Preparation and Study of a Rare Ternary Insulating Magnet

Thomas J. Wallin

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Preparation and Study of a Rare Ternary Insulating Magnet

by Thomas J. Wallin

A thesis submitted in partial fulfillment of the requirements for a degree with Honors in Chemistry from the College of William and Mary in Virginia
5/3/2010
Williamsburg, Va

Accepted for ____________________________
(Honors, High Honors, Highest Honors) ____________________________

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Abstract

Just previously in the advisor's laboratory, study of the magnetic properties of \( \text{Co}_{1-x}\text{Mn}_x\text{Ni}_y\text{Cl}_2\cdot2\text{H}_2\text{O} \) was initiated. Based on that work, it was clear that several additional compositions at least need to be prepared and measured in order to (a) complete the survey of two-dimensional composition space, and (b) accumulate enough information on the global behavior of the material as a function of composition to enable a reliable interpretation of the measured properties to be made. This mixed magnetic system is only the second ternary mixed magnet to be examined from this phase transition perspective. The pure components and binary mixtures of this system (Co/Mn/NiCl\(_2\cdot2\text{H}_2\text{O}\)) had been previously studied in this laboratory. However, the theory for ternary systems is far less developed than for the binary systems. As such, there is a very real possibility of uncovering qualitatively new phenomena in our study. Six new compositions, differing significantly from the previous seven, were prepared, characterized, and measured in the present work. The procedure was to measure the magnetic susceptibility as a function of temperature, between 1.5 and 300K; analyze the high temperature paramagnetic properties with appropriate basic theory; examine the data at low temperatures for signs of transitions; measure magnetization isotherms to look for indication of field-induced transitions and hysteresis; and also look for signs of the time dependence and associated fundamental irreversibility in any of the foregoing properties. Analysis of the data yields the beginnings of a magnetic phase diagram, that is a plot of ordering temperature versus the two composition variables, \( T(x,y) \). It is the second such plot ever determined and published.
Acknowledgements:

Funding for this research was provided by the William and Mary Charles Center Honors Research Fellowship, the William and Mary Chemistry Department, Patricia Kay Jue, and David Evans. Partial support was given by the donors of the Petroleum Research Fund of the American Chemical Society.

Thanks to:

Elizabeth Welshhans with preparing samples, collecting raw data, processing the data, and constructing the plots, particularly the isothermal data processing and plots.

John Potham and Andrew Hampton, whose work on the previous compositions of the same system was used to help complete the T(x,y) 3-D plots and Table 4.

Professor Robert Pike for help performing the X-ray crystallography and collecting raw data.

And of course, Professor Gary DeFotis. His invaluable experience, patience, and knowledge in this field provided important insight on numerous occasions.
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Introduction:
The Origin of Magnetism and Magnetic Moments:

According to Maxwell’s equations, moving electric charges generate a magnetic field. Therefore, at the atomic scale, any motion or spin of the charged electron and nucleus would cause magnetism. There are four possible sources of magnetism we must consider: 1.) the inherent spin of the electron about its axis 2.) the inherent spin of the nucleus about its axis, 3.) the motion of the electron in its orbital about the nucleus and 4.) the motion of the nucleus about the electron. The corresponding magnetism associated with these motions is discussed below.

The motion of the nucleus about the electron is quickly ignored because of its relatively large mass, its motion is much slower than that of the electron and is assumed stationary (as in the Born Approximation). In our study, any contribution from the spin of the nucleus can be ignored. First, not all our species have a nuclear spin (I=0 for Ni). Secondly, even with the nuclear species with spin (Co nuclei have a spin of 7/2 and Mn nuclei have a spin of 5/2)\(^1\), the contribution from these spins would be orders of magnitude smaller than those from the electron because the nuclear magneton is thousands of times smaller than the Bohr magneton. We simply are unable to detect the possible nuclear spin contributions with our apparatus\(^2\) (though it is possible elsewhere with heat capacity measurements).

