Magnetic phase diagram and spin glass behavior of (CH3)3NH(Co1-xNix)Cl3.2H2O.
by David Paul Raffaelle

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Physics
Montana State University
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Abstract:
The magnetic properties of the mixed system (CH3)3NH(Co1-xNix)Cl3 2H2O are reported. This system is a mixture of one dimensional, isomorphous antiferromagnets with competing orthogonal spin anisotropies. The magnetic phase diagram has been determined and a large region exhibiting spin glass behavior is found.
MAGNETIC PHASE DIAGRAM AND SPIN GLASS BEHAVIOR
OF \((\text{CH}_3)_3\text{NH}(\text{Co}_{1-x}\text{Ni}_x)\text{Cl}_3\cdot2\text{H}_2\text{O})\).

by
David Paul Raffaelle

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

MONTANA STATE UNIVERSITY
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December 1985
APPROVAL

of a thesis submitted by

David Paul Raffaelle

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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CHAPTER 1

Introduction

In this thesis a study is made of the magnetic properties of \((\text{CH}_3)_3\text{NH}(\text{Co}_{1-x}\text{Ni}_x)\text{Cl}_3 \cdot 2\text{H}_2\text{O}\). Of the pure constituents \((\text{CH}_3)_3\text{NH}\text{NiCl}_3 \cdot 2\text{H}_2\text{O}\) (TMANi) is a one dimensional XY like ferromagnet.\(^1\) \((\text{CH}_3)_3\text{NH}\text{CoCl}_3 \cdot 2\text{O}\) (TMACo) is a good realization of a one dimensional Ising system with ferromagnetic intrachain correlations.\(^2\) TMANi and TMACo are isomorphous with ordering temperatures of 3.6K and 4.13K respectively. In both systems chemical chains with strong ferromagnetic correlations occur along with crystallographic b axis. TMA \((\text{Co}_{1-x}\text{Ni}_x)\text{Cl}_3 \cdot 2\text{H}_2\text{O}\) is one dimensional in that the strong exchange is along the chain. However since the ordering owes to interchain coupling it is two dimensional in this case. In TMACo the spins align along the crystallographic c axis with a small net moment in a direction. In TMANi the z axis of the spin system is perpendicular to the chain axis.\(^1\) And in view of the experimental results, TMANi's spin system's easy axis is believed to lie in the a-b plane. The inherent randomness of the mixed system together with the frustration arising from competing interactions leads one to expect spin glass behavior. Indeed an unusual
magnetic phase diagram with an apparent spin glass region has been found. TMA(Co\textsubscript{1-x}Ni\textsubscript{x}) is one of the few examples of a non-metallic crystal with a spin glass phase. It is also a rare example of a "lower dimensional" magnet with a spin glass phase.

The second chapter of this thesis concerns itself with a general discussion of spin glasses. A short historical section is followed by descriptions of typical spin glass experiments and what they mean. Chapter three begins by describing the investigation into the magnetic and spin glass properties of TMA(Co\textsubscript{1-x}Ni\textsubscript{x}). Following that is a discussion of the experimental results and the spin glass behavior observed. Chapter four discusses the causes of the spin glass behavior in TMA(Co\textsubscript{1-x}Ni\textsubscript{x}). Finally a magnetic phase diagram is drawn and discussed.
CHAPTER 2

BACKGROUND

**Magnetic Interactions**

The term "magnetic interaction" is used to describe any dependence of the energy of a system on two or more magnetic moments. The most important contribution to this energy dependence is electrostatic and not magnetic in origin. "Magnetic" refers only to the effects of the interactions not their sources. These magnetic interactions are the cause of differences in energy of various electronic states. However, these energy differences are very small compared to the total energy of the system. Even using the exact Hamiltonian in real space coordinates usually does not give the desired energy difference precisely enough. To avoid this difficulty we replace the true Hamiltonian with a phenomenological spin Hamiltonian involving spin operators. This simplifies the problem of obtaining the energy levels of the system. The Heisenberg spin Hamiltonian for a two electron system is often given as

\[ H = -2JS_1 \cdot S_2 \]

where \( S_1 \) and \( S_2 \) are the vector spin operators for the two
electrons. Here $J = (1/2)(E_S - E_T)$ where $E_S$ is the energy of the singlet state and $E_T$ is the energy of the triplet state. This system will favor parallel spins if $J$ is positive and antiparallel spins if $J$ is negative. The energies of the singlet and triplet states are $(3/2)J$ and $-(1/2)J$ respectively.

The magnetic interaction just described is called the direct exchange because it comes from the direct Coulomb interaction among the electrons of the two ions. Because there are other sources of potential energy in a system the spin Hamiltonian is actually much more complicated in practice. The main additional terms come from the external fields, the spin orbit coupling and the crystal field. Introducing these terms, one can write the Hamiltonian as:

$$H = 2J_n \sum \hat{S}_n \cdot \hat{S}_{n+1} + \mu_B \sum \hat{S}_n \cdot \hat{g}_n \cdot \hat{S}_n + \sum \hat{S}_n \cdot \hat{D}_n \cdot \hat{S}_{n+1} + \sum \hat{S}_n \cdot \hat{D}_n \cdot \hat{S}_{n+1} + \sum \hat{D}_n \cdot \hat{S}_n \times \hat{S}_{n+1}$$

where the terms are the direct exchange interaction, the Zeeman interaction, the dipolar interaction, the anisotropic exchange interaction, and the antisymmetric exchange interaction respectively. Common limiting cases are the Heisenberg model ($J_x = J_y = J_z$), the $xy$ model ($J_x = J_y, J_z = 0$) and the Ising model ($J_x = J_y = 0$). For systems composed of arrays of chains the direct exchange interaction term is sometimes rewritten as:

$$H_{de} = -2J \sum \hat{S}_i \cdot \hat{S}_{i+1} - 2 \sum J'_{ik} \hat{S}_i \cdot \hat{S}_k - 2 \sum J''_{im} \hat{S}_i \cdot \hat{S}_m$$
where the sum over \( i \) is along the chain, the sum over \( i, k \) takes into account nearest neighbor chains and the sum over \( i, m \) takes into account next nearest neighbor chains.

