Magnetic phase diagram of the two-dimensional Heisenberg spin one-half canted antiferromagnet ethyl-ammonium tetrabromocuprate(II)

by Yadollah Hassani

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Physics

Montana State University

Abstract:
The magnetic susceptibility of (C2H5NH3)2CuBr4 has been studied as a function of an applied field (0-5500 Oe) and of temperature (1.85-120 K). The data show the antiferromagnetic ordering along b to occur at Tc =10.78 K, but the moments are canted toward the c-axis. The data in the paramagnetic region is fitted to the simple quadratic Heisenberg model. From this fit values for the exchange energy J/k = 18.5 K, Curie constant, C = .45 emu-K/mole, Curie-Weiss temperature,6 =37 K and J/kT. = 1.72 have been obtained. The anisotropic exchange field, Hd =2600 t)e, the inter-layer exchange field, Haf =300 Ge and out of layer anisotropy field, Ha =1550 Ge are obtained by means of mean field calculation. The magnetic phase diagrams have been constructed along a, b, and c axes by means of susceptibility versus temperature and magnetization curves. We find the bieritical point at 10.74 K and 60 tie, spin twist field, Hst =80 Oe, and derive the angle between the c- axis and the moment direction to be 53.2 degrees.

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Yadollah Hassani

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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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES-Continued

LIST OF FIGURES-Continued

LIST OF FIGURES-Continued

ABSTRACT

The magnetic susceptibility of $(C_2H_5NH_3)_2CuBr_4$ has been studied as a function of an applied field (0-5500 Oe) and of temperature (1.85-120 K). The data show the antiferromagnetic ordering along b to occur at T_c =10.78 K, but the moments are canted toward the c-axis. The data in the paramagnetic region is fitted to the simple quadratic Heisenberg model. From this fit values for the exchange energy J/k = 18.5 K, Curie constant, C = .45 emu-K/mole, Curie-Weiss temperature,θ =37 K and J/kT_c = 1.72 have been obtained. The anisotropic exchange field, H_d =2600 Oe, the inter-layer exchange field, H_{AF} =300 Oe and out of layer anisotropy field, H_a =1550 Oe are obtained by means of mean field calculation. The magnetic phase diagrams have been constructed along a, b, and c axes by means of susceptibility versus temperature and magnetization curves. We find the bicritical point at 10.74 K and 60 Oe, spin twist field, H_{ST} =80 Oe, and derive the angle between the c-axis and the moment direction to be 53.2 degrees.

CHAPTER ONE

INTRODUCTION

The purpose of this investigation is to analyze the magnetic properties of $[C_2H_5NH_3]_2CuBr_4$ and construct magnetic phase diagrams along all three axes. $[C_2H_5NH_3]_2CuBr_4$ is a member of the $[C_nH_{2n+1}NH_3]_2CuX_4$ family, hereafter abbreviated as C_nX where X represents a Cl or Br atom and n varies from 1 to 10. C_nX compounds have attracted special attention because they can serve as an approximation to the ideal two dimensional spin 1/2 Heisenberg ferromagnets. In the two dimensional Heisenberg S = 1/2 ideal system, exchange interactions are confined to two dimensions, and long range order above zero K cannot be sustained. However, C_nX compounds order at a temperature $[T_c]$ between 7 K to 16 K. This series of compounds deviate from the ideal system due to the presence of a weak anisotropy and coupling in the third dimension, which in turn causes the long range ordering at a temperature higher than zero K.

Yoshio reported this compound to be a weak ferromagnet. Weak ferromagnetism occurs mainly in antiferromagnetic crystals such as α-Fe_20_3, NiF_2, $MnCO_3$, and $CoCO_3$. The problem of weak ferromagnetism was first studied by Dzialoshinski [2] who contributed the weak ferromagnetism to an interaction of the form $d\circ[S_1XS_2]$. This term represents the antisymmetric part of the spin coupling. In contrast Yoshio claims that the source of the canting is symmetrical, i.e., of the

form $S_1 \circ K_s \circ S_2$. This discrepancy prompted us to do further investigation on this compound. Also, we have confusing ac susceptibility data.

