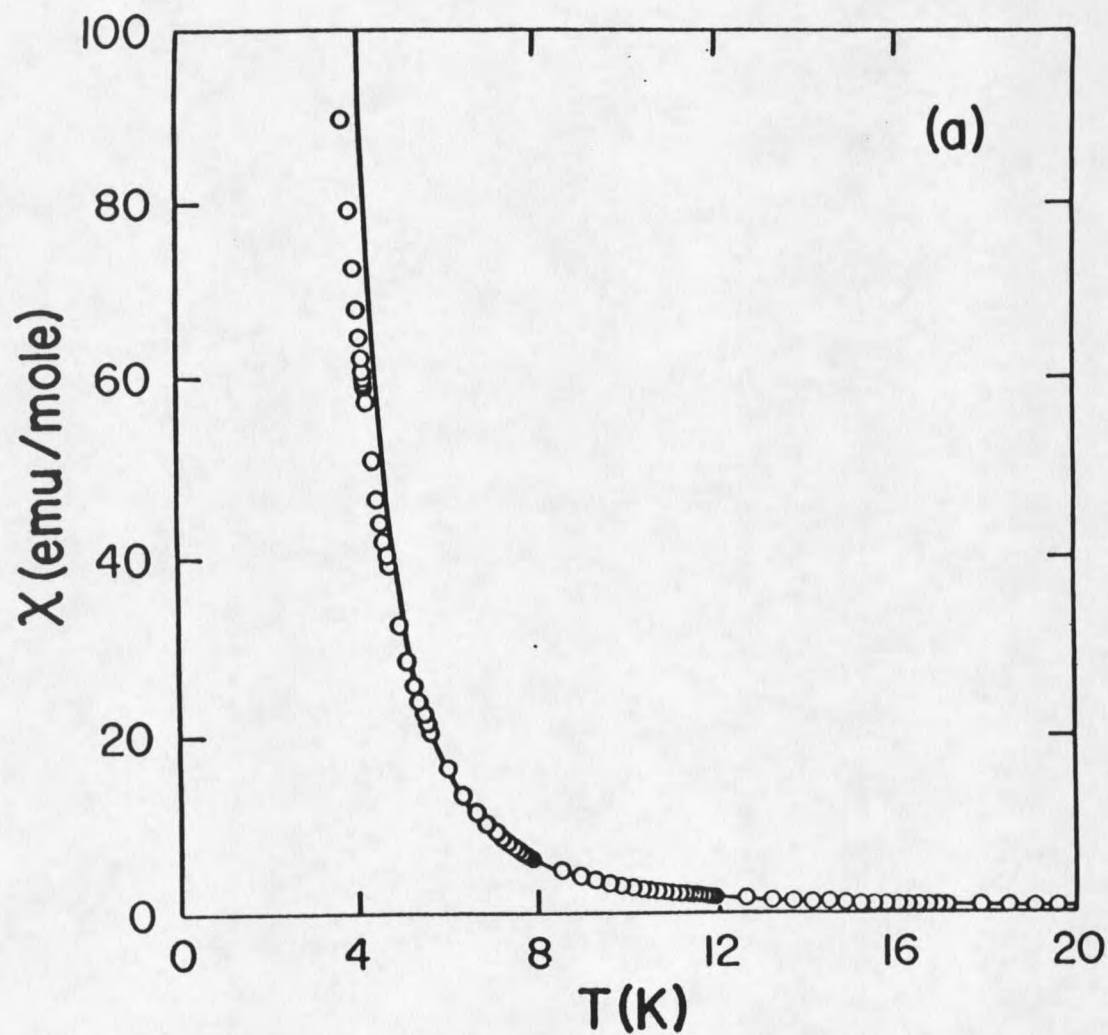


Figure 19. (a). χ vs T data for FeTAC at zero field. Solid line is the JB bound magnon susceptibility for $J/k=17.5\text{K}$, $\gamma=0.01$, and $g=7.5$.

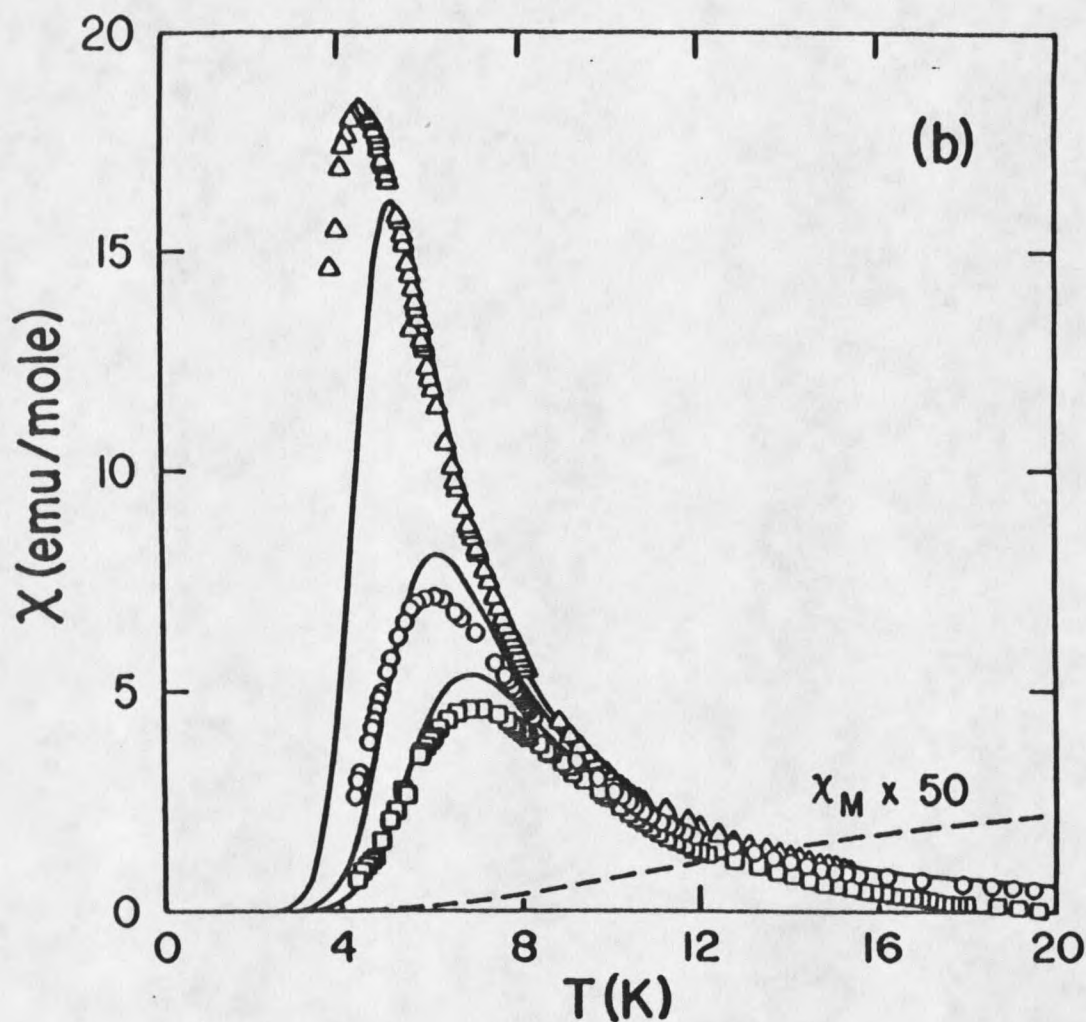


Figure 19. (b). χ vs T data for FeTAC in the fields of 500, 1000, and 1500 Oe. Data are represented by (Δ) for 500 Oe, (O) for 1000 Oe, and ($\square$) for 1500 Oe, and theoretical fits by lines. Solid lines are the JB bound magnon susceptibility for $J/k=17.5K$, $\gamma=0.01$, and $g=7.5$. Dashed line is the JB single magnon term multiplied by 50.

the magnon contribution (for 500 Oe) multiplied by a factor of 50. Except for small deviations which will be discussed below, the fit of the JB bound magnon term to the data is good, demonstrating that high- n excitations dominate the susceptibility of the 1D, Ising ferromagnet.

All four of the theoretical fits of $\chi_{JB,BM}$ to the data shown in Figure 19 are drawn for the same fitting parameters, $J/k = 17.5$ K, $\gamma = 0.01$, and $g = 7.5$. The JB theory is relatively insensitive to changes in γ near the Ising limit so this value cannot be taken as a measure of the extent of spin wave deviations from the Ising axis. $\chi_{1D,IF}$ gives identical results for the same exchange and g -factor, and these parameters are the same as those reported by Greeney et al.^[39] Since $\chi_{1D,IF}$ is exact, and fits the data in zero field, any deviation from the data must be attributed to either experimental error or nonideal 1D,IF behavior in FeTAC. The systematic variations of the 1500 Oe data from the theoretical line above 12 K are probably due to the drift in the background signal. The 500 Oe theoretical peak falls below the data peak because of the demagnetization effect. Although the data were corrected for demagnetization, applied field values were used in the theory. For the 500 Oe peak the demagnetizing field is about 50 Oe; using 450 Oe for the field in $\chi_{JB,BM}$ increases its height by a factor of 1.11. Other systematic deviations between the data and theory are not easily explained, but probably are due to the slight misalignment of the crystal and or due to the nonideal behavior of FeTAC.

Despite small deviations between data and theory, the general agreement of JB theory with data is obvious. Thus, these data provide further verification of the existence of bound magnons in the $S=1/2$, 1-D, Ising ferromagnet. Further, from the size of the magnon susceptibility shown in Figure 19(b) and the fits of the JB bound magnon term to the data, it is clear that magnon theory, based on single spin excitations, cannot possibly account for the observed behavior, and that high- n excitations (bound magnons) are

predominant in determining the susceptibility.

Discussion

It appears that demagnetization correction is a crucial part in all the calculations. Our method of calculating the demagnetizing factor is only an approximation. Because the shape of the sample is irregular, the demagnetizing field is not uniform. It is therefore important that we experimentally verify the estimated value of D/V . This can be approached in the following way. Recall:

$$\chi_{mea} = \frac{\chi_{corr}}{1 + \frac{D}{V}\chi_{corr}} = \frac{1}{\frac{1}{\chi_{corr}} + \frac{D}{V}}$$

For a first order phase transition $\chi_{corr} = \frac{dM}{dH} \rightarrow \infty$. This implies that $\chi_{mea} \rightarrow \frac{1}{D/V}$. Therefore if we measure χ as a function of the magnetic field at constant temperatures below T_c because χ reaches a maximum value of $\frac{1}{D/V}$ instead of a sharp peak we should obtain a plateau type curve. This technique was used by Landau *et al.*,^[43] on the metamagnet dysprosium aluminum garnet (DAG) and we present their results in Figure 20 as an example to illustrate this idea. In their notation $1/N$ represents $1/(D/V)$.