If the exchange interaction along the chain is dominant and ferromagnetic then one dimensional ferromagnetic correlations will be produced along the chain. As the temperature is lowered these correlations will grow. For a true one dimensional, Heisenberg system long range order will not occur above \( T=0 \). But because of interactions between chains, long range order may occur at some finite temperature. Three different types of interchain interactions can all lead to ordering if we neglect the antisymmetric exchange. These three types are: 1) ferromagnetic interactions between all chains \( J', J'' > 0 \); 2) ferromagnetic interactions between nearest neighbor chains but antiferromagnetic interactions between next nearest neighbor chains \( J' > 0, J'' < 0 \); and 3) antiferromagnetic interactions between nearest neighbor chains \( J'' < 0 \).

The systems of interest in this thesis all have at least one antiferromagnetic component. Systems with antiferromagnetic components will usually exhibit either spin flop or metamagnetic behavior when an external field is applied. Nearly all systems will have an "easy" or preferred direction along which the spins will tend to align. At some critical value an external magnetic field
applied along the easy axis of a metamagnet will break up the antiferromagnetic ordering. When this happens a first order phase transition to a paramagnetic state occurs. On the other hand in spin flop transitions it is the anisotropy not the antiferromagnetic exchange which is crucial. If a small external field is applied along the easy axis and then increased, a point will be reached where it is more energetically favorable for the spins to be aligned perpendicular rather than parallel to the easy axis. At this point the system undergoes a first order transition to the spin flop phase. If the external field is increased further the system will undergo a second order transition to a paramagnetic state.

In systems which have antisymmetric exchange there can be canted spin arrangements. For example, in an antiferromagnetic system where the spins on two different sublattices are canted each sublattice will have a component of magnetization in a particular direction. This may lead to a bulk magnetization or weak ferromagnetism. The canting may also be such that magnetization of the sublattices cancel each other in which case one has hidden canting.

Spin Glasses

As can be seen from the above discussion, magnetism comes in many forms. Over the last fifteen years another
distinct magnetic state known as the "spin glass" state has been recognized. The term "spin glass" was coined originally by B. R. Coles of Imperial College, London. The analogy between magnetic materials containing magnetic moments or spins and ordinary glasses comes from the apparent viscosity in the magnetization which seems to flow after a change in the applied field. Spin glass behavior was originally observed in alloys consisting of transition metal impurities in noble metal matrices. In 1972 V. Cannella and J. A. Mydosh found a sharp cusp in the a.c. susceptibility of such an alloy. This discovery sparked much interest in the spin glass problem because it supported the idea that a thermodynamic phase transition was occurring. This was supported by C. E. Violet and R. J. Borg who, using Mossbauer experiments, found that the spins were freezing at this same temperature. However other experiments such as the specific heat and resistivity showed no anomaly at some critical temperature. Thus these experiments indicate that there is no true transition taking place. In the 1970's spin glass behavior was found in many more compounds such as rare earth impurities and amorphous materials. In the last five years experimentalists have begun to use remnant magnetization and magnetic hysteresis measurements to study spin glasses. It was found that below the critical temperature the magnetization of the spin glass was
generally history dependent. There is still no agreement on whether or not there is a true thermodynamic spin transition to the spin glass state.

**Experimental Behavior**

Historically the experimental work done on spin glasses has far outweighed the theoretical research done on them. In most instances a substance is determined to be a spin glass by its behavior under certain conditions. It is important that before discussing the theory of spin glasses we review some of their characteristics.

With zero external field and small driving field the low-frequency a.c. susceptibility of transition metal ions in noble metal host alloys show a low temperature peak or cusp at some critical temperature \( T_g \). This is shown in Figure 1. \( T_g \) is known as the spin glass transition temperature and is in general a function of impurity concentration, measuring frequency and heat treatment. Above the critical temperature \( T_g \) the sample is paramagnetic. While below \( T_g \), in the spin glass phase, the impurity spins are no longer able to fluctuate with time but are locked or frozen in position.

The sharp cusps in the a.c. susceptibility suggest that a phase transition to a distinct spin glass state is occurring. However if a static magnetic field is applied the cusp is broadened, decreased in amplitude and shifted
to a lower temperature. This last observation indicates that the spin glass transition is not a true phase transition which leads to a new, distinct phase. Instead the spin glass phase is just a frozen configuration of spin clusters i.e. just one of an ensemble of low energy states separated in phase space from other such states by low energy barriers. The latter system would exhibit an inherent long term instability. The system could move through "phase space" due to thermal excitations. The spin glass state would then be characterized by long relaxation times. Strong support for the aforementioned model comes from the remnant magnetization and irreversibility characteristics of spin glasses.

Fig. 1 Low-field susceptibility $X_m(T)$ for alloys of AuFe, with 1 and 2% Fe impurities, showing the effect of increasing the external field. The full line represents the zero field limit. Flux density 10 mT; --- 20 mT; ... 30 mT. (after ref.7)
Spin glasses exhibit both isothermal remanent (IRM) and thermoremanent magnetization (TRM). The thermoremanent magnetization is obtained by cooling the system in an applied field and then switching the field off. Isothermal remnant magnetization is obtained by cooling the system in zero field, then an external field is applied for a short time and switched off. Under both conditions a slowly decaying magnetization $M_r$ appears in the spin glass sample, as can be seen in Figure 2.

Fig. 2 Dependence of the TRM and IRM for different values of the time $t$ (length of time the field is applied) for the Eu$_{4.8}$Sr$_{6.2}$S spin glass just below $T_g$ (after ref. 8)

In many cases, for times greater than 10 seconds, the time dependence of the IRM and TRM can be written as

$$ M = M_0 - Slnt $$

where $M_0$ is the initial value of the remanent magnetization and $S$ is a constant which depends on the field, temperature and material. Figure 3 shows the
remanent magnetization as a function of the natural logarithm of time.