The motion of the electron about the nucleus in its orbit is described quantum mechanically by the orbital angular momentum:

\[
\text{Orbital Angular momentum} = \hbar \ell
\]  

Where \(\hbar\) is Planck’s constant \((6.626\times10^{-34} \text{ m}^2\text{kg/s})\), and \(\ell\) is the orbital angular vector of the electron. The quantum number \(\ell\) corresponds to the orbital the electron is located in (\(\ell = 0\) for electrons in the s-
orbital, \( \ell = 1 \) for the p orbital, \( \ell = 2 \) for the d orbital, etc.). The corresponding magnetic moment (\( \mu_L \)) that originates from the orbital angular momentum is:

\[
\bar{\mu}_L = -\gamma_e \hbar \ell \quad (2)
\]

Where \( \gamma_e \) is the gyromagnetic ratio for the electron. Equation (2) can also be more conveniently expressed as the product of the Bohr Magneton and \( \ell \).

\[
\bar{\mu}_L = -\mu_B \ell
\]

Where \( \mu_B \) is the Bohr magneton and is just the product of the two constants \( \gamma_e \) and \( \hbar \).

Another magnetic moment is also created from the momentum associated with the spin about the electron on its axis. Similar to above, this spin angular momentum is given by:

\[
\text{Spin angular momentum} = \hbar \bar{s} \quad (3)
\]

Where \( s \) is spin quantum number (\( \frac{1}{2} \) for an individual electron). Equation 4 shows the magnetic moment associated with this spin (\( \mu_s \)).

\[
\bar{\mu}_s = -g \mu_B \bar{s} \quad (4)
\]

Where \( g \) is the spectroscopic splitting factor or “g-factor.” The value of \( g \) is approximately 2 for a free electron. The g factor is included so as to agree with experimental results, but also stems from relativistic quantum mechanics and quantum electrodynamics.

This is not the entire picture, as the orbital and spin motions add further complication by interacting with each other. For atoms and ions of relatively low atomic mass, the strength of this interaction is significant and Russell-Saunders coupling scheme is applied. However, in our study, the ions are those of transition metals in a ligand field. In this field, the orbital-spin interactions are not
great. Also, in ligand fields, the valence electrons are delocalized, the orbital angular momentum is
generalized, and \( L_z \) is no longer a constant of the motion. Hence we do not consider the orbital angular
momentum, only spin angular momentum. The net magnetic moment seems to depend heavily on the
quantum spin number \( s \), and is now given by:

\[
\bar{\mu} = -g \mu_B \bar{s}
\]  \hspace{1cm} (5)

It is important to note that there still does exist a slight spin-orbit interaction and as seen by the
divergence of \( g \) values from 2.00.\(^2\)
Crystal Field Splitting and D-electron Configuration for the System:

In order to see a magnetic moment in our system, we need a non-zero net electronic spin. Usually, the electrons in an atom are arranged in pairs with opposite spins (according to the Pauli Exclusion Principle) so the contributions from paired electrons offset. In filled subshells the electrons have cancelling orbital angular momentum and contribute nothing to the net magnetic moments. Thus, we need only consider electrons that are not in closed subshells.

We study Co_{1-x}Mn_{x}Ni_{y}Cl_{2}H_{2}O. In this system the chlorines act as bridging LX-type ligands\(^3\) (and the water is L type). With six ligands distributed evenly about the metal center, the geometry is roughly octahedral. It has been found that spins align along or nearly along the metal-water bonds.\(^4\)

Naturally, the metal complex carries a (+2) charge to offset the (-1) charge on each of the X-type ligands (chlorine). Co(II) has 7 d-electrons, Mn (II) has 5 d-electrons and Ni (II) has 8 d-electrons in the valence shell. The d-orbitals of atoms in ligand fields split based upon a variety of factors such as the geometry of the complex, the number of electrons on the metal ion, and the nature of the ligands (strong or weak field). The crystal field splittings of the d electrons in these complexes are shown below, following Pauli Exclusion and Hund’s rule for maximizing total spin. Water and chlorine are so called “weak-field” ligands: the electron pairing energy is much greater than the energy difference between

![Figure 1: Simplified Crystal Field of Complex](image-url)
the octahedral splitting. Consequently the metal ions prefer the spin case, as shown in Figures 2, 3, and 4.