This technique is particularly useful in FeTAC because the phase diagram is metamagnetic and the phase goes through a first order (discontinuous) transition from antiferromagnetic state directly to the paramagnetic state without passing through a spin-flop state ($T_c = 3.1K$, $H_c[T=0] = 90$ Oe).^[39] Details of this unusual case are as follows. In a usual antiferromagnetic system, say in an anisotropic Heisenberg antiferromagnet, the phase from AF $\rightarrow$ P (para) can go through in two stages: as the field increases (at constant temperature below T_c) the phase changes from AF $\rightarrow$ SF

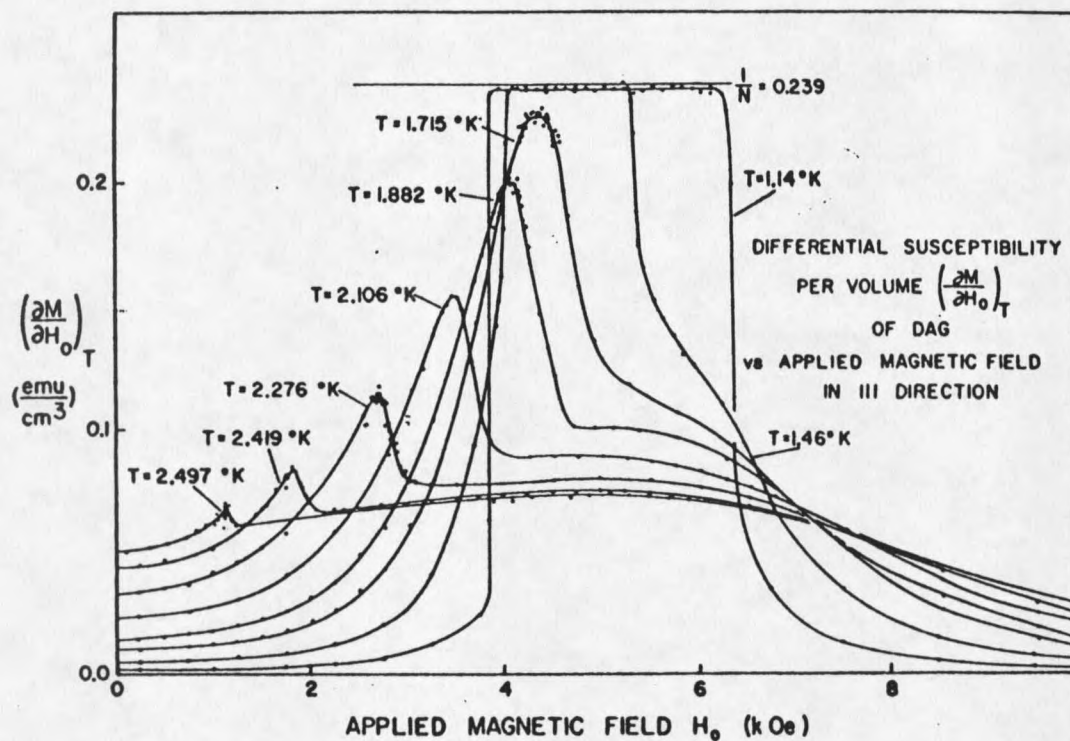


Figure 20. Figure taken from Reference [43] showing the observation of a plateau type curve instead of a usual sharp peak, due to the demagnetization.

(spin flop) $\rightarrow$ P. Because the interaction between the spins is antiferromagnetic the spins want to stay apart when they flip. Further increase in the applied field makes the spins point in the direction of the applied field and slowly brings the system to the paramagnetic phase. However, the SP phase depends on the anisotropy present in the system. If the anisotropy is strongly Ising-like, then the spins can only point either up or down. Hence, the phase transition occurs directly AF $\rightarrow$ P state without the intermediate SP phase. This case is referred to as metamagnetic. FeTAC is a strong Ising like system therefore the metamagnetic behavior is not surprising.

In order to verify the antiferromagnetic state and to check the value of T_c , we have measured the zero field susceptibility at temperatures as low as 2K (lower than the previous measurement). These measurements were taken on a different sample of FeTAC (21.5 mg). The data are shown in Figure 21 and show a sharp peak near 3.1K as an indication of a phase transition. Also note that χ goes to zero below 2K as expected for 3-D antiferromagnetic ordering.

In order to measure D/V experimentally, we measured χ as a function of magnetic field at constant temperatures near 3.1K (T_c). The data are shown in Figure 22. From the upper maximum value of the data at 3.3K, we obtained $D/V = 0.02 \text{ cm}^3$. On the other hand our estimated value is $D/V = 0.017 \text{ cm}^3$ which is reasonably close to the experimental value. For a more precise value, measurements should be taken to lower temperatures. However, the experimental value provides an upper limit for comparison with our estimated value.

The ac susceptibility measurements presented so far are the real component, χ' , of the complex susceptibility, $(\chi' + i\chi'')$. The component, χ'' is related to the energy losses

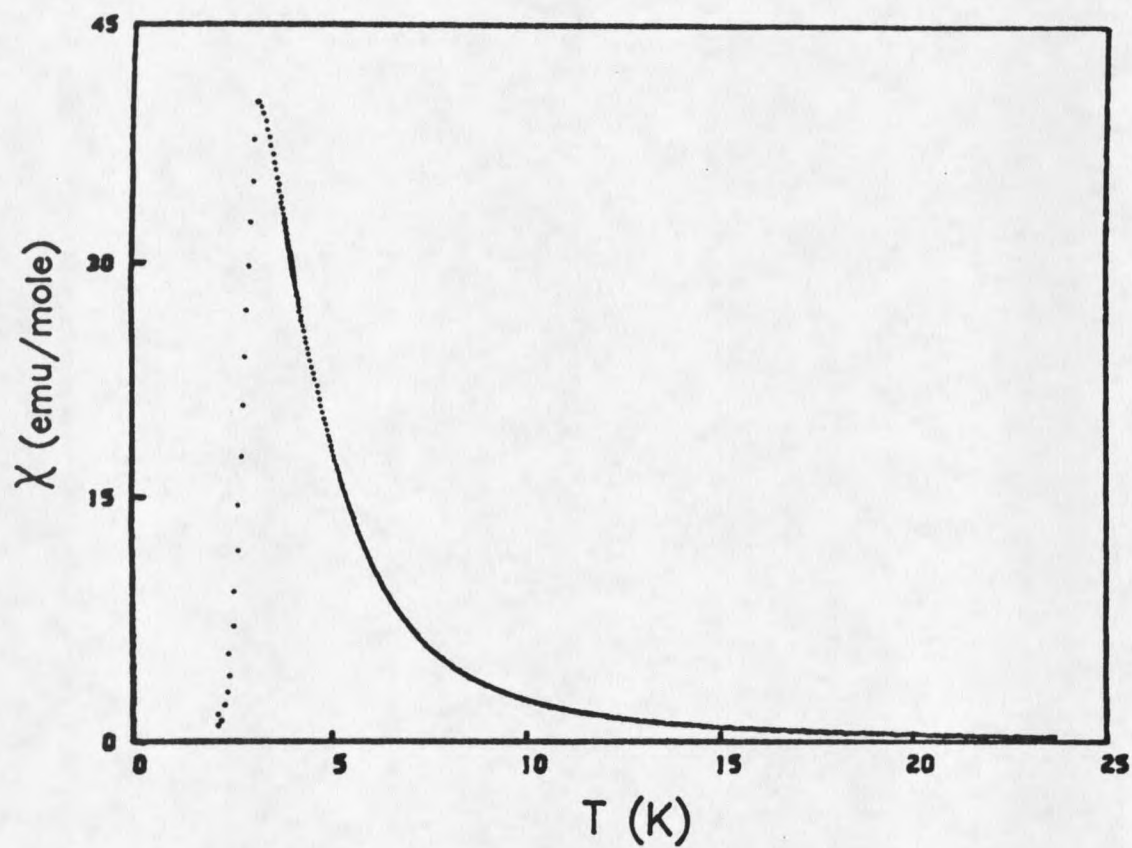


Figure 21. Zero field data of FeTAC showing long range ordering below 3.1K.

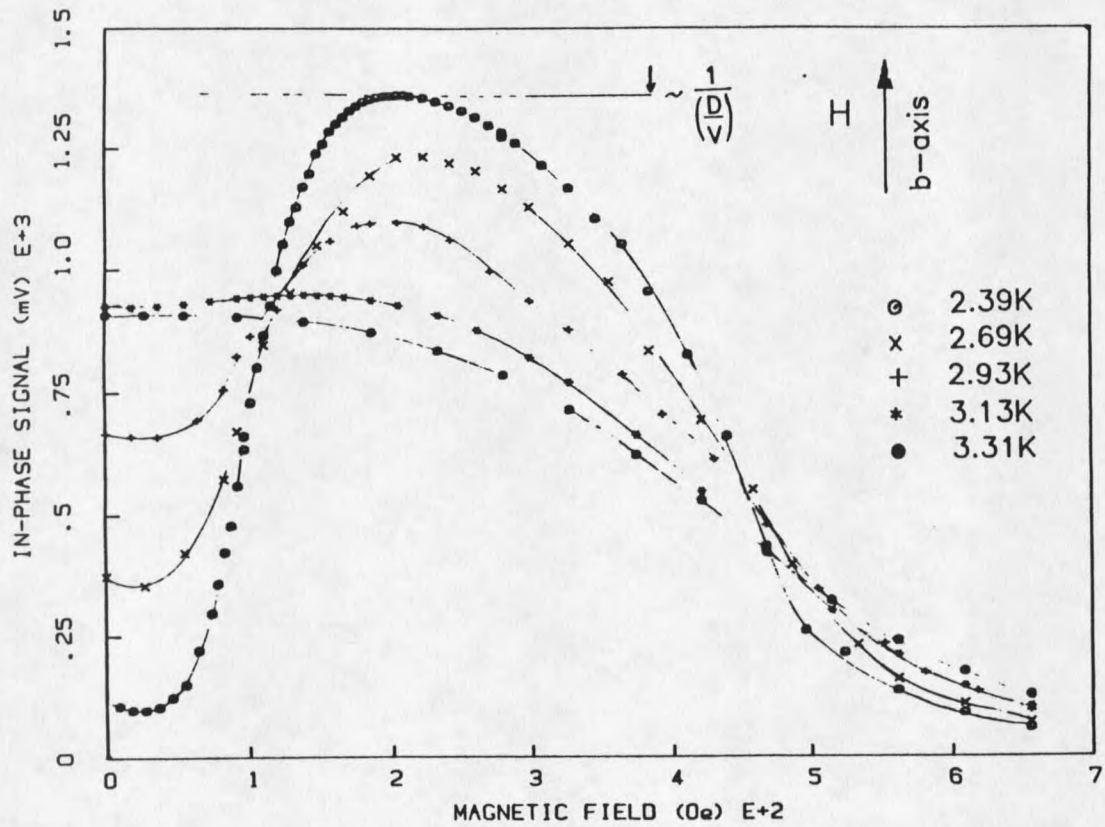


Figure 22. In-phase signal vs Magnetic field for FeTAC along the easy axis at various temperatures near $T_c=3.1K$. The maximum value of the data at 2.39K is approximately equal to the inverse of the demagnetizing factor.

which can occur in the system due to a spin relaxation mechanism. To understand the relaxation phenomena consider paramagnetic ions in a magnetic system that can occupy two energy levels, one with $m = -1/2$ (the magnetic moment aligned with H) and one with $m = +1/2$ (the moment antiparallel to H). If the oscillating component of the field is added to the static contribution (as in ac measurements) it is obvious that the paramagnetic ions should continuously redistribute over the two energy levels according to the Boltzmann distribution according to the temperature. This distribution requires a certain time constant τ . There is no problem if the change in external field dH takes place over a long time compared to this time constant; in this case the spins have time enough to reach equilibrium so that M is at equilibrium over the time scale of the experiment. Then the measured χ_{ac} is indeed equal to $\frac{dM}{dH}$ (the slope of the M vs H curve). In this case $\chi'' = 0$ and $\chi_{ac}(=\chi')$ is generally referred to as the isothermal susceptibility χ_T .

The situation is different if the oscillation of the ac field is fast compared to the time constant τ . The spins are then distributed over the energy levels and cannot relax on the time scale of the experiment. The measurement of χ_{ac} now gives the adiabatic susceptibility χ_{ad} (which is lower than χ_{ac}) since the magnetic system is effectively isolated from its surroundings. In this case also $\chi'' = 0$.

If the measurements are made at an intermediate frequency, the susceptibility will be frequency dependent and will give a value between χ_T and χ_S . A non-zero in-phase (χ') and a quadrature (χ'') signal results. The susceptibility is given by:

$$\chi(\omega) = \chi' + i\chi'' = \chi_S + \frac{(\chi_T - \chi_S)}{1 + i\omega\tau}$$

and can be illustrated in the so called Argand diagram which is a map of $\chi(\omega)$ in a complex plane. This diagram is particularly useful because it will be a semicircle for systems which have a single relaxation time, and will appear as a broadened curve for relaxation

processes not characterized by a single relaxation time (for example see our work on spin glass, ref. [44]). We will not discuss this further here.

For a regular paramagnet, the relaxation time is of the order of 10^{-11} sec. In our ac susceptibility measurements the excitation frequency was at 80 Hz ($\sim 10^{-2}$ sec). However, the measurements were taken in the temperature region where fluctuation of spin clusters exist. Thus, a distribution of relaxation times is expected. The excitation frequency was $\sim 10^{-2}$ so that the measurements were near χ_T . The imaginary component, χ'' , in most measurements was nearly zero or too small to be measured. Although the relaxation phenomena in a cluster system is not straightforward and needs further explanation, the simple idea of the relaxation time described above gives an insight as to how the frequency affects the ac susceptibility measurements.