Fig. 3 Schematic behavior of the remanent magnetization for T< Tg. The shaded area represents the time interval in which most experiments are performed. (after ref. 9)

The d.c. susceptibility and the a.c. susceptibility of a zero-field cooled sample are found to be the same. However, when a static field is applied to the sample an isothermal remnant magnetization slowly builds up causing the d.c. susceptibility to increase. The a.c. susceptibility remains small reflecting only the reversible part of the total magnetization, which is able to respond to the oscillating field. Tholence and Tournier have shown that the total susceptibility consists of reversible and irreversible components.\textsuperscript{10} The reversible part is defined by

\[ X_{\text{rev}} = \langle M(H)/H \rangle_{H \to 0} \]
and is obtained from the a.c. susceptibility data. While the irreversible part is

$$x_{\text{irrev}} = (\text{TRM}(H)/H)_{H \rightarrow 0}$$

and is obtained from the thermoremanent data. This leads some authors to believe that the true spin glass state is only reached after zero-field cooling.\(^{11}\) Applied fields distort the energy plane in phase space and favor some quasi-equilibrium state.

Another indication of the unusual properties of spin glasses is their history dependent magnetizations. The zero-field cooled magnetization and field-cooled magnetization differ for temperatures below the critical temperature \(T_g\) as seen in Figure 4. The zero-field cooled (ZFC) magnetization is obtained by cooling the sample from above \(T_g\) down to the measuring temperature in zero external field. Then a small field is applied and the magnetization is measured after waiting a short time. The field-cooled magnetization (FC) is obtained by turning on the field \(H\) above \(T_g\) and then cooling at constant field \((H \neq 0)\). For most systems the zero-field cooled magnetization is independent of the measuring time. However, for some systems like AuFe the ZFC magnetization changes slowly with time.\(^{12}\)

Upon heating, the field cooled magnetization is reversible. However if the ZFC magnetization is heated and then cooled back down, it is found to be irreversible.
Since the FC magnetization is reversible and always time independent, some authors speculate that field cooling will lead to the true spin glass equilibrium state.\textsuperscript{13}

![Graph showing zero field cooled and field cooled susceptibilities of CuMn with 1.08 and 2.02 at.% manganese. The field used in these measurements was H = 5.9 Oe.](after ref. 12)

The remanence and irreversible behavior of spin glasses has been seen in their hysteresis loops as shown in Figure 5. In that figure, curve (a) is the zero field cooled characteristic hysteresis loop of a spin glass. Below some critical field $H_{\text{crit}}$ the inner portion shown reversible. Once above $H_{\text{crit}}$ a small hysteresis and isothermal remanent magnetization develop corresponding to the outer loop of curve (a). Curve (b) is a typical
hysteresis for a field cooled spin glass. Curve (c) is a typical hysteresis loop for a ferromagnet included for comparison.

![Hysteresis Loop Diagram](image)

**Fig. 5** Hysteresis loops for (a) a spin glass cooled in 0 field, (b) a spin glass cooled in a magnetic field and (c) a ferromagnet. (after ref. 16)

Kouvel attempted to explain the displaced hysteresis of a field cooled spin glass in terms of a model with unidirectional exchange interaction. The sample remembers that it was cooled in a large field. A much smaller negative field is able to cause an abrupt reversal in the magnetization. Upon reducing this negative field the magnetization flips back to positive because the alloy still possesses its remembrance of the field cooling.

Many other experimental techniques have been used to
study spin glasses. At first, most experiments could be divided into those that showed an anomaly at $T_g$, the "freezing" temperature, and those which exhibited a broad change in behavior over a large temperature range. An example of the former is the a.c. susceptibility and an example of the latter is the electrical resistivity. With the increased study of spin glasses and the closer scrutiny of experimental techniques used in their study, it is no longer easy to divide the results into two such categories. One such technique, the measurement of the anomalous Hall effect, has proved to be a sensitive method for studying spin glasses. When magnetic impurities are present in a simple metal, such as an archetypical spin glass, there is an additional large component in the Hall effect due to spin orbit coupling between the conduction electrons and the localized moments. This coupling creates an asymmetric scattering for those moments which have been aligned by the magnetic field applied perpendicular to the current flow. This produces an additional contribution to the transverse electric field which is known as the skew component. This provides a good measurement of the degree of alignment in the magnetic field. This skew component is very sensitive to the rearrangement of the moments which occurs around the freezing temperature. This gives rise to a clear maximum at $T_g$ as shown in Figure 6. The sharp reduction below $T_g$
is due to the random freezing of the moments. The Hall effect is the only transport property with a very clear anomaly at $T_g$.

![Graph showing the temperature dependence of $\rho_H/B$](image)

Fig. 6 Temperature dependence of $P_H/B$ where $P_H$ is the Hall resistivity and $B$ is the magnetic flux density for 8.0 at.% AuFe alloy at: $\circ\circ\circ$, 20 mT; ..., 50 mT; $\Delta\Delta\Delta$, 100 mT. (after ref. 17)

As in many studies of magnetic compounds, the specific heat of spin glasses is of considerable interest. However, the expected anomaly at $T_g$ has not been found. Martin, using alloys with very small concentrations of magnetic impurities has found a "knee" at the freezing temperature in a plot of $C_m/T$ versus $T$. His work is the
first that shows any clear feature in the heat capacity of a spin glass. As of yet, no definite conclusions have been drawn from his results.

**Spin Glass Theories**

A wide variety of techniques have been applied to the spin glass problem producing a large amount of theoretical work. Many excellent reviews can be found such as the one by Mydosh. The first theories have been concerned with explaining the cusp in the a.c. susceptibility. One early theory that has had much influence on the spin glass problem is that of Edwards and Anderson. They postulated that despite the random arrangement of spins, there is nevertheless a certain configuration which minimizes the potential energy of the system and which corresponds to the ground state. They introduced the order parameter \( q \) such that if \( s_i^{(1)} \) is the value of the spin at \( t_1 \), then there is a nonvanishing probability that at a later time \( t_2 \) the spin \( s_i^{(2)} \) will be pointing in the same direction. So that

\[
q = \langle S_i^{(1)} . S_i^{(2)} \rangle 
\]

is not zero for \( T<T_g \)

and

\[
q = 0 \quad \text{for} \quad T>T_g
\]

and \( q \) increases towards unity as the temperature approaches absolute zero. This theory predicts not only a cusp in the a.c. susceptibility but also in the specific
heat. However, the original theory was classical in nature in that it did not consider quantization of the impurity spins.