Figure 2: Mn (II) Electron Configuration for Weak Field Octahedral Splitting

![Diagram of Mn (II) electron configuration for weak field octahedral splitting]

Figure 3: Co(II) Electron Configuration for Weak Field Octahedral Splitting

![Diagram of Co(II) electron configuration for weak field octahedral splitting]

Figure 4: Ni (II) Electron Configuration for Weak Field Octahedral Splitting

![Diagram of Ni (II) electron configuration for weak field octahedral splitting]

The net spin of the metal complexes is obviously (3/2) for Co, (5/2) for Mn, and (1) for Ni. A nonzero net spin contributes a non-zero magnetic moment and leads to a net magnetic moment in the metal complexes of our sample. For more information on crystal field splitting see Miessler.³
Magnetization and Susceptibility:

Now that it is understood that non-zero magnetic moments can exist in the transitional metal ions present in our sample (due to the spin angular momentum), the existence of a net magnetization or net induced magnetic moment ($M$) can be rationalized.

$$\overline{M} = \sum \mu$$  \hspace{1cm} (6)

Where the magnetization ($M$) is simply the sum of all magnetic moments ($\mu$) in the macroscopic sample.

Though each individual metal complex has a magnetic moment, in a large collection of complexes, without an applied magnetic field there is no preference for direction of the moment. Thus the random alignment of the moments, caused by thermal motion of the molecules, cancels out and there is no expected net magnetization under ordinary circumstances.

However, polarization of the moments through the application of a magnetic field destroys this random orientation can be destroyed. Now there is a Hamiltonian Energy from the applied field ($H$) and the magnetic moment:

$$E = -\vec{\mu} \cdot \vec{H}$$  \hspace{1cm} (7)

Although thermal energy can still randomize the orientation of the individual moments, not all the directional components will cancel and a net magnetization results. As you increase the field strength, you increase the energy associated with the Hamiltonian causing more polarization in the moments (one could also decrease the temperature and consequently thermal energy to achieve the same effect).
Magnetic susceptibility measures quantitatively the magnetic moment’s response to an applied field. This relationship is shown in equation 8.

\[ \bar{M} = \chi \bar{H} \quad \text{or} \quad \chi = \frac{\bar{M}}{\bar{H}} \quad (8) \]

Where \( \chi \) is the magnetic susceptibility per unit volume (a molar susceptibility can be obtained by multiplying the volume susceptibility by the ratio of molecular weight to density).

A high magnetic susceptibility means that the individual magnetic moments are easily polarized by an applied magnetic field. Since the thermal energy of a material tends to randomize the orientation of the moments, the susceptibility shows temperature dependence.
The Curie Law:

The Curie Law demonstrates this temperature dependence for non interacting spins. If we substitute the magnetic moment from equation (5) into the Hamiltonian energy of equation (7) we get:

\[
E = -\vec{\mu} \cdot \vec{H} = g \mu_B \vec{S} \cdot \vec{H} = g \mu_B m_s H
\]

(9)

Where \( m_s \) is the spin component in the z direction (\( H \) is applied in the z direction so the dot product uses only the z component of \( s \)). For electrons \( m_s \) is \( \pm \frac{1}{2} \). Thus, the moments become polarized and a splitting develops based upon whether the \( m_s \) value is \( +\frac{1}{2} \) or \( -\frac{1}{2} \).

\[
\Delta E = \left( \frac{1}{2} \right) g \mu_B H - \left( -\frac{1}{2} \right) g \mu_B H = g \mu_B H
\]

(10)