The same picture can be used to explain qualitatively the relaxation time in the EPR measurements where the ac excitation field is the microwave perturbation. Our EPR experiments were performed at the very high frequency of 9.2 GHz corresponding to a period of $\sim 10^{-10}$ sec. Unlike ac measurements (where an total moment of all the spins are measured) EPR measurements single out each spin. The spins at resonance absorb the microwave energy and may pass it on to the other spins which are not at resonance. This energy transfer is possible by means of the dipolar and exchange interactions. The rate at which the energy transfers, $\frac{1}{T_2}$, in this case, is referred to as spin-spin relaxation. The spin system also transfers energy to the lattice at the rate $\frac{1}{T_1}$, where T_1 is the spin-lattice relaxation time. Usually T_2 is smaller than T_1 ($T_2 \ll T_1$). Since the line width (ΔH) of the resonance line is inversely proportional to the relaxation time T_2 ($\Delta H \sim \frac{1}{T_2}$), the line width will be broader for faster relaxation times.^[45] Recall Figure 16 in which the line widths are plotted as a function of temperature in the region $4K < T < 10K$. Note that the line width for the "broad" signal is about 600 Oe (near 4K) whereas for "strong"

signal it is only about 80 Oe. This means that the "broad" signal is relaxing much faster than the strong signal. This is due to the strong spin cluster fluctuations at this temperature. Also note that the signal broadens further as the temperature is increased from 4K to 10K. This means that the fluctuations are greater and the spins may not stay coupled long enough to observe EPR resonances ($t_{\text{microwave}} = \frac{1}{\omega_{\text{microwave}}} = \frac{1}{10^{10}\text{Hz}} = 10^{-10}\text{sec}$). Therefore, spin cluster resonances associated with 3,4,5,...spin clusters relax too quickly so that the resonances of the higher order spin clusters are too broad to be seen.

In summary, the ac susceptibility data of FeTAC and the analysis based on JB theory clearly show that the bound magnons do exist in the one-dimensional, $S=1/2$, Ising ferromagnet and in fact the susceptibility data are almost entirely represented by the contribution from bound state excitations. The evidence for the spin cluster resonance is clear from the appearance of the broad signal in the EPR spectrum, and further confirms the existence of bound magnons above T_c .

TMCuCl₃ - S=1/2, 1-D, Nearly Isotropic Heisenberg Ferromagnet

Tetramethylammonium copper chloride, TMCuCl₃, (CH₃)₄NCuCl₃, has been reported to be a good S=1/2, nearly Heisenberg linear ferromagnet.^[46] The structural properties of TMCuCl₃ were described by Weenk and Spek^[47] as consisting of linear chains of magnetic ions surrounded by face-sharing chlorine octahedra. The chains are well separated by large tetramethylammonium ions and show a high degree of one dimensionality $J'/J \sim -10^{(-4)}$. TMCuCl₃ grows as a very small needle crystal, therefore, most of the data which have been published so far are on powdered samples. Landee and Willett estimated the value of J/k to be 29K from their susceptibility measurements by fitting to Baker's high temperature series expansion for S=1/2, isotropic Heisenberg systems.^[46] There are discrepancies in the reported value of J/k (35K - 45K) presumably due to inherent impurities in the sample.^[48] Dupas and Renard measured the susceptibility at low temperatures and showed that TMCuCl₃ orders at T_N = 1.25K and has a SF-P phase diagram with H_c = 600 Oe.^[49] Our experimental measurements which we describe next were all carried out at temperatures far from the 3-D ordered state region (T > 1.24K) to ensure the 1-D behavior. TMCuCl₃ powdered samples and tiny needle crystals were obtained from Professor Roger Willett at Washington State University, Pullman, Washington.

Susceptibility at Zero Field

Differential susceptibility measurements were made on a powdered sample using the SQUID susceptometer. The single crystals were not big enough to get a good signal in the susceptometer so zero field measurements were made on a 46.9 mg powdered sample in the temperature range of 2K ≤ T ≤ 18K. An excitation field of 7.5 mOe and

frequency of 80 Hz was used. Zero magnetic field was adjusted prior to data runs using a Pb sphere as described in Chapter 3. Temperatures as low as 2K were obtained by pumping the sample space. Experiments were repeated several times to ensure the reproducibility of the data.

In Figure 23, the data are plotted as χT vs T . This figure shows that the magnetic susceptibility increases continuously as the temperature is lowered at a rate greater than the $1/T$ dependences predicted by Curie law ($\chi = C/T$), indicating the presence of ferromagnetic interactions. For interacting spins the susceptibility at $T \gg T_c$ follows the Curie-Weiss law which is given as

$$\chi = \frac{C}{T - \theta} = \frac{C}{T} \left(1 + \frac{\theta}{T} + \dots \right)$$

and implies:

$$\chi T = C + C \frac{\theta}{T} + \dots$$

where C is the Curie constant and θ is a parameter which is introduced to account for the possible interaction between spins. Therefore, if the interaction is ferromagnetic ($\theta > 0$) the χT vs T graph will curve upwards as the temperature is lowered, and for antiferromagnetic interaction ($\theta < 0$) this graph will curve downwards.

Zero field data are also shown in Figure 24(a)-(b), plotted as χ vs T . The reported value for the long range ordering temperature is $T_N = 1.24\text{K}$ which is lower than the lowest temperature that we can obtain in our system. These data are compared with the expressions of Takahashi and Yamada and of Schlottmann for the $S=1/2$, isotropic Heisenberg ferromagnet (equations 2.4 and 2.5). For fitting the g -value was kept at 2.1 and the value for J/k was adjusted for a good fit. Very good fit was obtained for Takahashi

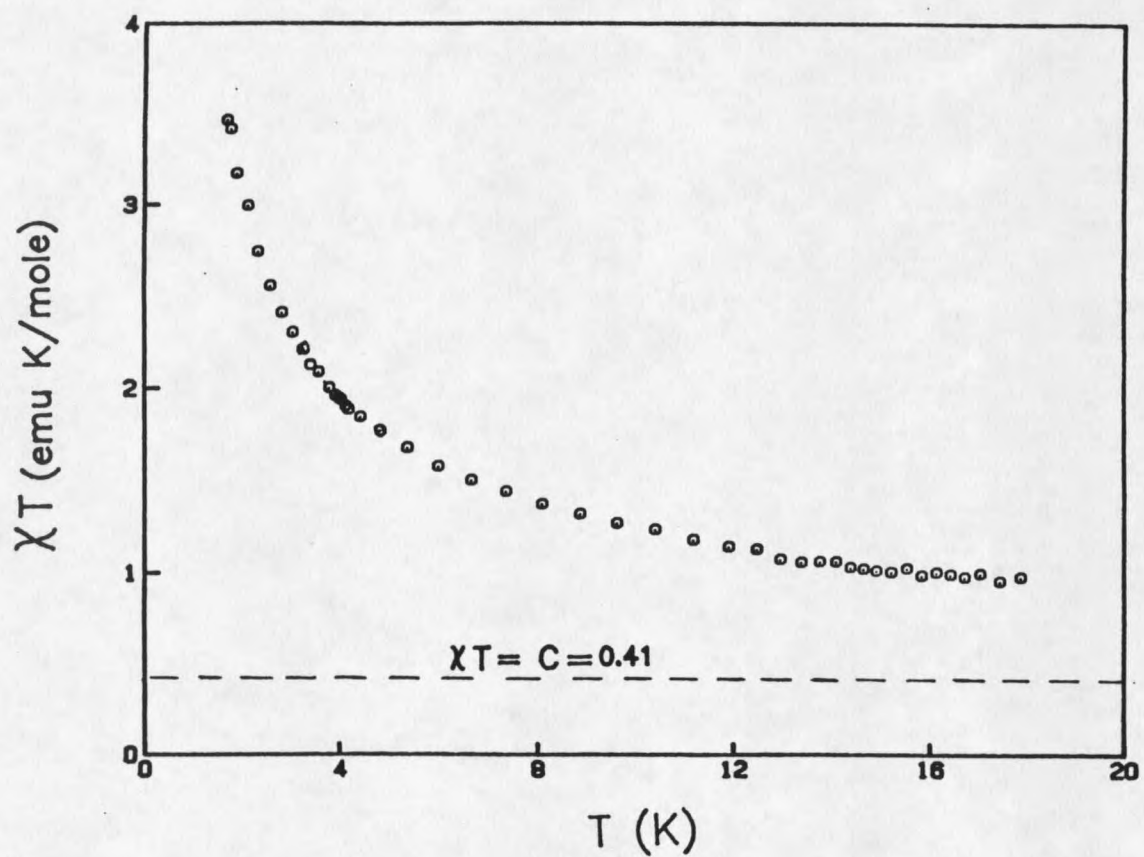


Figure 23. Zero field susceptibility data for TMCuC plotted as χT vs T . The data curving upwards indicates the presence of ferromagnetic interaction.

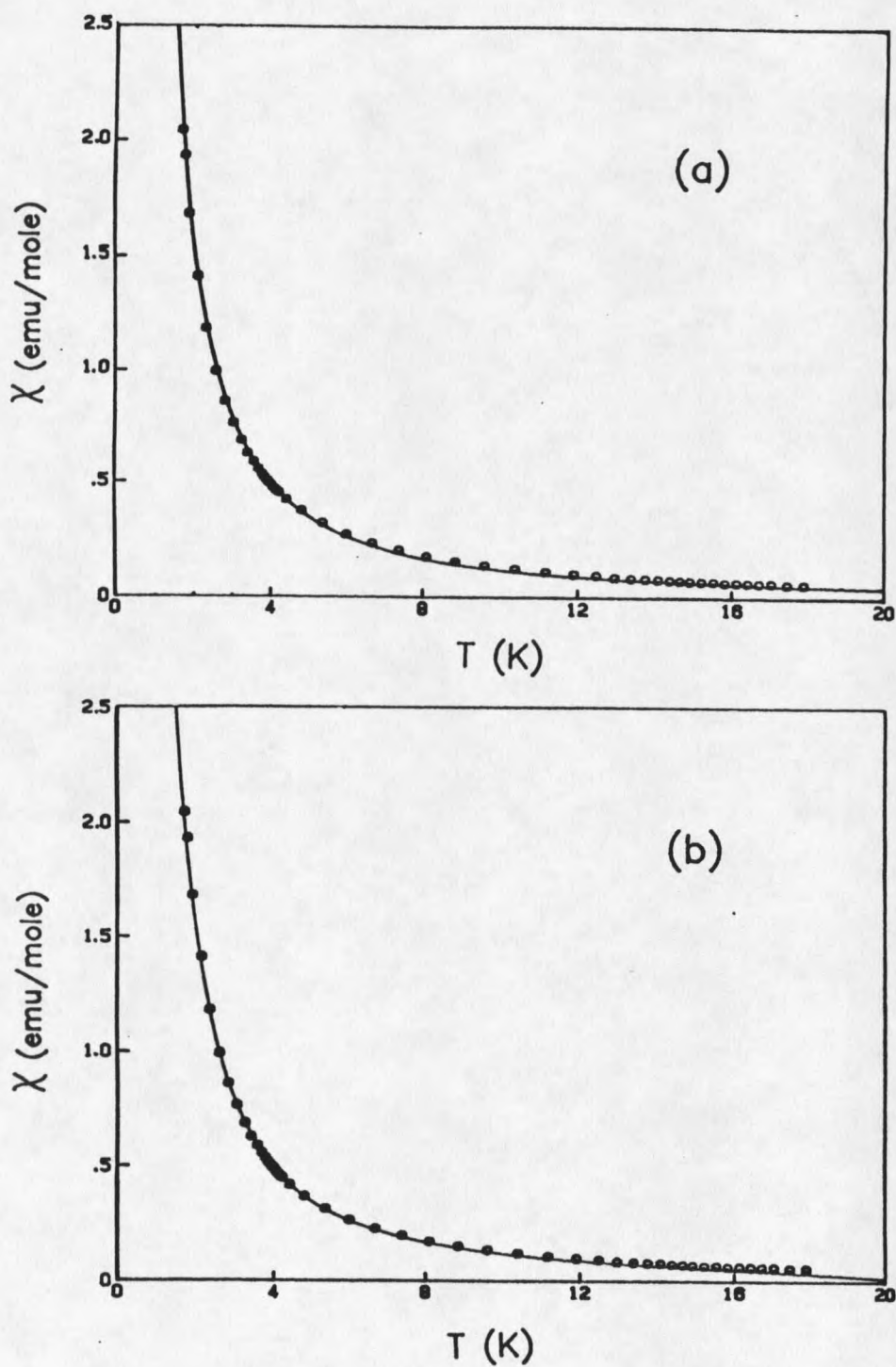


Figure 24. Zero field susceptibility data of TMCuC. Solid lines represent (a). Takahashi and Yamada's expression for $J/k=50\text{K}$ and $g=2.1$ (b). Schlottmann's expression for $J/k=38\text{K}$ and $g=2.1$.

and Yamada's expression (equation 2.4) with $J/k = 50K$ (solid line in Figure 24(a)) and Schlottmann's expression (equation 2.5) with $J/k = 38K$ (solid line in Figure 24(b)). The discrepancy in the J/k value may be attributed to the discrepancy seen in their expressions in Figure 4, as discussed in chapter 2. Attempts made to fit the Johnson and Bonner expression with a small anisotropy (4-5%) gave poor agreement with data. Comparing all these fittings it appears that the zero field (powdered sample) data can be best described by an isotropic Heisenberg model with an average g value ≈ 2.1 .