Electrical resistivity and neutron scattering experiments on spin glasses suggest that to some extent the spins are correlated into magnetic clusters at temperatures above the freezing temperature. Examples of these micromagnetic clusters are shown in Figure 7. These micromagnetic clusters arise from concentration fluctuations in the compound. The tendency to form clusters is opposed by thermal disorder. It was the Grenoble group\textsuperscript{10} which first suggested that Neel's theory of superparamagnetism\textsuperscript{22} could be applied to such a system. As the temperature is lowered, the micromagnetic clusters become larger and more numerous. If the temperature is low enough a cluster may become "blocked" i.e. no longer able to overcome an energy barrier. If it is blocked for a long enough time, there is a chance it will not be sensed by the measuring technique and will appear frozen. From the Neel theory of superparamagnetism, the relaxation time of a magnetic cluster is given by

\[ t = t_0 \exp\left(\frac{E_a}{kT}\right) \]

where \( t_0 \) is a characteristic relaxation time for the spins and \( E_a \) is an anisotropy energy. This is the well known Arrhenius equation. Dipolar coupling is the largest contributor to the anisotropy energy but cluster shape and
surface effects can add to it. Guy has given a full account of Neel's theory of superparamagnetism and its applications to spin glasses.

![Diagram of a spin glass with about 10 at.% of impurities showing micromagnetic clusters.](after ref.16)

The ideas presented above are similar to those used by G.S. Grest and C.M. Soukoulis in their work on spin glasses. Grest and Soukoulis have calculated the metastable states of the spin glass free energy surface. They believe that over and intermediate time scale a spin glass can move along a given minimum on the free energy surface as it evolves without changing $H$ or $T$. Their
results have shown good qualitative agreement with experiment. Some of these results will be presented in the next chapter.

Yet another theory by Soukoulis and Levin combines intracluster interactions with intercluster interactions. The strong interactions between the spins within the clusters are treated exactly. While the much weaker intercluster interactions can be approximated using mean field theory. This model successfully predicts both the cusp in the a.c. susceptibility and the broad maximum in the specific heat.

Once thought important the so called RKKY interaction plays a lesser role in modern spin glass studies. Impurity spins in alloys interact with each other by polarizing the conduction electrons. The interaction, \( J(r) \), between two spins depends only on their relative separation.

\[
J(r) \approx \cos \frac{2k_Fr}{(k_Fr)^3} \text{ as } r \to \infty
\]

\( k_F \) here is the Fermi wave vector. The RKKY interaction is shown in Figure 8. We see that because \( J(r) \) is oscillatory, the interaction between two spins can be either ferromagnetic or antiferromagnetic depending on \( r \). Then because of the random distribution of impurities the magnetic interactions are also random. These conditions can lead to a large amount of frustration in the system. The concept of frustration which is essential in the
understanding of spin glasses will be presented shortly.

![Diagram of the RKKY interaction](image)

**Fig. 8** The RKKY interaction $J(r)$ between two magnetic impurities as a function of their separation $r$. If one magnetic moment is fixed at the origin 0, then a second situated at $r=0A$ will couple antiferromagnetically. A second impurity at $r=0B$ will be coupled ferromagnetically but less strongly.

A theoretical approach used on dilute alloys has been to replace the random array of spins with RKKY interactions by a regular array of spins with a Gaussian distribution of interactions. If $J_{ij}$ is the interaction between spins $i$ and $j$, a possible distribution would be

$$P(J_{ij}) = C \exp\left[-\frac{(J_{ij}-J_0)^2}{2J^2}\right]$$

where $J_0$ is the mean and $J$ is the variance. Using these ideas and the "replica trick" a magnetic phase diagram with a spin glass phase was found. Unfortunately, this model also predicted a negative entropy for the system at zero temperature.
Frustration

Over the last couple of years, spin glass behavior has been found in a variety of systems. The one thing that all these systems have in common is that they all contain interactions between spins which are in conflict with each other due to some disorder in the system. No conventional long range order can occur. But, nevertheless, experiments indicate a transition to a new state. In a classical spin glass, i.e. a nonmagnetic metal diluted with a few percent of magnetic ions, the RKKY interaction $J(r)$ strongly oscillates with the distance between magnetic ions $r$. Then due to the randomness of $r$ conflicting interactions between spins are produced. In $\text{Eu}_x\text{Sr}_{1-x}\text{S}$, the nearest neighbor exchange is ferromagnetic, $J_1>0$, and the next nearest neighbor interaction is antiferromagnetic, $J_2 = -J_1/2$. It is this competition between $J_1$ and $J_2$ that leads to spin glass behavior in $\text{Eu}_x\text{Sr}_{1-x}\text{S}$. In concentrated amorphous systems such as $\text{Gd}_{0.37}\text{Al}_{0.63}$, $J$ is random due to structural disorder. Systems with purely antiferromagnetic bonds should also exhibit spin glass behavior if the structure of the system leaves part of the bonds unsatisfied, i.e. frustrated.

To have spin glass behavior it is essential that the randomness of $J$ in the system leads to frustration. Or in other words there should be no ground state where all the
bonds are satisfied. One of the simplest examples is a triangular structure with nearest neighbor antiferromagnetic bonds, as shown in Figure 9. Another example is a two dimensional square lattice with Ising spins and interactions $J_{ij}$. When $J_{ij} > 0$, the ground state is ferromagnetic and for $J_{ij} < 0$, the ground state is antiferromagnetic and if $J_{ij} = \pm 1$ at random then one has a disordered magnet. On the next page, Figure 10 represents a perfect ferromagnetic configuration. In Figure 11 the sign of $J$ on all bonds around the central point are reversed but they are still all satisfied. The energy of the spin configuration is the same in figures 10 and 11. Figure 12 however, represents a frustrated system because there is no way of choosing the spins at the sites around the square so that all the bonds are satisfied. A note of caution though, to have genuine spin glass behavior frustration without disorder is not sufficient.