Although the crystal structure of C_nX compounds are similar, the magnetic behaviors of the members of this family differ from one another. For instance, the ferromagnetic layers may couple antiferromagnetically as in C_2Cl [1]. In C_1Cl, the coupling between layers is ferromagnetic [1]. On the other hand, in C_3Br a weak ferromagnetic moment appears along the c-axis [1]. The ferromagnetic intra-layer exchange constant, J/k, varies from 15.4 K for C_4Cl to 22 K for C_5Br [3]. Inter-layer interaction, J'/k, is very weak compared to that of in-plane interaction, $J'/J=1.7\times10^{-3}$ for C_1Br and $J'/J=10^{-5}$ for $C_{10}Cl$ [4]. For C_2Br, different values of J'/J have been reported. Yoshio reports $Z'|J'|/ZJ=7\times10^{-4}$ where Z is the number of nearest neighbors in the plane and Z' is the number of nearest neighbors in the next plane. If we take Z=4 and $Z'=8$ then we get $J'/J=3.5\times10^{-4}$. L. de Jongh gives a value of 1.7×10^{-3} which is about 4.8 times larger than Yoshio's J'/J value. Although inter-layer exchange coupling is small, it plays a major role in the magnetic behavior of C_nX compounds below the transition temperature. The anisotropy field within the layer is of the order of 10^{-5} to 10^{-4} of the ferromagnetic exchange field. The out-of-plane anisotropy remains the same for all compounds and is of order of 10^{-3} of the ferromagnetic exchange field [4].

The crystal structure of the known members of the C_nX family is orthorhombic [4], which means the axes of a unit cell are perpendicular and also $a\neq b\neq c$. In this series of compounds a and b are nearly equal,

but the distance between the planes increases as n is increased. Table I is taken from reference [5] where d_1 is the distance between copper ions within a layer and d_2 is the distance between nearest neighbor copper ions in different layers. It also shows lattice constants up to n=6. For C_2Br a transition of 10.72 K is given. We measured the transition temperature to be 10.75 ± 0.05 K . Professor K. E. Emerson, of Montana State University, has measured the lattice constants of C_2Br to be a=7.9525, b=7.7187, and c=21.4191 Angstrom which is in agreement with Table 1.

The second chapter of this thesis is concerned with the theoretical behavior of antiferromagnets. Chapter Three deals with methodology, and includes a discussion of susceptibility versus temperature and field. In Chapter Four, mean field calculations are carried out and numerical values for magnetic parameters are given. Finally, in Chapter Five, magnetic phase diagrams along three axis are constructed and discussed.

Table 1: Curie temperature and lattice constants

Compound	T_c(K)	a_o(Å)	b_o(Å)	c_o(Å)	d_1(Å)	d_2(Å)
C_1Cl	8.9	7.54	7.3	18.55	5.24	9.99
C_2Cl	10.2	7.47	7.35	21.18	5.24	11.22
C_3Cl	7.61	7.65	7.33	24.66	5.29	12.89
C_4Cl	7.27					
C_5Cl	7.25	7.51	7.38	34.81	5.26	17.8
C_6Cl	7.65					
C_2Br	10.72	7.95	7.72	21.5	5.54	11.44
C_3Br	10.41	8.00	7.69	24.32	5.54	12.78

CHAPTER TWO

THEORETICAL BEHAVIOR OF ANTIFERROMAGNETS

Susceptibility as a Function of Temperature

An antiferromagnet consists of two or more magnetic sublattices. The simplest antiferromagnetic arrangement is one in which the magnetic atoms can be subdivided into two sublattices, A and B, so that moments belonging to sublattice A point in one direction, and those belonging to sublattice B point in the opposite direction. The magnetic interaction between the sublattices is such that, below the Neel temperature [T_N], spins on the sublattice A point in a positive direction and those of sublattice B point in a negative direction, leading to zero net moment. The direction of the magnetization of each sublattice below the Neel temperature will be along the direction of the anisotropy field. This is called easy direction or easy axis.

Cooling a paramagnet in zero applied field leads to a transition from the paramagnetic to antiferromagnetic state at the Neel temperature. Above the Neel temperature, the system behaves as a paramagnetic system and obeys the Curie-Weiss law:

$$\chi=C/(T-\theta)$$

where C and θ are called Curie constant and Curie temperature, respectively. The susceptibility below the Neel temperature along the

easy axis decreases reaching a finite value at T=0. This is illustrated in Figure 1.

In cooling a paramagnetic system, if a constant external field is applied normal to the easy axis, the applied field will produce a torque that tends to rotate the sublattice magnetization. The internal field will oppose this rotation. One can show, by molecular field calculation, that the susceptibility below the Neel temperature remains constant and assumes a value of C/2 (see Figure 2).