Now applying the Boltzmann distribution to the population of the \( m_s = \frac{1}{2} \) and \( m_s = -\frac{1}{2} \) energy levels, we see the following temperature dependence:

\[
\frac{N_{+1/2}}{N} = \frac{e^{-\Delta E/2kT}}{e^{\Delta E/2kT} + e^{-\Delta E/2kT}}
\]

(11)

\[
\frac{N_{-1/2}}{N} = \frac{e^{\Delta E/2kT}}{e^{\Delta E/2kT} + e^{-\Delta E/2kT}}
\]

(12)

Where \( N \) is the total population, \( N_{1/2} \) and \( N_{-1/2} \) are the populations in the \( m_s = -\frac{1}{2} \) and \( m_s = \frac{1}{2} \) states respectively, \( \Delta E = g \mu_B H \) (as given by equation(10)), \( k \) is the Boltzmann constant and \( T \) is the absolute temperature in Kelvin. Since the induced magnetic moment is the sum all the magnetic moments, and there exist two states, we get:

\[
\bar{M} = N_{1/2} \mu_{1/2} + N_{-1/2} \mu_{-1/2}
\]

(13)

We know that \( \mu_{1/2} = -\mu_{-1/2} \), substituting in equations (11) and (12), substituting 2 in for \( g \), and recognizing the hyperbolic tangent, we can rewrite the above as:
\[ M = N \frac{1}{2} \mu - N \frac{1}{2} \mu = N \mu \frac{e^{\mu H} - e^{-\mu H}}{e^{\mu H} + e^{-\mu H}} = N \mu \tanh \left( \frac{\mu H}{kT} \right) \]  \hspace{1cm} (14)

Now, the following approximations for the hyperbolic tangent can simplify equation (14).

\[ \tanh x \quad = x \quad \text{for} \quad x \ll 1 \]  \hspace{1cm} (15)

\[ \tanh x \quad = 1 \quad \text{for} \quad x \gg 1 \]  \hspace{1cm} (16)

Looking at the low temperature behavior, where kT is much smaller than \( \mu H \), using the second, large x, approximation for \( \tanh \), we get:

\[ X = \frac{M}{H} = \frac{N \mu \tanh \left( \frac{\mu H}{kT} \right)}{H} = \frac{N \mu}{H} \]  \hspace{1cm} (17)

This predicts saturation magnetization, with all of the moments aligning directly along the applied field.

Similarly, for high temperatures, where kT is much larger than \( \mu H \), the first approximation yields:

\[ X = \frac{M}{H} = \frac{N \mu \tanh \left( \frac{\mu H}{kT} \right)}{H} = \frac{N \mu}{H} \left( \frac{\mu H}{kT} \right) = \left( \frac{N \mu^2}{k} \right) \frac{1}{T} \]  \hspace{1cm} (18)

Or written more generally:

\[ X = \frac{C}{T} \]  \hspace{1cm} (19)

Where it can also be shown in general that \( C = Ng^2 \mu_0^2 s(s+1)/3k \). Equation (19) is known as the Curie Law. It predicts that at high temperatures, where the \( \tanh \) approximation holds, susceptibility is inversely proportional to the temperature.
Deviations from the Curie Law and the Curie-Weiss Law:

The Curie law assumes that each individual metal spin does not interact with any other metal spin. The single most common and important source of deviations from Curie law behavior is in the exchange interaction. The Heisenberg Hamiltonian accounts for this exchange in insulators:

\[ \hat{H}_{ex} = -2J \sum_{i>j} \vec{s}_i \cdot \vec{s}_j \]  

(20)

Where J is the exchange integral which depends on the quantum mechanical details of the system. If J is positive, having the spins antiparallel lowers the energy of the system. If J is negative, the opposite holds and the system energetically favors the spins aligning parallel (e.g., ferromagnetism). This added spin-spin exchange interaction changes the high temperature behavior and the Curie-Law from above.