![Fig. 9 A simple system with frustration.](image-url)
Fig. 10 A ferromagnetic configuration of bonds.

Fig. 11 All the bonds around the central site have been made negative, but all can still be satisfied.

Fig. 12 A frustrated configuration of bonds.

The Existence of a Phase Transition

At this time, most authors agree that neither from an experimental nor from a theoretical point of view has the question of whether there is in fact a phase transition to a spin glass state been resolved. Gerard Toulouse, however, has presented a method which he believes can resolve this question. At high
temperatures, the theory predicts, for the magnetization

\[ M(H) = XH - aH^3 + O(H^5), \quad T > T_C \quad (1) \]

where \( x \) varies continuously with temperature, that the coefficient \( a(T) \) will diverge for \( T \rightarrow T_C \) as

\[ a(T) = (T - T_C)^{-q}. \quad (2) \]

At \( T = T_C \), the expected behavior is

\[ M(H) = XH - bH^{1+2/z} + \ldots \quad (3) \]

as this type of behavior is suggested by the Mattis model. 27

In mean field theory, one finds \( q = 1 \) and \( q = 2 \). Toulouse goes on to state that the change in behavior from equation (1) to equation (3) as \( T \rightarrow T_C \) is proof of a transition. So far little experimental work has been directed toward the determination of \( q \) and \( z \). Concerning the exponent \( z \) values range from \( z = 1,3 \) and \( z = 5,28,29,30 \).
CHAPTER THREE

INVESTIGATION

SAMPLE PREPARATION

Samples of \((\text{CH}_3)_3\text{NH})(\text{Co}_{1-x}\text{Ni}_x)\text{Cl}_3\cdot2\text{H}_2\text{O}\)
\((\text{TMA(}\text{Co}_{1-x}\text{Ni}_x)\text{)}) were prepared by mixing
concentrated aqueous solutions of \(\text{TMA(Cl}_3\text{H}_2\text{O})\) and
\(\text{TMA(NiCl}_3\text{H}_2\text{O})\), filtering and letting the resultant
solution evaporate. These were provided to us by K.E.
Emerson. Data were taken on samples which contained 5, 10,
15, 30, 34, 44, 60, 85 and 100% Nickel.

Crystal Structure

\(\text{TMA(}\text{Co}_{1-x}\text{Ni}_x)\) consists of bibridged chains of edge
sharing \(\text{trans-(Co}_{1-x}\text{Ni}_x)\text{Cl}_4(\text{OH}_2)_2\) octahedra with the
chains running parallel to the \(b\) axis of the orthorhombic
unit cell as shown in Figure 13. Figure 14 shows that
another chlorine atom in the lattice links these chains
together via hydrogen bonds to form sheets in the \(b-c\)
plane. The remaining trimethylammonium ions are found as
interstitial ions and separate the sheets in the \(b-c\)
plane. The symmetry here allows for spin canting. For a
more detailed description, see the paper by D. Losee et al.
Fig. 13 Three dimensional representation of the unit cell of TMA(\text{Co}_{1-x}\text{Ni}_x). For clarity atoms bonded to Co atoms on the edges are not shown. (after ref. 2)
Fig. 14 Projection of a portion of the crystal structure of TMA(Co$_{1-x}$Ni$_x$) onto the b-c plane. The dashed lines give unit cell boundaries. (after ref. 2)
Experimental Procedure

Susceptibility and magnetization measurements were made using a VSM model 155 Princeton Applied Research vibrating sample magnetometer. A variable temperature helium cryostat and a calibrated Lakeshore Cryotonic carbon-glass resistor provided temperature measurement. The magnetometer was calibrated with a MnF$_2$ crystal obtained from the International Bureau of Standards. The magnetic moments of powdered samples of .7g to .95g were measured over a temperature range of 2 to 200 degrees Kelvin. Susceptibility data were taken in an external field of 50 Gauss for temperatures below 20 Kelvin. An external field of 500 Gauss was used when taking data at temperatures between 20 and 200 degrees Kelvin.

We used a unique method in taking magnetization data which exhibits the thermoremanent characteristics of the spin glass. This set of magnetization, or susceptibility, data was obtained by cooling the sample in a field of $H = 2000$ Gauss from about 10K to 2K. The applied field was then turned off leaving an external field of 13 Gauss. After waiting approximately 3 minutes, susceptibility data were taken while slowly increasing the temperature. The temperature was raised past the critical temperature, $T_c$, and then lowered again down to $T=2.0K$ again taking
susceptibility data all the while. Note all the data were taken in a field of H=13 Gauss.

Standard thermoremanent magnetization data were also taken on a few samples. The sample would be cooled in a large field of 1000 or 2000 Gauss. The field would then be turned off and magnetization versus time measurements were taken.

The zero-field cooled and field cooled susceptibility data were obtained in the following manner. With the external field turned off (H< 4 Gauss) the sample was taken down in temperature from T=100K to T=2.0K. Then the external field was turned on to H=50 Gauss and after waiting approximately 30 seconds susceptibility data were taken while the temperature was raised past the critical temperature T\(_c\). Then reversing directions, data were taken while lowering the temperature back down to T=2.0K.

**Results and Discussion**

The susceptibility as a function of temperature was found for compounds of TMA(Co\(_{1-x}\)Ni\(_x\)) with various percentages of nickel. Shown in Figures 15 and 16 respectively, are the low and high temperature susceptibilities of TMA(Co\(_{0.60}\)Ni\(_{0.30}\)). These are representative of all the data. The complete set of results is given in the appendix. In the appendix, Figures 24 through 29 give the susceptibilities at temperatures
below 10K for the various compounds. And Figures 30 through 34 give the high-temperature susceptibilities of the same compounds.