On the other hand, if the external field is applied parallel to the easy axis, the susceptibility decreases below the Neel temperature and goes to zero at T=0, as shown in Figure 2. This is because there is a strong interaction between the moments of the two sublattices and a relatively small applied field cannot turn over the moments of the negative sublattice to the direction of the field (Figure 2).

In a powder sample in which the easy directions are distributed at random, the susceptibility is given by

$$\chi_{pow} = (1/3)\,\chi_{pa} + (2/3)\,\chi_{pe}$$

where χ_{pa} and χ_{pe} denote the parallel and perpendicular susceptibility, respectively, as shown in Figure 2.

Magnetization as a Function of Field

A magnetization curve [M vs H] yields an important feature of a magnetic system, the strength of the anisotropy field. For an antiferromagnet, we can consider two cases: field applied 1] normal to the easy axis and 2] parallel to it.

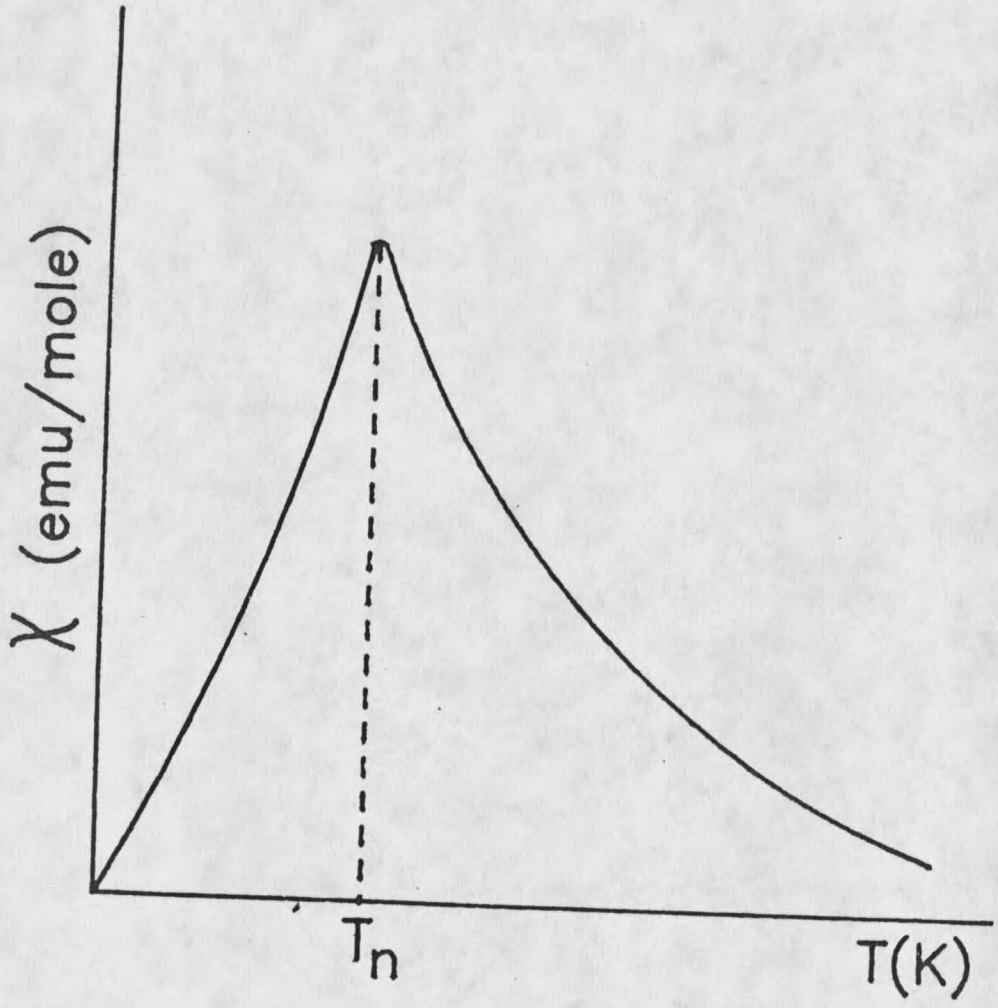

Figure 1. The magnetic susceptibility of an antiferromagnet at zero field

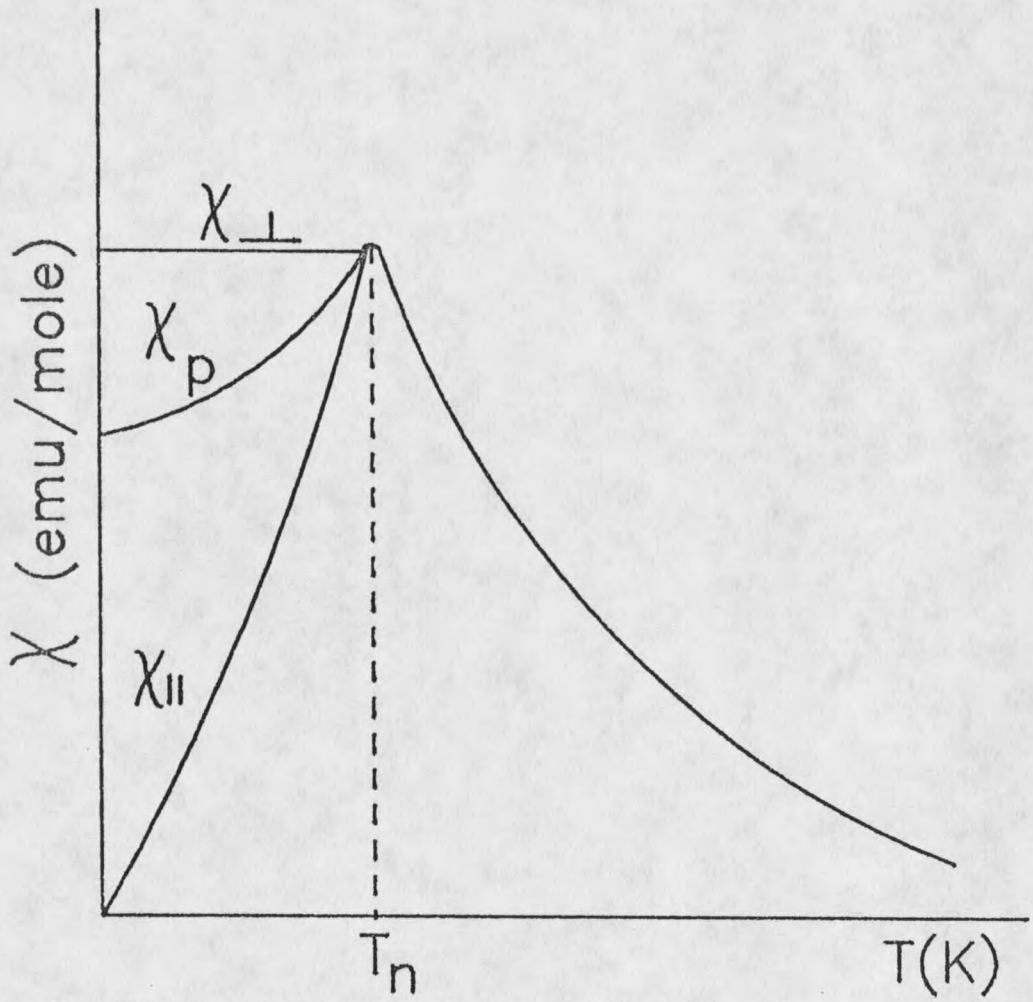

Figure 2. Thermal variation of molar susceptibility of an antiferromagnetic in the presence of relatively weak field

1] Field normal to easy axis: an increasing applied field, H, will turn each sublattice magnetization away from the easy axis and tends to align it in the direction of the applied field. As field is increased, magnetization will increase linearly until saturation is achieved. This gives the magnetization versus field curve shown in Figure 3.

2] Field parallel to easy axis: for a field applied in the direction of the easy axis, the applied field will be resisted by the anisotropy field until the applied field equals that of the anisotropy field. This field is called spin-flop field. At the spin-flop field two sublattice magnetization will reorient themselves such that they are perpendicular to the direction of the applied field. As the field is increased further, magnetization will increase linearly as a function of the applied field until saturation is acheived. This is shown in Figure 4.

We will show that, below some critical temperature, an antiferromagnetic ordering develops in C_2Br. In contrast to the usual antiferromagnets, the magnetization vectors of the sublattices are not exactly antiparallel to each other, but are inclined at some angle. In C_2Br spin-flop does not occur. However, a spin rearrangement occurs, which we will call a spin-twist transition.

Magnetic Phase Diagram

A magnetic phase diagram [H_a vs T] can be constructed for an ordered system to illustrate the phases that occur. A hypothetical phase diagram for an antiferromagnet when small anisotropy with the external field applied parallel to the easy axis is shown in Figure 5.