Susceptibility at Finite Fields

Measurements were made on the same sample in the temperature range of $4.2 \leq T \leq 20K$ and in the fields of 1, 1.5 and 2 Tesla. The desired field was obtained by carefully setting the superconducting magnet current. For each run the bridge was rebalanced to cancel any background signal that could arise due to the changes in the field. The measurements at higher fields were very difficult to make. These measurements were made point by point by slowly changing the temperature and allowing enough time for the SQUID to stabilize. The data are shown in Figure 25; different symbols are used for different fields.

The zero field data can be best described by the isotropic Heisenberg model. Therefore, in the presence of a magnetic field, one would expect the spins to point in the direction of the field, and the nature of the exchange interaction between the spins to be unaffected. Unfortunately there are not any theoretical expressions available with which to compare the finite field data in the isotropic case. Neither Takahashi nor Schlottmann have extended their expressions for finite field.

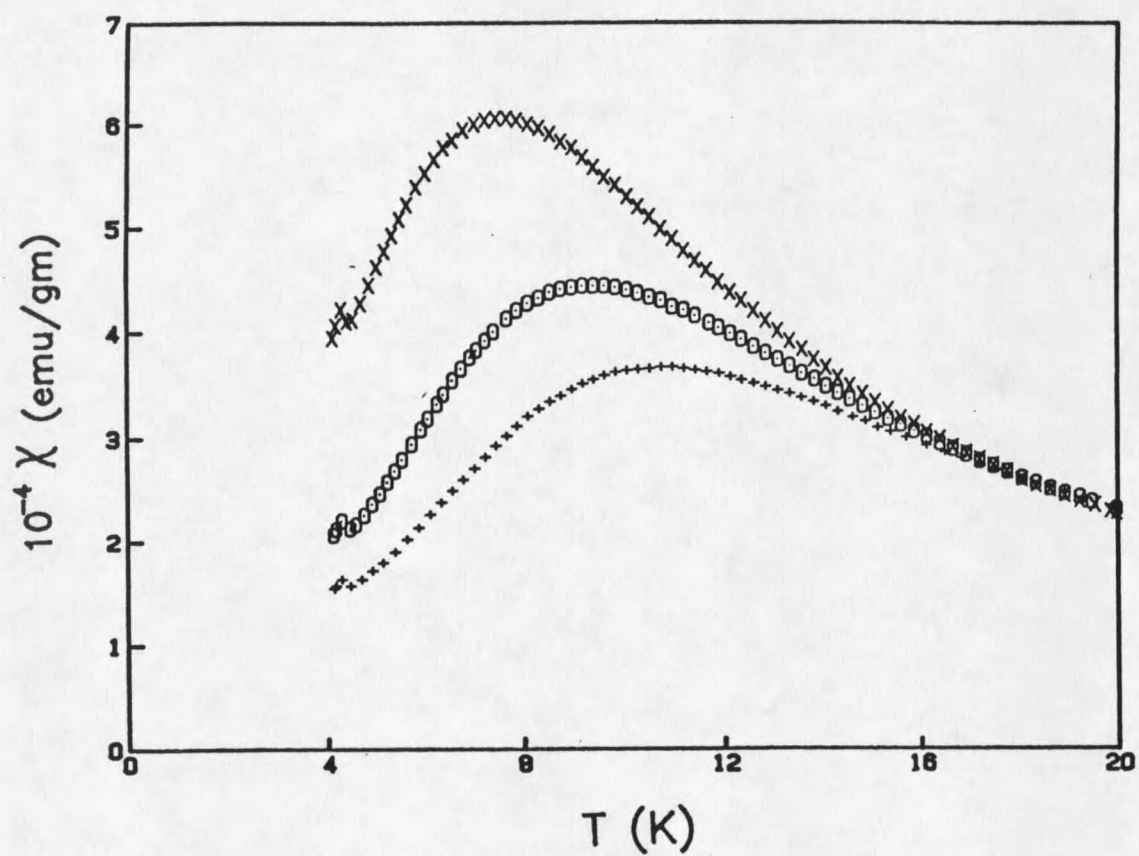


Figure 25. χ vs T data for TMCuC at different magnetic fields. (X) for 1 Tesla, (O) for 1.5 Tesla and (+) for 2 Tesla.

Our approach, in collaboration with Professor George Tuthill of our department to analyse our experimental results, has been to numerically diagonalize a finite chain Hamiltonian. Numerical results of a 12-spin ring of $S=1/2$, isotropic Heisenberg ferromagnet at fields of 0, 1 and 2 Tesla are shown in Figure 26. Takahashi and Yamada's zero field expression is drawn for comparison. The zero field result, as seen in figure is in fairly good agreement with Takahashi and Yamada's expression as low as $T/(J/k)=0.2$. Corresponding results for 14-spins are shown in Figure 27 which indicates that the zero field results approach Takahashi and Yamada's expression very reasonably as the number of spins in the calculation is increased. In order to improve the results it will be necessary to extend the spin calculation to larger number of spins. Nevertheless, it can be seen that the 14-spin results for 1 and 2 Tesla calculation appear to make no significant change compared to 12-spin results. Therefore the 14-spin results are adequate for the analysis of our data at 1 and 2 Tesla.

The 14-spin results for the parameters $J/k=50K$ and $g=2.1$ are plotted in Figure 28. The results are not particularly encouraging since the peaks occur at much lower temperatures as compared to the data; for example peak for 1 Tesla occurs near 5K whereas the data show the peak near 7.5K. Although these sets of parameters give a very good fit for zero field data with Takahashi's expression, in the presence of a field this system can no longer be represented by an isotropic Heisenberg model with the same fitting parameters. The reason may be that a powdered sample is used, therefore the measured susceptibility is the average of the susceptibilities along all three principal axes. In a moderate field any possible anisotropy should be taken into account.

Next we will analyze our data in terms of the Johnson and Bonner expression (equation 2.1) for infinite chains with small anisotropy. The data points and theoretical curves for the fields of 1, 1.5, and 2 Tesla are shown in Figure 29(a)-(c). The dashed line

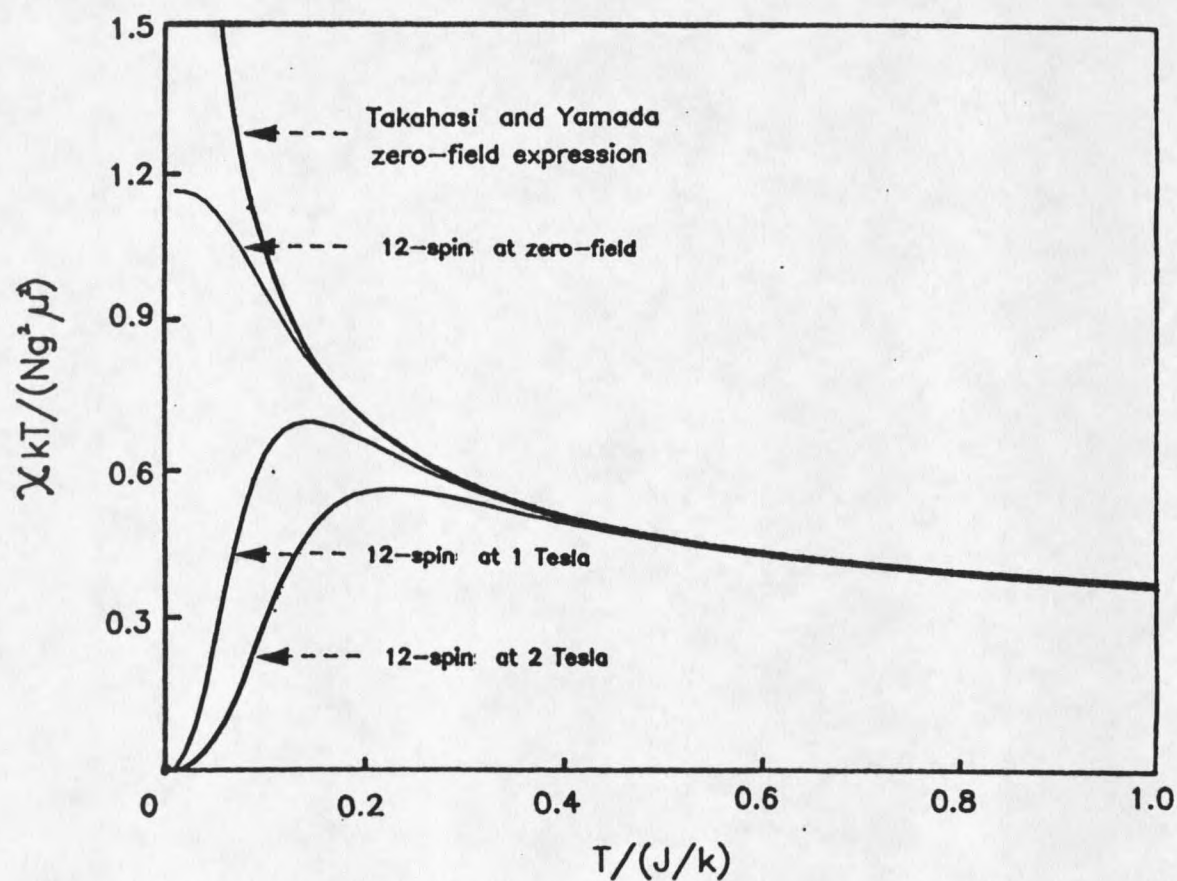


Figure 26. Numerical results of a 12-spin ring of $S=1/2$, isotropic Heisenberg ferromagnet at fields of 0, 1 and 2 Tesla. Takahashi and Yamada's zero field expression is drawn for comparison.