From the low-temperature data, T<10K, graphs of 1/X versus T were made. Figure 17 is the graph of 1/X vs. T for TMA(Co_{0.90}Ni_{0.10}). This graph is representative of all the 1/X vs. T graphs. The remainder of these graphs are shown in Figures 35 through 39 of the appendix. From the 1/X vs.T graphs, the 3 dimensional ordering temperature $T_0$ was estimated by noting the temperature where the data leveled off. For all the samples the values of $T_0$ were very close ($4.1 < T_0 < 4.5$) with a slight lowering of $T_0$ being seen as the percentage of Nickel in the sample was increased. From the literature values of $T_0$ were obtained for the "pure" samples.$^1,2$ For TMACo $T_0 = 4.33K$ and given for TMANi is $T_0 = 3.6K$.

In the low-temperature susceptibility data, shown in Figures 24 through 29 of the appendix, we note that as the percentage of Nickel in the sample increases, we lose the peak in the susceptibility near $T_0$. The peak is typical for a powdered sample in its antiferromagnetic phase. For ferromagnets there is no peak in the susceptibility. TMANi is known to contain ferromagnetic chains.$^2$ However powder susceptibility data indicates that TMANi is slightly antiferromagnetic.$^2$ TMACo is also an antiferromagnet. The structure of TMACo is also one of ferromagnetic chains.
Fig. 15 Low-temperature susceptibility of TMA(Co₀.7₀Ni₀.3₀).
Fig. 16 High-temperature susceptibility of TMA(Co$_{0.70}$Ni$_{0.30}$).
Fig. 17 Low-temperature inverse susceptibility of TMA(0.90Ni.10)
with a much smaller interaction between chains, $J_2$, being antiferromagnetic. We suspect that the antiferromagnetic to spin flop phase transition in TMANi occurs at a field below 50 Gauss. If this is the case, then while taking data in a field of 50 Gauss the spins at the nickel atom sites are in the spin flop phase. Instead of aligning antiferromagnetically the spins were beginning to align along the applied field. This would cause the sample to lose some of its antiferromagnetic properties and behave more like a paramagnet. Then because of this we tend to lose the low-temperature peak in the susceptibility as the percentage of nickel in the sample is increased.

The effects of a thermoremanent magnetization in our compound can be seen in the graph given in Figure 18. The upper curve is due to the fact that the sample was cooled in a field of 2000 Gauss. The field was then turned down to 13 Gauss and susceptibility data were taken. The dramatic drop in $X$ is due to the near shutting off of the field. But just below $T_c$ and after a considerable amount of time ($t=3$ min.) we see that slope of the upper curve decreases rapidly. This is because the sample contains a thermoremanent magnetization. The spins have been frozen in position when the sample was cooled below some critical temperature $T_g$ into what we suggest is the spin glass phase. The sample apparently remembers that it has been cooled in a large field and attempts to keep this "frozen
Fig. 18 Susceptibility of TMA(Co$_{0.95}$Ni$_{0.05}$) taken in an external field of 13 Gauss after the sample had been cooled in a field of 2000 Gauss.
After heating and then recooling the sample, in a field of 13G, we get the lower part of the data shown. We note that after heating and recooling, the susceptibility we measure is slightly larger than that which was observed before. This unexpected rise in the susceptibility is observed in all samples and is nearly uniform in size. As of yet this is unexplained but it may be an effect similar to the displaced hysteresis curves found in the M vs. H graphs for field cooled spin glasses. The temperature where the upper curve meets the lower susceptibility curve is \( T_g \), the spin glass transition temperature. This type of data was taken for various samples and the results are shown in Figures 40 through 43 of the appendix. From these graphs \( T_g \) was calculated for all samples.

Figure 19 is a graph of the data obtained when a sample of TMA(Co_{0.95}Ni_{0.05}) was field cooled and zero-field cooled. This example is representative of the results observed in all samples. These data were obtained in the following manner. The sample was cooled in zero field, \( H<4\text{G} \). The field was then turned on to \( H=50 \text{ Gauss} \) and after waiting approximately three minutes we began taking \( X \) vs. \( T \) measurements. Upon initially raising the temperature we obtained the lower curve shown in the graph. This is the ZFC or zero-field cooled susceptibility. We continued to raise the temperature until we had passed the three
Fig. 19 Zero-field cooled and field cooled susceptibilities of TMA(Co$_{0.95}$Ni$_{0.05}$) taken in a field of 50 Gauss.
dimensional ordering temperature. We then reversed directions and began lowering the temperature. This then produced the upper curve of the data shown, the field cooled (FC) susceptibility. Note that both curves were obtained in a field of 50 Gauss. However the samples history is different in each case. The ZFC susceptibility curve proved to be irreversible. When we stopped raising the temperature and then lowered it, while at a point on the ZFC curve, we found that the susceptibility remained at its present level. The FC susceptibility on the other hand is reversible. The steep rise around 2K in the ZFC curve is due to the fact that the sample was still responding to the recently turned on field at the time. \( T_g \) is taken as the point where the ZFC susceptibility intersects the FC susceptibility. Here, below some characteristic temperature \( T_g \), we find typical spin glass behavior in that the sample's susceptibility is history dependent. We see that after the steep initial rise the ZFC susceptibility levels off somewhat and is lower than the FC susceptibility at temperatures below \( T_g \). These results support the theory that the spin glass state represents a frozen configuration of spin clusters. The results from all samples investigated in this manner are given in Figures 44 through 48 of the appendix. In Figures 46 and 48 the samples were cooled in exactly zero field instead of 4 Gauss. This accounts for their dissimilarity
with respect to the other figures.

Thermoremanent magnetization studies were done on selected samples. The samples were cooled in a large external field which was then shut off. Immediately following this magnetization versus time measurements were taken at constant temperature. The 5, 10, 15, 30, 44 and 60% nickel samples all showed thermoremanent magnetizations at temperatures around 2K, well below $T_g$. These can be seen in Figure 20. A more extensive study of the thermoremanent magnetization was conducted on TMA(Co$_{56}$Ni$_{44}$). The results are shown graphically in Figures 21 and 22. From Figure 21 we observe that the thermoremanent magnetization disappears around 3.6K, an indication of $T_g$ for TMA(Co$_{56}$Ni$_{44}$). This fits well with the other measurements of $T_g$. Figure 22 is a plot of magnetization versus time and shows definite thermoremanent magnetization below $T_g$ at 3.0K. These results represent the long relaxation times that characterize compounds in the spin glass phase.