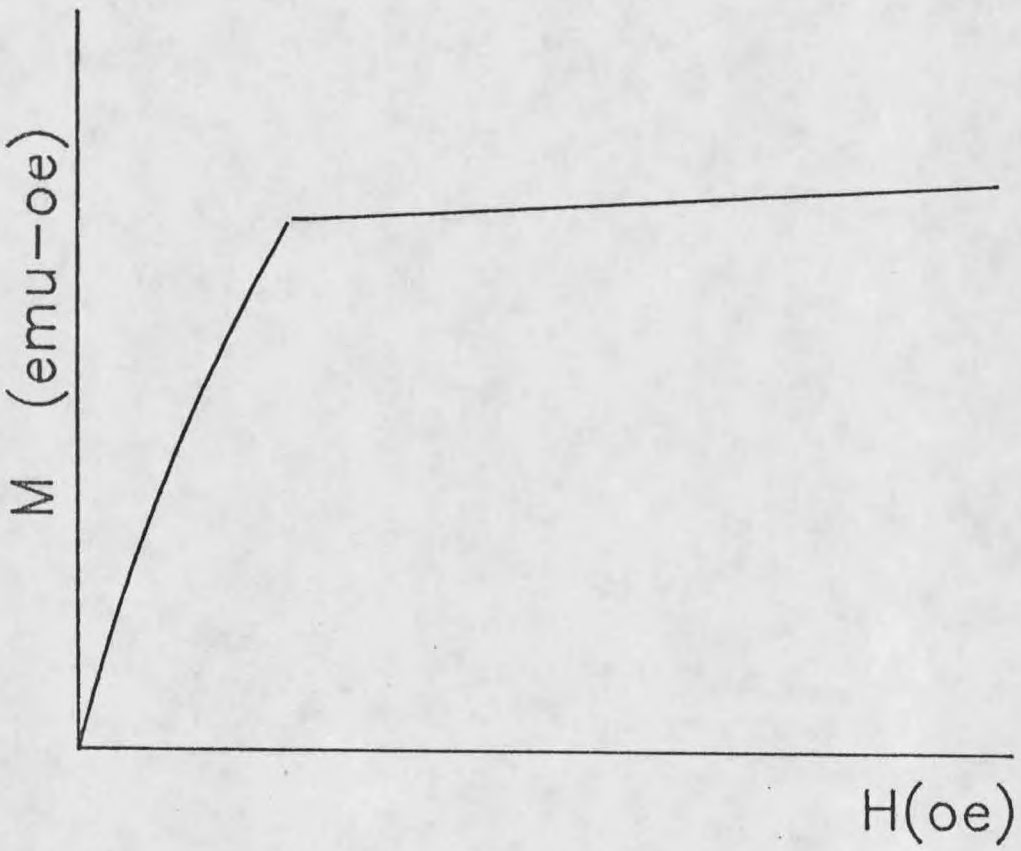

Figure 3. Magnetization versus field. Field is applied perpendicular to the easy axis