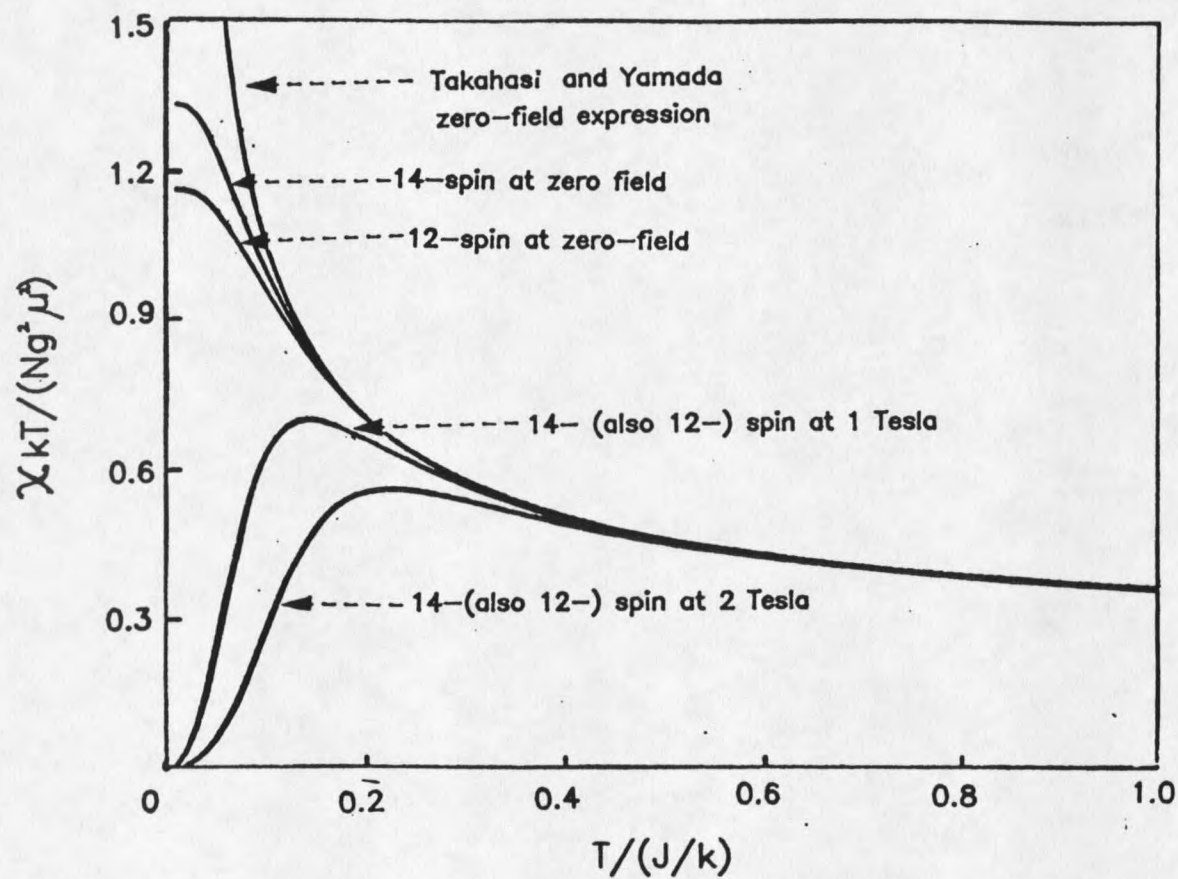


Figure 27. Numerical results of 14-spin are compared with 12-spin results and Takahashi and Yamada's expression.

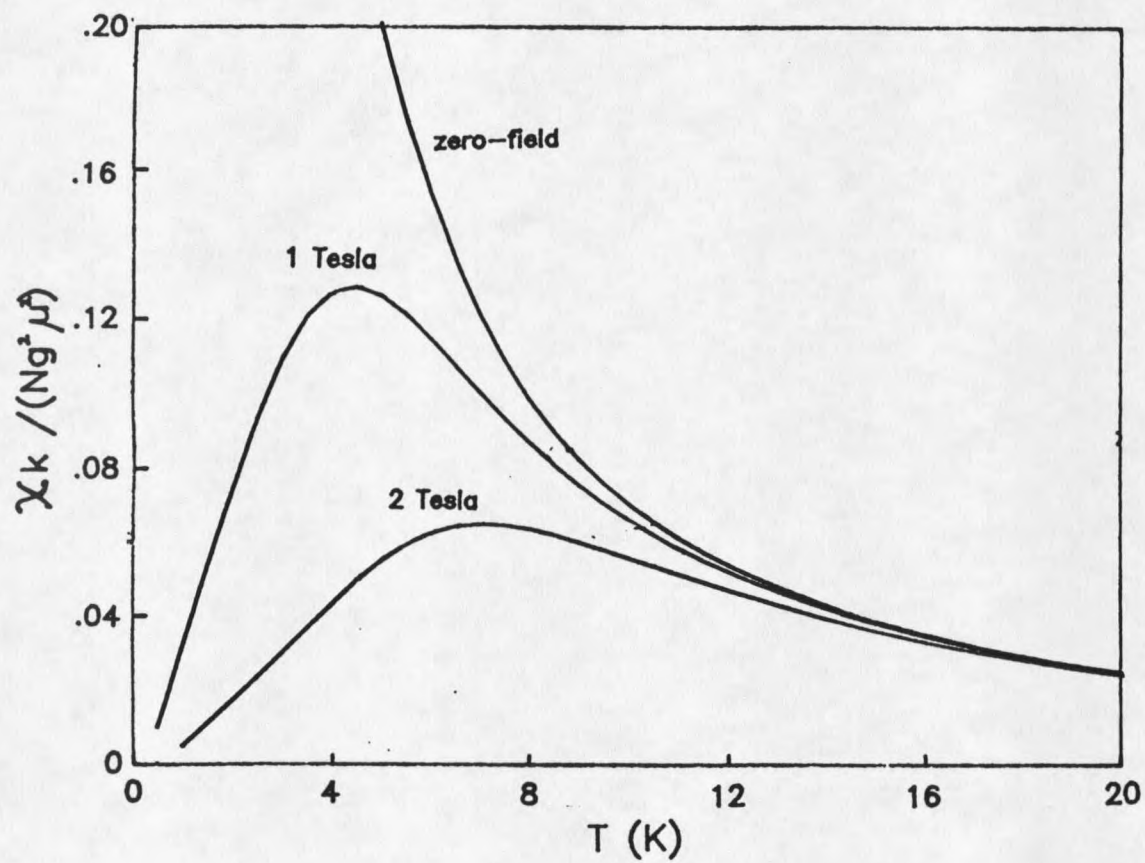


Figure 28. 14-spin results for $J/k=50$ K and $g=2.1$.

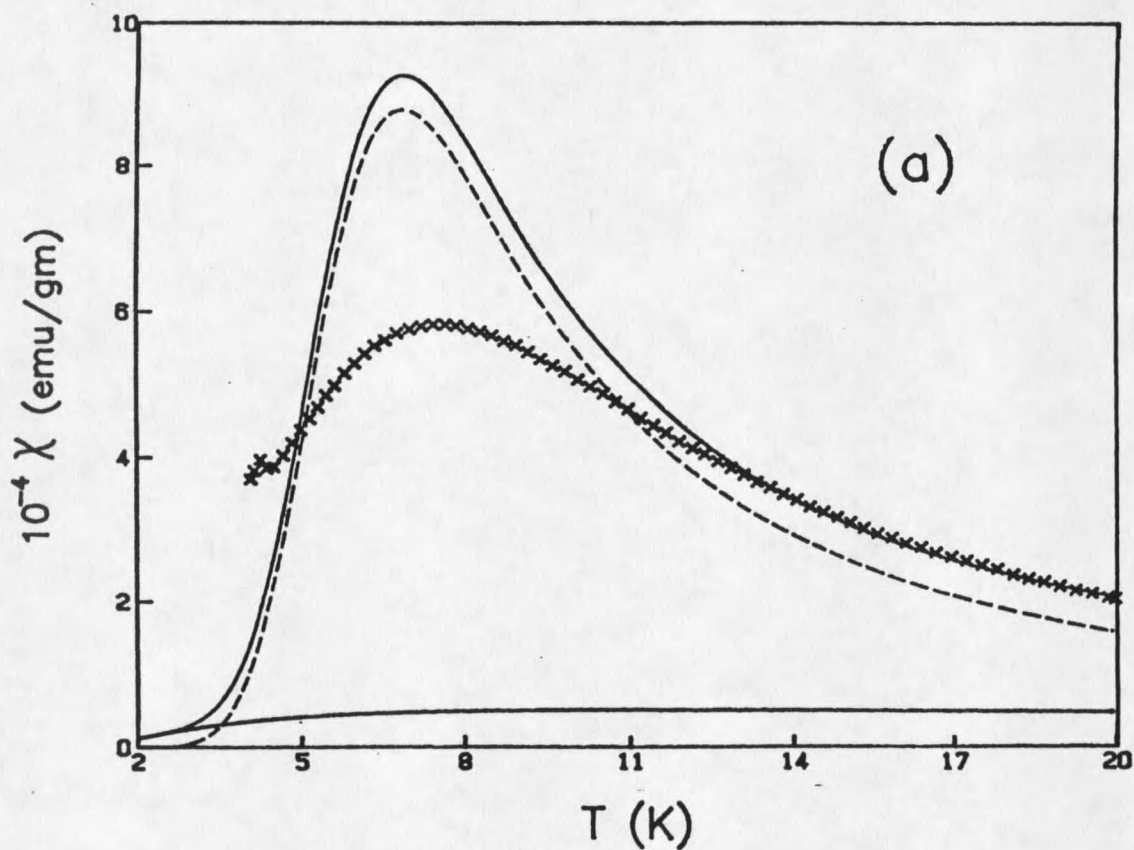


Figure 29. χ vs T data for TMCuC powder measured at different fields: (a). at 1 Tesla (X), (b). at 1.5 Tesla (O), and (c). at 2 Tesla (+), are compared with JB expression for $J/K=45K$, $\gamma=0.01$, and $g=2.1$. The dashed lines are the bound magnon contribution and the line just above the temperature axis are spin wave contribution.

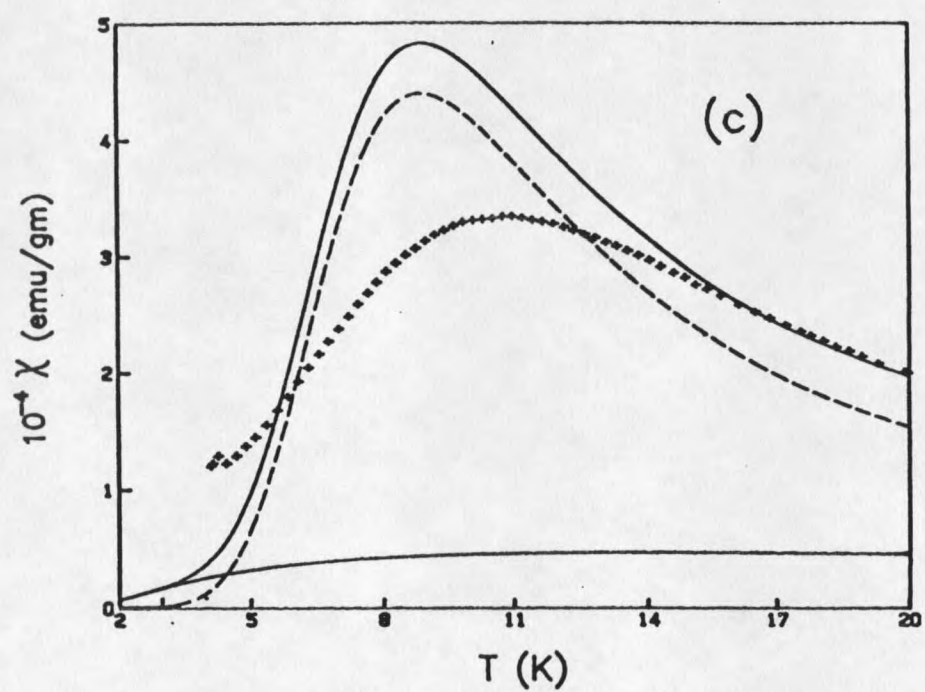
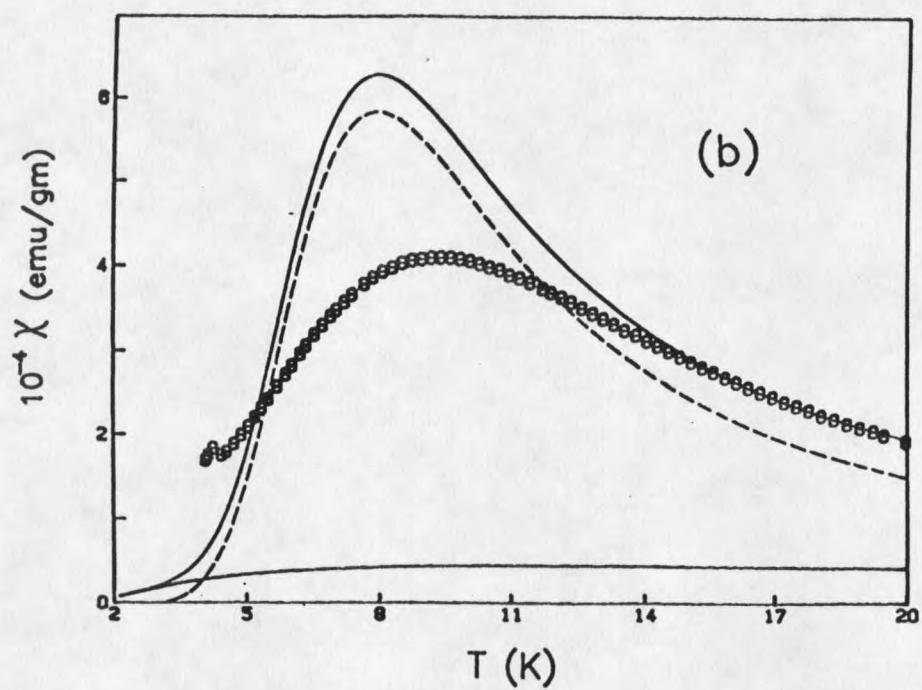