Transition temperatures from all the data taken have been compiled in Tables 1 through 3. Table 1 contains the values for the three dimensional ordering temperatures taken from the $1/X$ vs.$T$ graphs. Values for $T_g$ taken from the thermoremanent data correlated well with the values for $T_g$ taken from the ZFC and FC data. The observed values of $T_g$ are listed in Tables 2 and 3.
Fig. 20 Thermoremanent magnetizations of $\text{TMA(Co}_{1-x}\text{Ni}_x$) with $x = 0.05, 0.10, 0.15, 0.30, 0.44,$ and $0.60$. 
Fig. 21 Dependence of the thermoremanent magnetization of TMA\(\text{Co}^{0.56}\text{Ni}^{0.44}\) on temperature.
Fig. 22 Thermoremanent magnetization of TMA(Co,56Ni,44) at 3.0K.
Table 1. Three dimensional ordering temperatures taken from graphs of $1/\chi$ vs. $T$ for TMA(Co$_{1-x}$Ni$_x$).

<table>
<thead>
<tr>
<th>% Ni</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.3 (4.25)*</td>
</tr>
<tr>
<td>10</td>
<td>4.4</td>
</tr>
<tr>
<td>15</td>
<td>4.5 (4.3)*</td>
</tr>
<tr>
<td>30</td>
<td>4.4</td>
</tr>
<tr>
<td>34</td>
<td>4.2*</td>
</tr>
<tr>
<td>60</td>
<td>4.15</td>
</tr>
<tr>
<td>85</td>
<td>4.17</td>
</tr>
</tbody>
</table>

* Values in parentheses after ref. 32

Table 2. Spin glass transition temperatures taken from thermoremanent magnetization data for TMA(Co$_{1-x}$Ni$_x$).

<table>
<thead>
<tr>
<th>% Ni</th>
<th>$T_g$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.86</td>
</tr>
<tr>
<td>10</td>
<td>3.94</td>
</tr>
<tr>
<td>15</td>
<td>4.02</td>
</tr>
<tr>
<td>30</td>
<td>4.04</td>
</tr>
<tr>
<td>60</td>
<td>3.80</td>
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</tbody>
</table>

Table 3. Spin glass transition temperatures taken from the zero-field cooled magnetization data for TMA(Co$_{1-x}$Ni$_x$).

<table>
<thead>
<tr>
<th>% Ni</th>
<th>$T_g$ (K)</th>
</tr>
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<tr>
<td>5</td>
<td>3.715</td>
</tr>
<tr>
<td>10</td>
<td>4.085</td>
</tr>
<tr>
<td>15</td>
<td>4.038</td>
</tr>
<tr>
<td>34</td>
<td>(3.95)*</td>
</tr>
<tr>
<td>60</td>
<td>3.80</td>
</tr>
<tr>
<td>85</td>
<td>3.84</td>
</tr>
</tbody>
</table>

* after ref. 32
CHAPTER 4

CONCLUSIONS

**Cause of Spin Glass Behavior in TMACo\(_{1-x}\)Ni\(_x\)Cl\(_3\).2H\(_2\)O**

Spin glass behavior is known to exist in a variety of compounds. The two ingredients which are necessary for spin glass behavior are disorder and frustration. For this mixed system the disorder we assume comes about naturally from the method used to prepare the samples. TMACoCl\(_3\).2H\(_2\)O and TMANiCl\(_3\).2H\(_2\)O are isomorphous. They both mainly consist of chemical chains running parallel to the crystallographic b axis. When the two systems are mixed we expect the same chemical chains as before except with randomly placed Co and Ni atoms.

The frustration that arises in this system is somewhat unique. In TMACo the spins align along the crystallographic c axis. In TMANi it is only known that the easy axis of the spin system is in either the a-b or the c-b plane. If the easy axis of TMANi was in the c-b plane we would probably not have any frustration in the mixed system TMA(Co\(_{1-x}\)Ni\(_x\)) due to the crystal structure and without frustration we would not observe any spin glass behavior. Therefore we conclude that in TMANi the easy
axis is in the a-b plane. So in the mixed system when there is a Co atom in the chain the easy axis for the spin system is along the c axis. And when there is a Ni atom in the chain the easy axis of the spin system is in the a-b plane perpendicular to the easy axis at the site of a Co atom. Now both TMACo and TMANi have strong intrachain ferromagnetic interactions which want to align all the spins in one direction. We therefore have competition between the differing spin anisotropies due to the ferromagnetic intrachain correlations. This competition leads to frustration along the chains in the mixed system. Then with both disorder and frustration we find, as expected, spin glass behavior.

**Magnetic Phase Diagram**

From the observed transition temperatures $T_c$ and $T_g$, a magnetic phase diagram has been constructed and appears in Figure 23. All the phases are labeled as paramagnetic P, antiferromagnetic AF, or spin glass SG. As far as we know only two other magnetic phase diagrams of this type have been found.$^{33,34}$

The structure of the present diagram is somewhat different from those previously seen. Tetracritical points can be found in systems with suitable competing spin anisotropies and indeed in both of the other phase diagrams previously mentioned, DeFotis et al. have
reported tetracritical points. In our diagram a
tetracritical point is not directly observable. However
further data could possibly indicate such a tetracritical
point in our compound.

As seen on the phase diagram, the $3d$ ordering
temperatures $T_c$ of the pure components are connected by a
continous phase boundary. The data cannot tell us
conclusively whether a continous phase boundary is seen or
whether there are two distinct lines of paramagnetic to
antiferromagnetic phase transitions. In other systems with
competing orthogonal spin anisotropies, a discontinous
upper boundary in the magnetic phase diagram was observed.