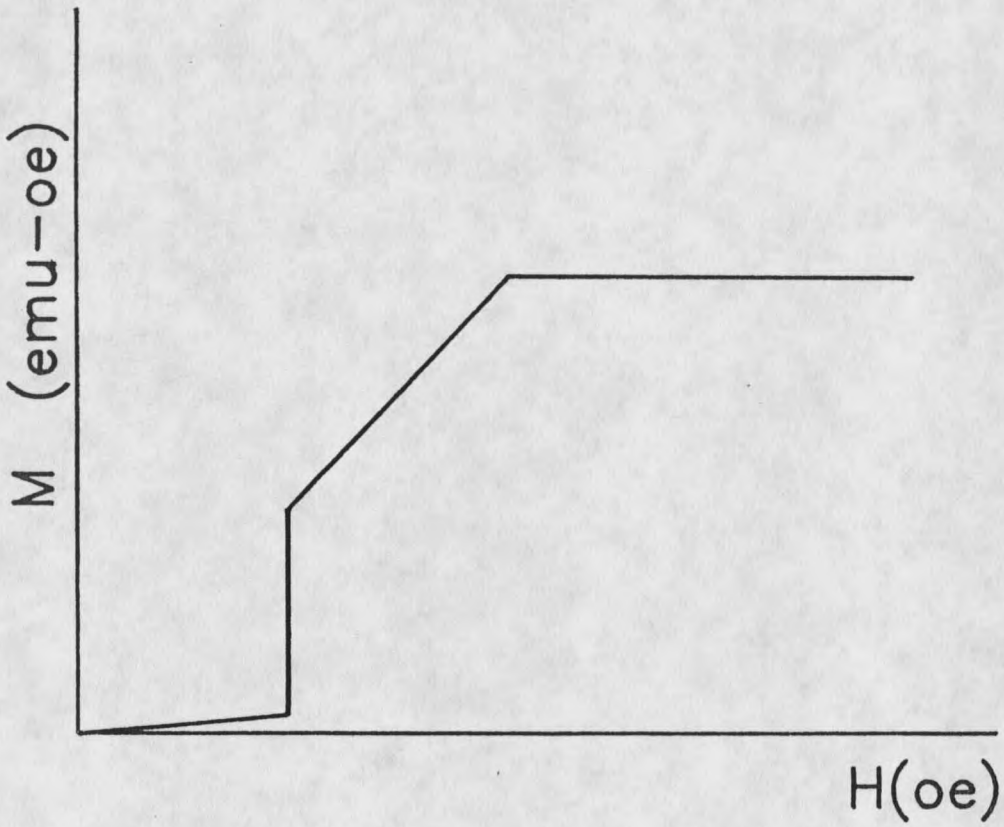

Figure 4. Magnetization versus field. Field is applied parallel to the easy axis

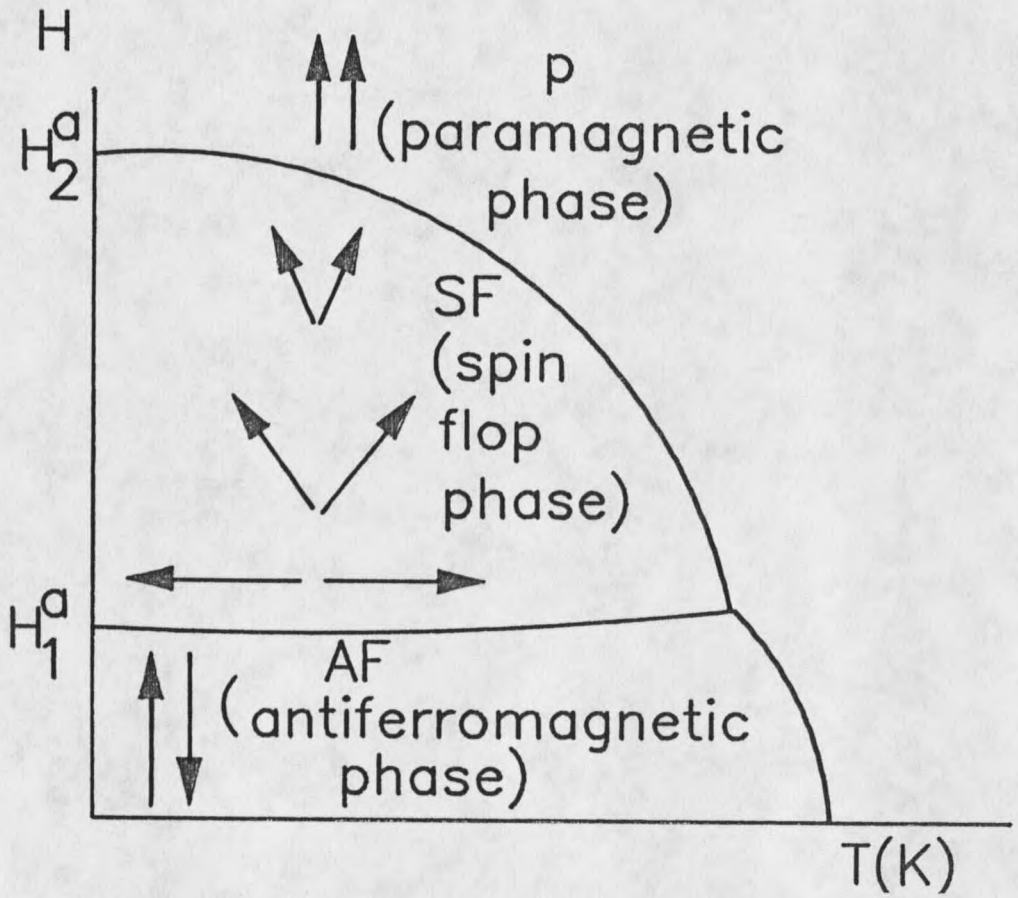

Figure 5. Phase diagram for an antiferromagnet with small anisotropy. The external field is applied parallel to the easy axis

This figure illustrates three distinct phase boundaries. These are: 1] paramagnetic [P] to antiferromagnetic [AF]; 2] AF to spin-flop [SF]; and 3] SF to P phase boundaries. When a field is applied along the easy axis of an antiferromagnet, a competition is set up between the applied field and the internal field, causing $T_c[H_a]$ to drop to a lower value as H_a increases. This is a second order phase transition and forms the P-AF phase boundary.