Figure 29 continued

in the Figure indicates the Johnson and Bonner theoretical contribution due to bound magnons and the line just above the temperature axis shows the contribution due to spin-waves (magnons). The solid lines represent the total contribution. All these lines are drawn for the same fitting parameters: $J/k = 45\text{K}$, $\gamma=0.955$ (anisotropy 4.5%) and $g_{\text{ave}} = 2.1$. From the figure it can be seen that the spin-wave contribution is very small and cannot represent the data. The total contribution is mainly from the BM term and it correctly predicts the broad maximum at higher fields. The fact that the SW expression cannot be made to fit to the data for any values of parameters suggests that linear SW theory fails in TMCuC. Similar failure was seen in the analysis of the low temperature ac susceptibility measurements on CHAC, a $S=1/2$, 1-D, nearly isotropic Heisenberg ferromagnet.^[14] It appears that SW theory should be suspect in any other Heisenberg linear ferromagnetic chains and that this failure is not due to the excitation of too many SW's, as is commonly assumed in 1-D, but rather due to the presence of BM's, which are the non-linear excitations resulting from anharmonic terms in the Hamiltonian. This conclusion is supported by the work of Taylor and Muler who find that the SW theory does not correctly give the $T=0$ dynamics structure factor of certain 1-D systems which are ordered at $T=0$.^[50]

Although JB theory clearly indicates the relative importance of the BM contribution, there are some difficulties. In particular the fittings are by no means perfect in that the peaks in the data are consistently lower than the theoretical expression. The deviation may be attributed to one or more of the following: first a powder sample was used. Therefore the measured susceptibility is an average value of easy-and hard-axis single crystal susceptibility which is lower than the value along the easy axis. Second, because the sample was powder, no corrections were made for the demagnetizing effect. It is apparent from the work of Landau, *et al.*, that careful measurement on samples of spherical

or ellipsoidal shapes are necessary in order to gain precise thermodynamic information.^[43] Irregular-shaped samples have a distribution of demagnetizing fields which will, in turn, broaden the susceptibility peak. Third, this sample possibly contains small amounts of two impurity micro-crystallites. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is most expected and it is evident from the small peak which appears in the data near 4.3K, since $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ orders antiferromagnetically at $T_N = 4.357\text{K}$.^[50] $((\text{CH}_3)_4\text{N})_2\text{CuCl}_4$ could also be present. It could be possible that the impurities are greater than expected and mixed into the TMCuC crystallites give inhomogeneous exchange. However, if the JB theory is assumed correct for the susceptibility in the presence of an applied field, and the above mentioned variations from the ideal 1-D system are the cause for deviations from a perfect fit, then the JB theory shows that bound spin wave excitations play a major role in the magnetic behavior of TMCuC.

CuCl₂.DMSO -- S=1/2, Heisenberg, 1-D, Ferromagnet

The third linear chain compound that we have chosen for the bound magnon analysis is CuCl₂.DMSO (copper-chloride-dimethylsulfoxide). This compound has been reported to show a predominantly ferromagnetic intrachain coupling, $J/k = 45\text{K}$, and a significant antiferromagnetic interchain coupling, $J'/k = -1.6\text{K}$ in the paramagnetic phase.^[52,53] It orders antiferromagnetically near $T_c = 5.0\text{K}$. The structure of CuCl₂.DMSO has been reported to be monoclinic with the chain axis parallel to the c-axis and the interchain superexchange pathway connecting chains in the bc-plane.^[52] The crystals grow as parallelepipeds with the long axis along the c-axis. It has been reported from the magnetization measurements that the spin anisotropy is very small and therefore the spin interaction is nearly of Heisenberg type.^[53] In this section we report our preliminary ac susceptibility measurements along the c-axis. The sample was provided by Prof. Roger Willett from Washington State University, Pullman, Washington.

Ac Susceptibility Measurements

A single crystal weighing 24.5 mg was used in these measurements. Ac susceptibility was measured using the ac-SQUID susceptometer at a frequency of 80 Hz and an excitation field of 90 mv peak to peak amplitude. Unlike the VSM, in the SQUID system the orientation of the sample cannot be rotated once the sample is placed in for measurements. Any orientation has to be done visually so for this reason the sample was mounted with the chain axis (c-axis) parallel to the magnetic field for the preliminary measurements. Also along the long axis the demagnetizing effect is small so that the largest signal is expected. From the dimension of the sample, the demagnetizing factor along the c-axis was estimated to be $D/V = 0.007 \text{ emu}^{-1} \text{ mole}$.

Zero field data in the temperature region of $4.2\text{K} < T < 25\text{K}$ is shown in Figure 30. These data have been corrected for demagnetizing effect. Note that the susceptibility is increasing as the temperature is lowered until near the temperature 5K and below, where it falls off as an indication of antiferromagnetic ordering. When the lower temperature data are extrapolated to zero temperature, the susceptibility does not reach zero as would be expected along the easy axis. This is in agreement with the magnetization data which has been reported to show the easy axis to be in the ac-plane but not coincident with the c-axis.^[56]

These data are compared with Takahashi and Yamada's zero field expression for $S=1/2$, 1-D, isotropic Heisenberg ferromagnet (solid line). For this approach his expression (equation) has been modified by the addition of a meanfield correction to account for the interchain interaction using the basic equation^[54,55]:

$$\chi' = \frac{\chi_c}{1 - \frac{2zJ'}{Ng^2\mu^2}\chi}$$

where z is the number of nearest-neighbor chains and J' is the exchange integral for the magnetic interaction between nearest-neighbor chains. The solid line is drawn for the parameter $J/k = 45\text{K}$, $g = 2.15$ and $zJ'/k = -2\text{K}$. This line only fits the data above 13K. The mean field correction does not give a reliable fit in the low temperature region near the transition temperature because of strong critical fluctuations associated with the onset of long-range order. The value for J/k is in excellent agreement with the previously reported value, whereas the value for zJ'/k is about a factor of 2 smaller than the reported value.^[52,53] It should be noted that Swank *et al.*^[52] obtain this value (for J/k) by fitting

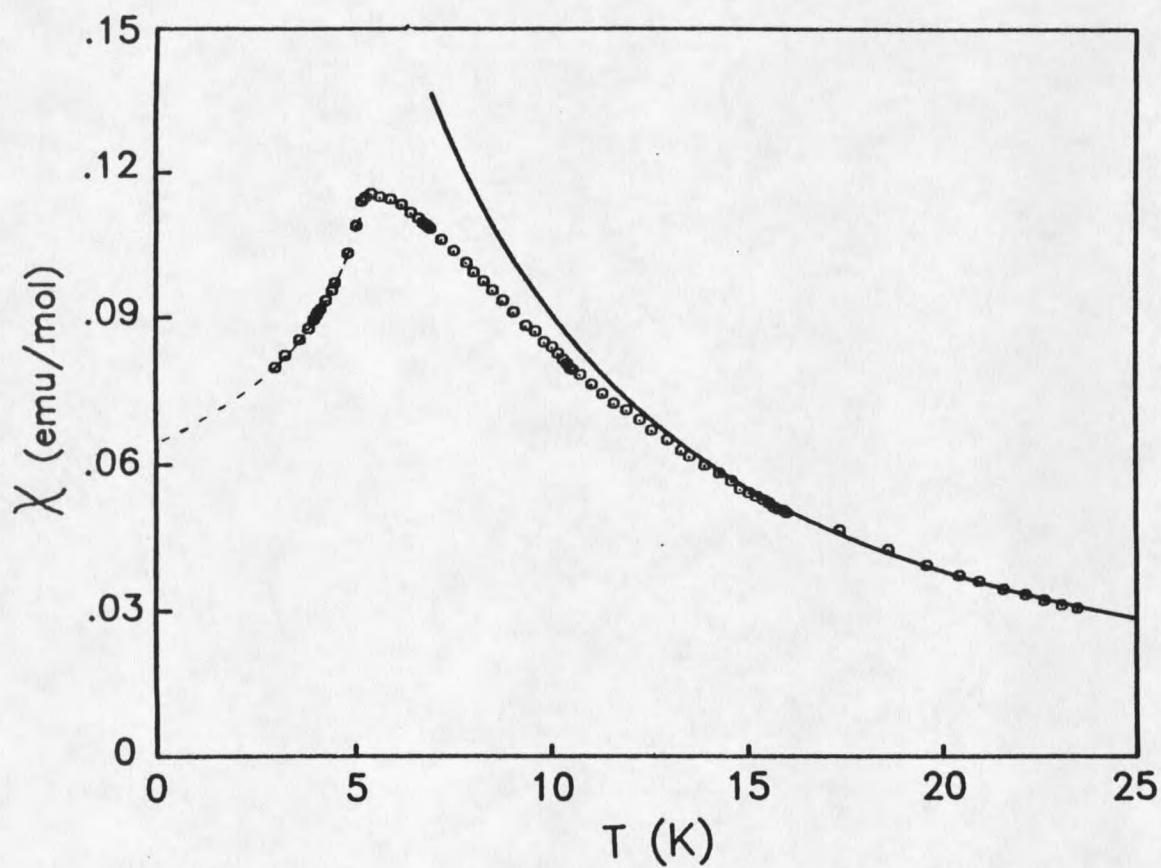


Figure 30. χ vs T data for $\text{CuCl}_2\cdot\text{DMSO}$ measured along the c -axis. Solid line is Takahashi's expression for $J/k=45\text{K}$ and $g=2.15$ with a mean field correction $zJ'/k=-2\text{K}$.

the high temperature data on a powdered sample to a Pade approximation of the high temperature expansion for a $S=1/2$, 1-D, Heisenberg system^[56]. The value $g = 2.15$ is reasonable because the angular dependence study of the EPR resonances on a single crystal in the ac-plane has been reported to give $g_{\max} = 2.211$ and $g_{\min} = 2.090$ with the value along the c-axis lying in between.^[57]

Zero field data are also plotted as χT vs T in Figure 31. Note that as the temperature is lowered, χT increases upward until near the temperature 13K and then decreases toward zero. This means that the dominant interaction is ferromagnetic above 13K and antiferromagnetic below this temperature and explains why the theoretical curve deviates from the data below this temperature in Figure 30.

In an attempt to understand the possible bound magnon effect on this compound we have tried to analyze the zero field data with the JB theory. However, due to the significant interchain interaction J' the actual one dimensional behavior is not so clear below 13K and for this reason we were unable to separate the bound magnon effect from the deviation due to the critical fluctuation.