The lower curves on the phase diagram are the spin
glass phase boundaries. Above these curves the compound
does not exhibit spin glass behavior. Again it is
uncertain whether or not two distinct lines of spin glass
to antiferromagnetic transitions are observed. A continous
spin glass phase boundary is just as likely. It is also
uncertain whether or not these lines are second order. The
compound is unusual in that a very large spin glass phase
is observed. The pure constituents, $\text{TMACo}$ and $\text{TMANi}$, have
no frustration or disorder therefore we do not expect them
to have a spin glass phase. We expect then that the spin
glass phase boundaries will drop down and intersect
the horizontal axis of the diagram. This was partially
verified. $\text{TMANi}$ was investigated and showed no
Fig. 23 Magnetic phase diagram for TMACo$_{1-x}$Ni$_x$ showing antiferromagnetic (AF), paramagnetic (P), and spin glass (SG) phases.
Summary and Future Investigations

The experimental evidence obtained in this investigation indicates that TMA\((Co_{1-x}Ni_x)\) is a spin glass in that it exhibits spin glass behavior under certain conditions. Namely temperatures less than 4.1K and in external fields on the order of 50 Gauss. Spin glass behavior in TMA\((Co_{1-x}Ni_x)\) indicates, since the weak interchain coupling is two dimensional, that the lower critical dimensionality of spin glasses is at least two.

Figure 22 shows the time dependence of the thermoremanent magnetization in our sample at 3.0K for a cooling field of 1000 Gauss. Analysis reveals that a logarithmic time dependence cannot account for the decay. However for results similar to these a "stretched" exponential has been found to account fairly well for the data.\(^{33}\)

Due to its spin glass nature more experimental work on this compound is planned. A wider range of samples will be investigated in order to fill in the phase diagram as completely as possible. More extensive studies of the thermoremanent magnetization may be done. In that case one hopes that an equation may be fit to the data which in turn would help us to understand the relaxation process in the spin glass phase. The temperature where the thermoremanent magnetization disappears could also be an
accurate measurement of $T_g$. Further studies on the structure of the compound would certainly be useful in understanding the disorder and frustration in the system.

This investigation has led to a magnetic phase diagram with a definite spin glass phase. Despite an enormous amount of effort by research scientists in the last 10 years, our overall understanding of spin glasses is still very incomplete. The emphasis now seems to be on the fundamental concept of frustration and its application not only to spin glasses but also to a vast class of condensed matter phases.
REFERENCES CITED


[32] J. Rubenacker, personal communication

[33] G.C. DeFotis, D.S. Mantus, Co$_{1-x}$MnxCl$_2.2$H$_2$O: A New Kind of Spin Glass, unpublished

APPENDIX

This appendix is a compilation of the data obtained for TMA(Co$_{1-x}$Ni$_x$) during the course of this investigation. Figures 24 through 34 give the susceptibility as a function of temperature for compounds of TMA(Co$_{1-x}$Ni$_x$) containing various percentages of Nickel. Figures 35 through 39 are graphs of $1/X$ vs. $T$ for temperatures below 10K. Figures 40 through 43 show the susceptibilities of various samples of TMA(Co$_{1-x}$Ni$_x$) taken in a field of 13 Gauss after cooling in a field of 2000 Gauss. And Figures 44 through 48 are graphs of the zero field cooled and field cooled susceptibilities taken in fields of 50 Gauss.
Fig. 24 Low-temperature susceptibility of TMA(-Co.95Ni.05).
Fig. 25 Low-temperature susceptibility of TMA(\text{Co}_{0.9}\text{Ni}_{0.1}).
Fig. 26 Low-temperature susceptibility of TMA(Co,85Ni,15).
Fig. 27 Low-temperature susceptibility of TMA\text{Co}_{0.70}\text{Ni}_{0.30}.
Fig. 28 Low-temperature susceptibility of TMA(Co_{40}Ni_{60}).
Fig. 29 Low-temperature susceptibility of TMA(Ni)Cl$_3$.2H$_2$O.
Fig. 30 High-temperature susceptibility of TMA(Co.95Ni.05).
Fig. 31 High-temperature susceptibility of TMA(Co.90Ni.10).
Fig. 32 High-temperature susceptibility of TMA(Co$_{0.85}$Ni$_{0.15}$).
Fig. 33 High-temperature susceptibility of TMA(Co_{70}Ni_{30}).
Fig. 34 High-temperature susceptibility of TMA(\text{Co}_{40}\text{Ni}_{60}).
Fig. 35 Low-temperature inverse susceptibility of TMA(Co_{0.95}Ni_{0.05}).
Fig. 36 Low-temperature inverse susceptibility of TMA\(_{10}\%\).
Fig. 37 Low-temperature inverse susceptibility of TMA(Co,85Ni,15).
TMA 30%

Fig. 38 Low-temperature inverse susceptibility of TMA(Co<sub>0.70</sub>Ni<sub>0.30</sub>).
Fig. 39 Low-temperature inverse susceptibility of $\text{TMA(Co}_{.40}\text{Ni}_{.60})$. 

$1/X$ (mole/emu) vs $T$ (K) for TMA 60%.
Fig. 40 Susceptibility of TMA(Co$_{0.95}$Ni$_{0.05}$) taken in a field of 13 Gauss after cooling in a field of 2000 Gauss.
Fig. 41 Susceptibility of TMA(Co₉₀Ni₁₀) taken in a field of 13 Gauss after cooling in a field of 2000 Gauss.
Fig. 42 Susceptibility of TMA(Co.70Ni.30) taken in a field of 13 Gauss after cooling in a field of 2000 Gauss.
Fig. 43 Susceptibility of TMA(Co₄₀Ni₆₀) taken in a field of 13 Gauss after cooling in a field of 2000 Gauss.
Fig. 4.4 Zero-field cooled and field cooled susceptibilities of TMA(Co,0.95Ni,0.05) taken in a field of 50 Gauss.
Fig. 45 Zero-field cooled and field cooled susceptibilities of TMA(Co$_{0.85}$Ni$_{0.15}$) taken in a field of 50 Gauss.
Fig. 46 Zero-field cooled and field cooled susceptibilities of TMA(Co$_{0.66}$Ni$_{0.34}$) taken in a field of 50 Gauss.
Fig. 47 Zero-field cooled and field cooled susceptibilities of TMA(Co$_{0.40}$Ni$_{0.60}$) taken in a field of 50 Gauss.
Fig. 48 Zero-field cooled and field cooled susceptibilities of TMA(Co.35Ni.65) taken in a field of 50 Gauss.
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