If an increasing field is applied, at a constant temperature below the Neel temperature, along the easy axis of an antifeorrmagnet, nothing will happen until the applied field becomes equal to that of anisotropy field. When the applied field slightly exceeds the anistropy field, the moments flop [nearly] perpendicular to the direction of the field. The field at which moments flop, is called spin-flop field. The transition is first order and this is a thermodynamically favored state. This forms the AF-SF phase boundary. A second order transition occurs when the moments line up with the field and the system enters into a paramagnetic state [SF-P transition].

Next we will drive the zero-T critical field by the method of mean field calculation and follow closely the format given by Drumheller, Rafaelle, and Baldwin (6).

The spin-Hamiltonian for a two-sublattice antiferromagnet can be written

$$H=-g\mu_B H\cdot S_i+2J\sum S_i\cdot S_j+LS_{iz}^2 . \qquad (1)$$

The first term is the Zeeman term. The second term represents the antiferromagnetic interaction between S_i and S_j. The exchange energy,

J, is assumed to be positive. The third term indicates the z-axis is the hard axis. We will subdivide the lattice of magnetic atoms into two sublattices, A and B, such that sublattices A and B point in opposite directions. According to the molecular field theory all magnetic atoms are identical and equivalent and S_k can be replaced by its average value <S>. Then the energy of Equation (1) can be written:

$$E = - (1/2)\, g\mu_B H\cdot\langle S_A\rangle - (1/2) g\mu_B H\cdot\langle S_B\rangle + Jn\langle S_A\rangle\cdot\langle S_B\rangle + L\langle S_z^2\rangle \qquad (2)$$

where n is the number of the nearest neighbor ions. We will use the coordinate system shown in Figure 6. The angle between sublattice spins and the hard axis (z-axis) is defined as θ. Energy for the AF phase, from Equation (2) is

$$E_{AF} = - JnS^2, \qquad (3)$$

For simplicity, we have written S for <S>. For the spin flop phase, Equation (2) becomes

$$E_{SF} = - g\mu_B HS \sin\theta - JnS^2 \cos 2\theta + LS^2 \cos_2\theta \qquad (4)$$

since E_{SF} is a function of θ,it can be minimized by setting $dE/d\theta = 0$. This gives

$$\sin\theta = g\mu_B HS/(4JnS^2 - 2LS^2). \qquad (5)$$

From Equation (5) cosθ and cos2θ can be found. Substituting these into Equation (4) will result in

$$E_{SF} =[-(g\mu_B HS)^2-8(JnS^2)^2-4(LS^2)^2+12(LS^2)(JnS^2)]/4(2JnS_2-LS^2) \qquad (6)$$