Phase Diagram Along the c-axis

Figure 32 shows the corresponding ac susceptibility data at magnetic fields of 2000 Oe and 6000 Oe in the temperature region of $4.2\text{K} < T < 16\text{K}$. There is no significant change in the data above T_c compared to the zero field data. However, below T_c , there is a strong divergence in the susceptibility at 6000 Oe indicating a first order phase transition. In order to further observe the field dependence below T_c , we measured the susceptibility as a function of magnetic field at different constant temperatures (isothermal measurements). Figure 33 shows the in-phase signal at the temperature of 4.16K. This shows a sharp peak near 5.5 kOe, and above 5.5 kOe the susceptibility

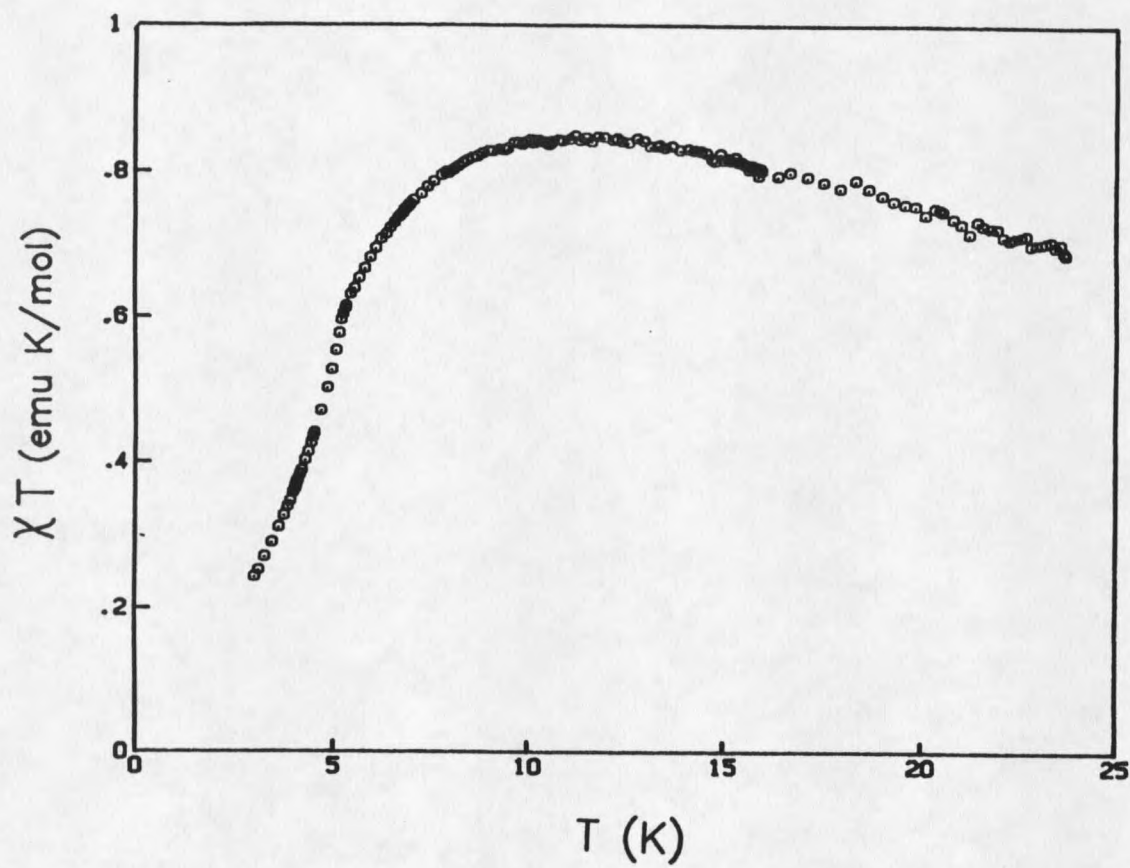


Figure 31. Data shown in the last figure plotted as χT vs T .

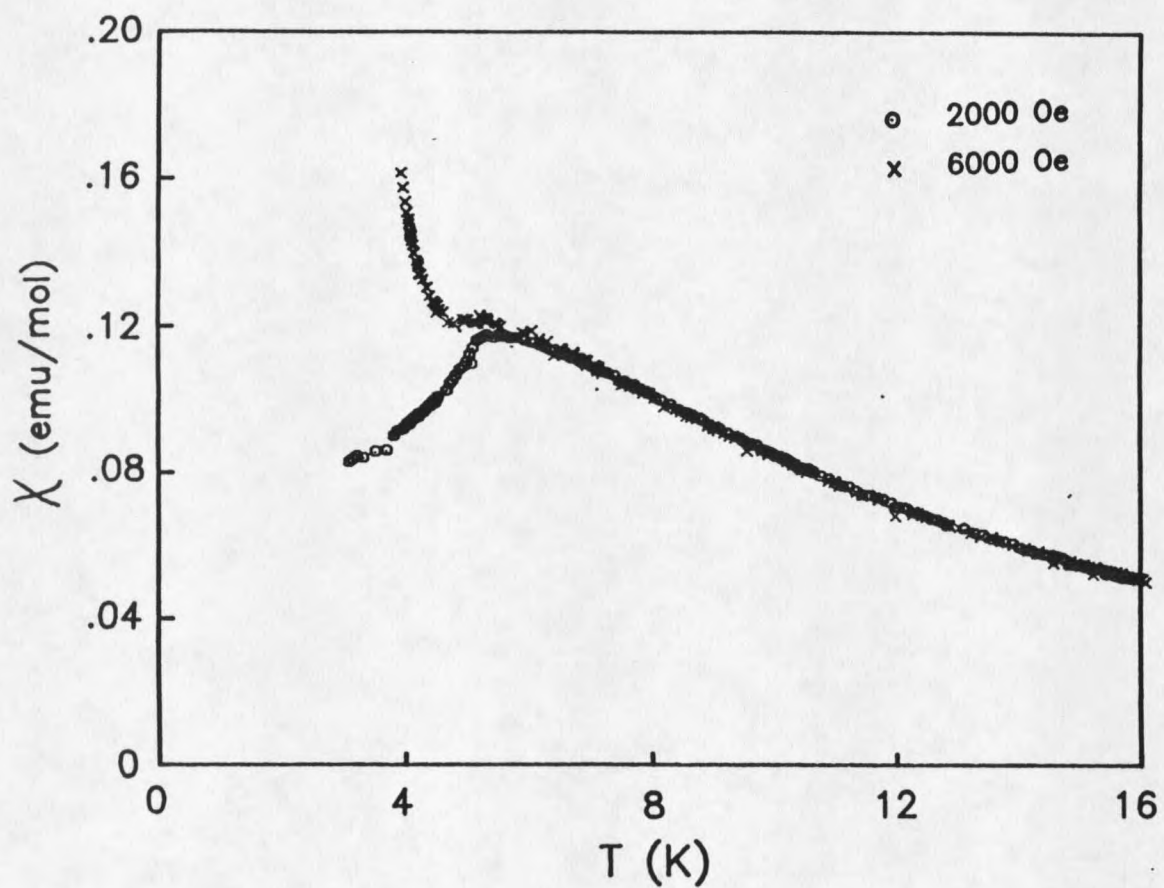


Figure 32. χ vs T data for $\text{CuCl}_2 \cdot \text{DMSO}$ measured along the c-axis at fields of 2000 and 6000 Oe.

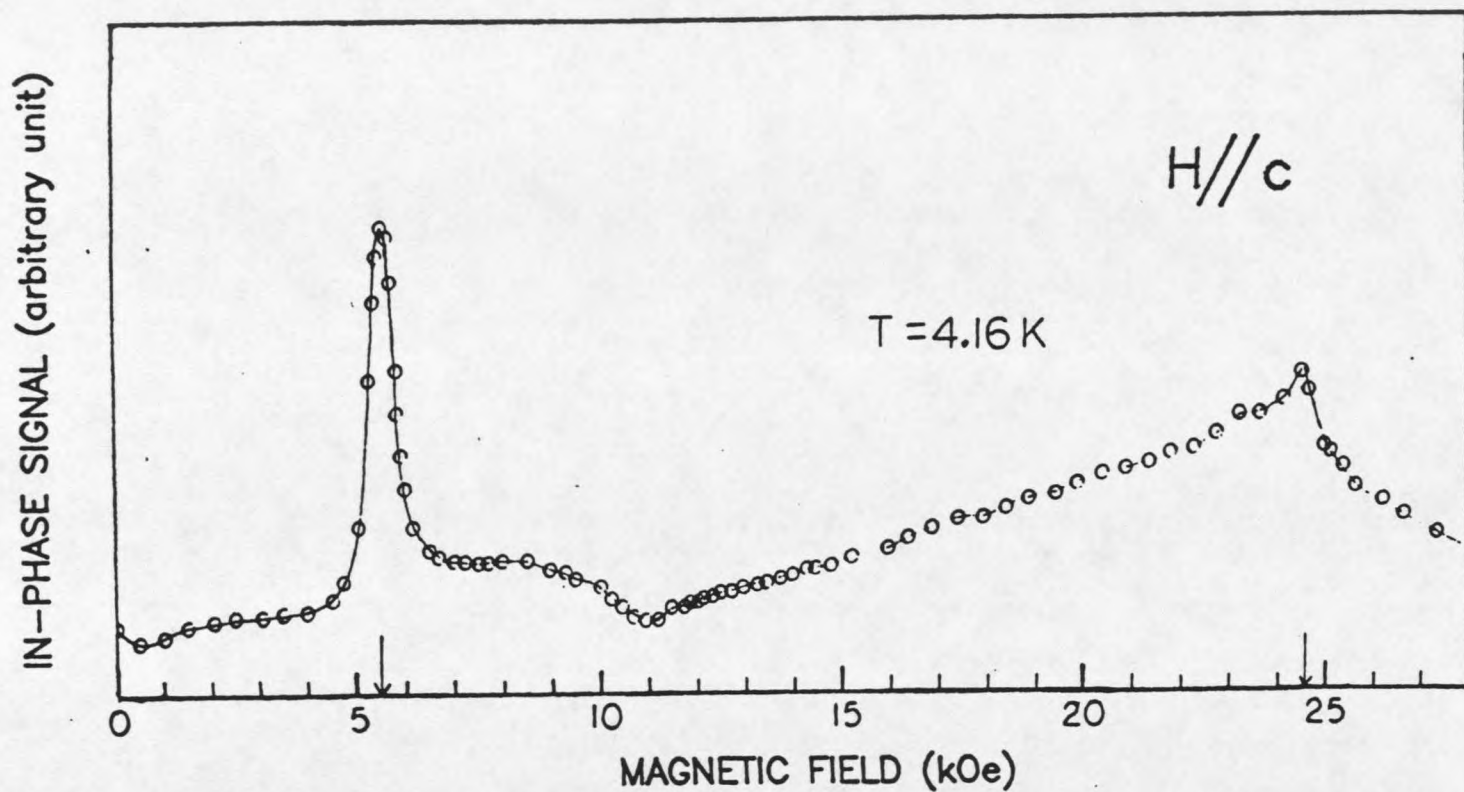


Figure 33. Inphase signal vs Magnetic field for CuCl₂.DMSO at 4.16K. H is applied parallel to the c-axis.

decreases and then increases almost linearly until there is a sudden drop in χ at 24.5 kOe.

A qualitative explanation can be given by considering a two-sublattice model. First consider the expected behavior along the easy axis for a nearly Heisenberg antiferromagnetic system. Any anisotropy K , causes the spins to establish a preferred (easy) axis in the absence of an external field. In the presence of a small applied field the ordering is the expected antiferromagnetic (AF) phase. However, when the field is increased to a certain value along the "easy-axis", the spins will suddenly flop (SF) to a position where they are nearly perpendicular to the applied field as well as the easy axis, although still nearly oppositely aligned to one another. In so doing, they gain the magnetic energy $\frac{1}{2}(\chi_{\perp} - \chi_{\parallel})H^2$, where $\chi_{\parallel}$ and $\chi_{\perp}$ are the susceptibilities corresponding to the parallel and perpendicular orientation of the spins with respect to the field. The critical field, H_1 , at which the spin flop occurs is then given by:

$$K = \frac{1}{2}(\chi_{\perp} - \chi_{\parallel})H_1^2$$

A further increase of field will gradually rotate the sublattice moments, until at the critical field H_c their mean direction is parallel to the field and the paramagnetic phase is entered. At this point on the SF-P boundary, the antiferromagnetic interaction is balanced by the applied field and anisotropy field.^[58]

The expected ideal behavior (at $T=0$) of magnetization and ac susceptibility based on this model are sketched in Figure 34.^[58] Note that there is a discontinuity in the magnetization (first order transition) at the spin-flop transition (H_1) and there is a discontinuity in the susceptibility (second order) at the SF-P transition (H_2). Also note that the susceptibility is constant in between these region. Comparing this easy axis behavior with our data, a generally similar behavior can be seen except that the