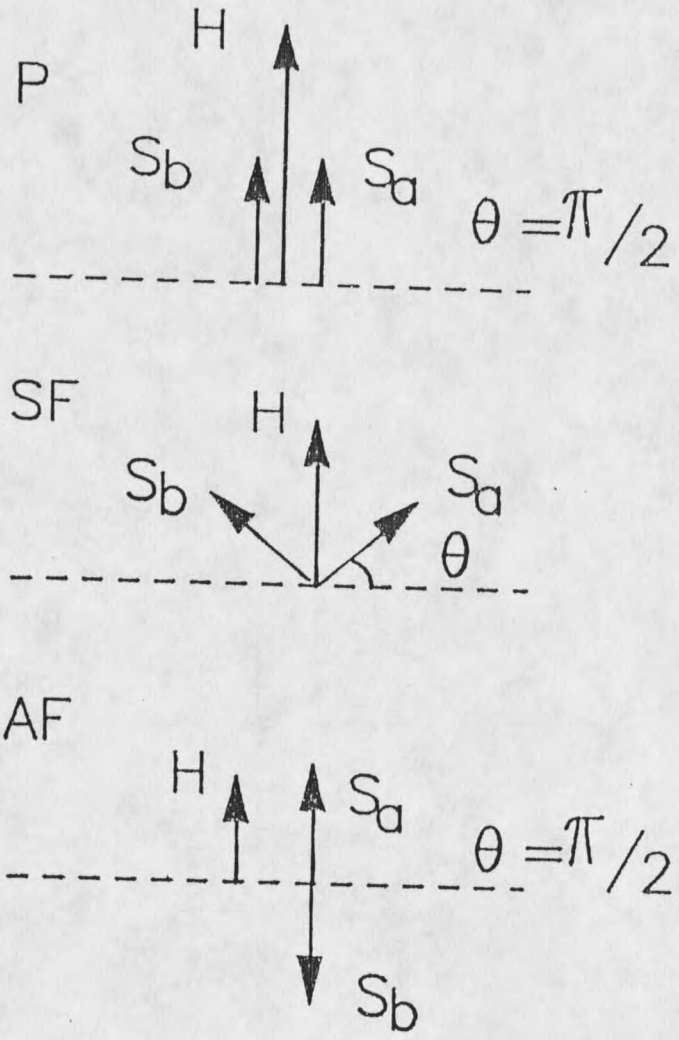

Figure 6. The coordinate system, discussed on page 14

At the spin-flop transition, Equations (6) and (3) are equal. This gives

$$(g\mu_B HS)^2 = 4[(2LS^2)(JnS^2) - (LS^2)^2], \tag{7}$$

dividing Equation (7)] by $(g\mu_B s)^2$, results in

$$H^2 = 2(2nJS/g\mu_B)\,(2LS/g\mu_B) - (2LS/g\mu_B)^2\,. \tag{8}$$

We define $H_{AF} = (2nJ/g\mu_B)$ and $H_A = (2LS/g\mu_B)$ and relabel H as H_{SF}, then Equation (8) becomes

$$H_{SF} = [2H_{AF}H_a - H_a{}^2]^{1/2}\,, \tag{9}$$

H_{SF} is the value of the antiferromagnetic to spin-flop transition field extrapolated to zero K. The field of the spin-flop to paramagnetic transition can be obtained by replacing θ by $\pi/2$ in Equation (5), this yields

$$H_c = 2H_{AF} - H_a\,. \tag{10}$$

These equations or appropriately similar ones will be used for our analysis in Chapter 5.

CHAPTER THREE

EXPERIMENTS

Sample Preparation

The $(C_2H_5NH_3)_2CuBr_4$ crystals were prepared by Professor K. E. Emerson of Montana State University. The ratio of the mole weight of $C_2H_5NH_3Br$ and $CuBr_2$ is two to one. Two parts of $C_2H_5NH_3Br$ and one part of $CuBr_2$ were dissolved in alcohol. The solution was filtered and put in a closed beaker in the presence of ether. By this method, good single crystals of fairly thin plates were obtained.

Crystal Structure

Although the crystal structure of $(C_2H_5NH_3)_2CuBr_4$ has not been solved in detail, dimensions of the unit cell and the distance between the copper-copper within the layer and between neighboring layers are known (Table 1). The crystal structure of known compounds of the $(C_nH_{2n+1}NH_3)_2CuX_4$ series are all orthorhombic with space group P_{bca}. These compounds consist of nearly isolated magnetic sheets of CuX_4 (X = Cl or Br), which are separated by two sheets of alkyl-ammonium groups. The cell constants a, b, and c for C_2Br are 7.9525, 7.7187, and 21.4191 Angstrom, respectively (7). Preliminary studies of this compound have shown that the unit cell is orthorhombic and the space group is P_{bca} (7).

The Vibrating Sample Magnetometer

Data were obtained using an EGG PAR Model 155 magnetometer. In addition to the magnetometer console and head, the system includes an electromagnet with field control and a cryostat with temperature control and measurement. The system is interfaced to an Apple II computer.

A schematic of the magnetometer head is shown in Figure 7 (8). It consists of the following: a mechanical vibrator, a long rod, a magnet, pick up coils, and a capacitor plate assembly. The sample is attached to the end of a long rod and placed between the pole faces of the magnet. The rod and the sample are vibrated perpendicular to the applied field by the mechanical vibrator at a frequency of 82.5 hertz. The magnetization of the sample induces a voltage in pick up coils placed on the magnet pole faces. The induced voltage has a frequency of 82.5 hertz and an amplitude proportional to the magnetization of the sample and to the amplitude of the vibration (9). The purpose of the capacitor is so that the detected voltage can be made independent of vibrational amplitude. A nickel standard is used to calibrate the magnetometer, since the saturation magnetization of nickel is known.

Temperatures over a range of 1.7 K to room temperature were controlled by both a current heater mounted below the sample and an adjustable gaseous flow rate. Temperatures at the lowest range were obtained by pumping on the sample chamber. The temperature was measured with a carbon glass resistor mounted directly above the