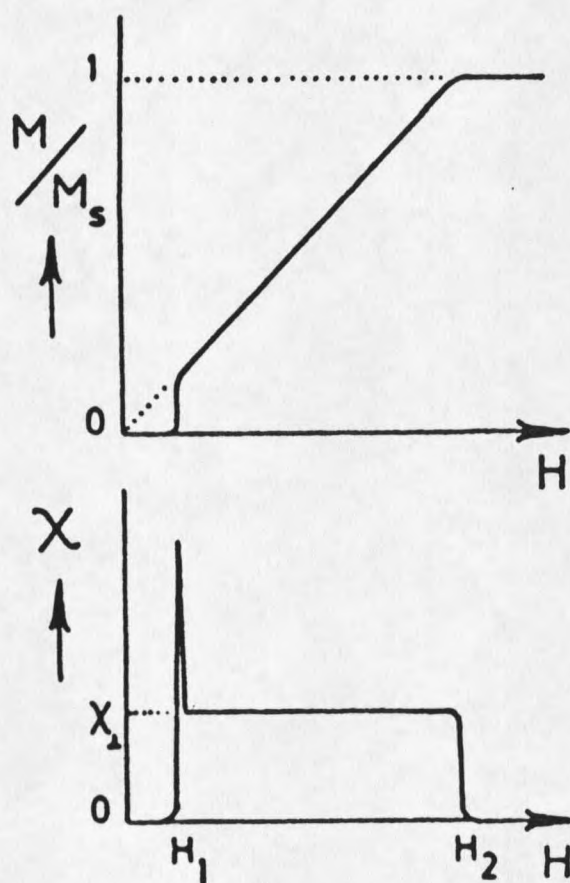


Figure 34. Expected behavior of Magnetization and Susceptibility of a weakly anisotropic Heisenberg antiferromagnet along the easy axis.

susceptibility is not constant in the region between the critical fields. Also the first peak is not very sharp as expected for a first order transition. This is probably because the applied field is not exactly along the easy axis. Here we point out the work by Chepurmykh^[59] and Rohrer and Thomas^[60] who studied the angular dependence of SF transition on antiferromagnets. They showed that at $T=0K$, a first order spin-flop transition exists only for angles between the easy axis and the applied field less than a critical angle which is of the order anisotropy/exchange. For angles larger than this critical angle the sublattice magnetization turn continuously from an antiferromagnetic-like configuration into a spin-flop-like configuration. We interpret the first peak in the susceptibility data as an indication of this continuous transition from AF-like configuration to SF like configuration, and the sudden drop at the higher field as an indication for the spin flop state to paramagnetic state transition.

Figure 35 shows the in-phase signal as a function of field at different but constant temperatures. The sharpness of the peaks corresponding to the SF phase get smaller as the temperature approaches the critical temperature $T_c(H=0)=5K$, and disappears above 5K as expected. The discontinuity corresponding to the SF-P phase transition also slowly disappears as the temperature approaches T_c . The phase diagram obtained from the critical fields is shown in Figure 36. It seems that the AF-SF boundary is almost linear in the temperature region shown. It appears that the bicritical point is near 4.9K. However, more measurements near this temperature are necessary to further confirm this tricritical point. Also note in Figures 35 and 36, there is an indication for some kind of transition near 11 kOe. This appears constantly even above T_c . The origin of this transition is not clearly understood.

In summary, we have measured the ac susceptibility along the chain axis. The zero field results suggests that the 1-D behavior is dominant only above 13K; the data fit

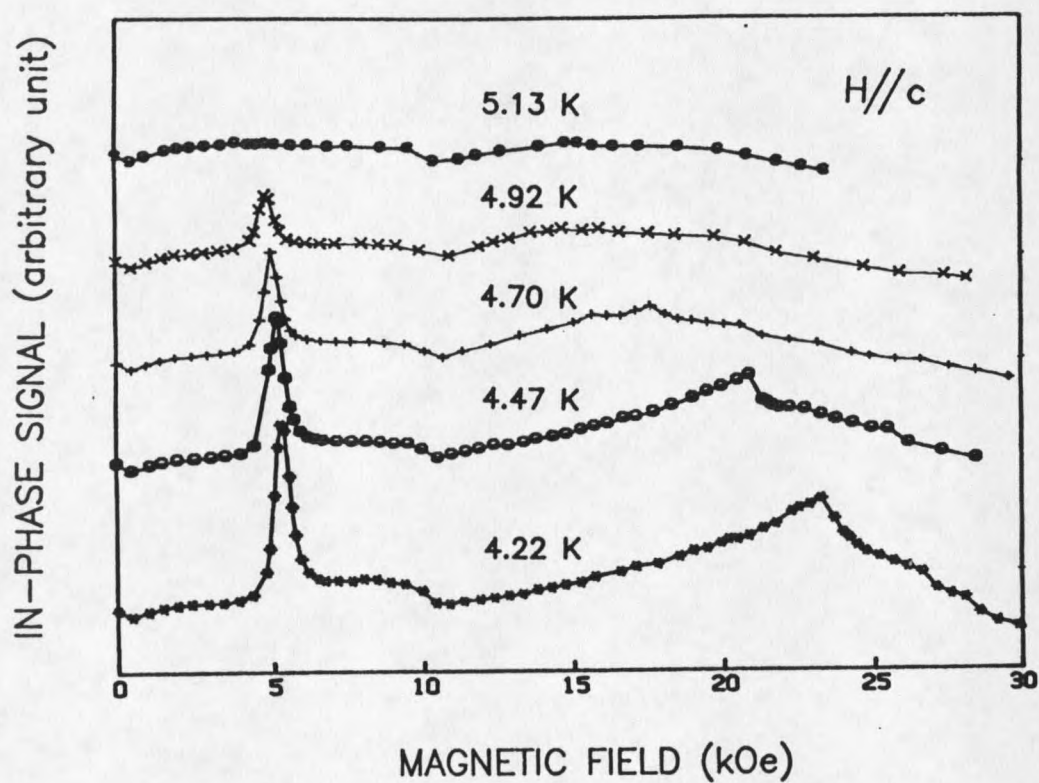


Figure 35. In-Phase signal vs Magnetic field for $\text{CuCl}_2 \cdot \text{DMSO}$ at different temperatures.

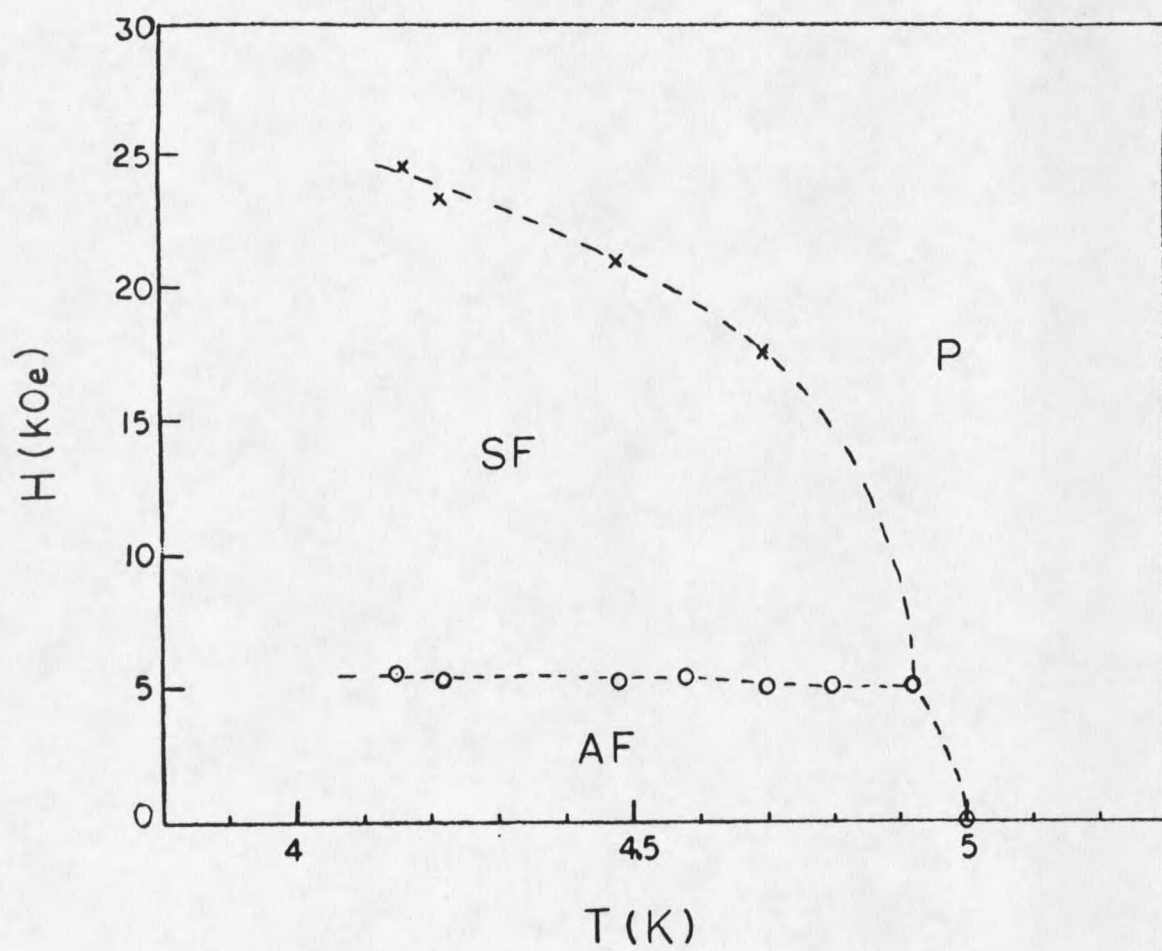


Figure 36. Magnetic phase diagram for $\text{CuCl}_2 \cdot \text{DMSO}$ for fields parallel to the c-axis.

Takahashi and Yamada isotropic Heisenberg expression. Compared to the other 1-D compounds that we have studied (TMCuC, FeTAC), this compound shows significant 3-D fluctuations due to the interchain exchange J' , and for this reason the bound magnon effect, which is definitely a 1-D effect, cannot be clearly identified at low temperatures. From the isothermal measurements as a function of field at different temperatures ($T < T_c$), we were able to map the phase boundaries, especially the SF-P boundary at higher fields which had not been accessible to the maximum field (9.5 kOe) in the magnetization measurements reported by Landee *et al.*^[53]

CHAPTER 5

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

The ac susceptibility data for FeTAC and TMCuC show general agreement with the Johnson and Bonner theory and confirm the existence of bound magnons in the Ising and Heisenberg systems. Further, from the size of the magnon susceptibility shown in Figures 19 & 29 and the contribution from the JB bound magnon term to the data, it is clear that the magnon theory, based on single spin excitations, cannot possibly account for the observed behavior, and that bound magnon excitations are predominant in determining the low temperature susceptibility.

The observation of the broad signal in the low temperature EPR spectrum clearly indicates the 2-fold spin cluster resonance in FeTAC and further confirms the existence of bound magnons in the Ising system. This is the first observation of spin cluster resonance above T_c . It would be interesting to extend these measurements to a different microwave frequency, perhaps higher than 9.2 GHz, and also at temperatures below the long range ordering temperature $T_c=3.1K$.

In $CuCl_2 \cdot DMSO$ because it significantly deviates from the ideal one-dimensional behavior, the bound magnon effect cannot be clearly identified. However the existence of strong 3-D fluctuations above T_c make this compound an interesting system for further study. For example one could extend the ac susceptibility measurements to a wide range

of frequencies, this would give a better understanding of the spin cluster dynamics involved. Another possible candidate for bound magnon analysis is the recently discovered compound pyrrolidinium CuCl_3 . Our preliminary magnetization data indicate this compound to behave as a good Heisenberg, $S=1/2$, chain, above the Neel temperature 4.8K, and it appears to be one of the strongest quasi-one-dimensional ferromagnets ($J=56\text{K}$, $J'/J = -10^{-2}$).

From a theoretical point of view, the one-dimensional, $S=1/2$, isotropic Heisenberg model still remains to be solved for finite magnetic fields; the method could perhaps be an extension of the work of Takahashi or of Schlottmann. Although JB theory allows one to investigate the effect of bound magnons of the $S=1/2$, one-dimensional Ising-Heisenberg system, as far as we know, no attempt has been made in the development to include the effect of spin canting, out of plane anisotropy or other terms in a realistic Hamiltonian. Although, bound magnons in a $S=1/2$ system are the quantum analogue of the soliton-antisoliton pairs in the classical sine-Gordon chains, how the classical soliton is related to Bethe-Ansatz is not fully elucidated.

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