Instead, we now write the Curie Weiss law:

\[ X = \frac{c}{T - \theta} \]  

(21)

Where \( \theta \) is the Weiss constant, often used as a measure of J in uncomplicated systems (if \( \theta > 0 \) so is J and if \( \theta < 0 \) so is J). It can be shown that the Weiss constant is given by:

\[ \theta = \frac{2s(s+1)zJ}{3k} \]  

(22)

Where s is the spin quantum number, z is the number of complexes that interact by the exchange integral J.

The Curie Weiss-Law is also not infallible. Deviations occur at low temperatures and/or high fields, where the \( \tanh(x) = x \) approximation fails. Other departures from this law occur when zero-field splitting occurs, when T is not substantially larger than |\( \theta \)|, or when more complex interactions between spins exist.
**Types of Magnetism:**

A system can exhibit many different classifications of magnetic behavior such as: paramagnetism or diamagnetism, and ferromagnetism, antiferromagnetism or ferrimagnetism. Paramagnetism is the magnetic behavior that occurs when the only interactions that exist occur between the magnetic moment and the applied field. Diamagnetic is the temperature-independent effect of orbital electronic motion readjusting to oppose an applied field. According to Lenz’s Law, diamagnetism occurs in all materials to some degree in response to the application of a magnetic field.

The exchange integral explains ferromagnetism. When J (and θ) is greater than zero, the energy is lowered when the dot product of the interacting spins is greatest. This occurs when the moments align. A ferromagnet at low enough temperatures has the tendency for the spins to align and not cancel out even in the absence of a field. Consequently, it exhibits a spontaneous magnetization. The cut off temperature for spontaneous magnetization is the Curie temperature, which is typically less than the Weiss Constant, θ. However, even though spins tend to orient, there usually is no macroscopic magnetic behavior in a ferromagnet without an applied field.

Ferromagnetic behavior tends to occur in “domains.” In a given domain, all the spins are parallel to each other. However, the domains themselves do not orient, as seen in Figure 6 (please note that this depicted domain pattern is not a physically realistic one). Hence, over a large enough collection, the magnetic moments of the larger domains will cancel out just like the individual complexes moments can cancel out. Also like individual complexes, application of a field can cause these domains themselves to align.
Antiferromagnetism occurs when it is energetically more favorable to have each moment be pointed in the opposite direction to that of its neighbors. This results when $J(\theta)$ is less than zero, and the spins aligned antiparallel minimizes the Heisenberg Hamiltonian (thus causing the dot product to be negative). Below a critical temperature, typically lower than $|\theta|$, the magnetic moments take on this antiparallel arrangement.

Ferrimagnetic behavior occurs in an antiferromagnet with different spin values, and magnitudes of magnetic moments, between adjacent complexes. Ferrimagnetism is shown in Figure 8.

A material can show multiple forms of these magnetic behaviors. Along a chain the moments can be antiferromagnetic, but ferromagnetic between chains themselves, and so on. Again, any ordering that occurs does not do so on a macroscopic scale, but within smaller domains.

We now describe the motivation for the present work and our goals. Just previously in the advisor’s laboratory, study of the magnetic properties of $\text{Co}_{1-x}\text{Mn}_x\text{Ni}_y\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ was initiated. Based on that work, it was clear that several additional compositions at least need to be prepared and measured in order to (a) complete the survey of two-dimensional composition space, and (b) accumulate enough information on the global behavior of the material as a function of composition to enable a reliable interpretation of the measured properties to be made. We want to: measure the magnetic susceptibility as a function of temperature; analyze the high temperature (>30K) paramagnetic properties with the appropriate basic theory; examine the data at low temperatures (<20K) for signs of magnetic transitions; measure the magnetization isotherms to look for any field induced transitions and
hysteresis; look for signs of time dependence and associated fundamental irreversibility in any of the
foregoing properties; create a magnetic phase diagram, that is a plot of ordering temperature versus the
two composition variables \((x,y)\). Six new compositions, differing significantly from the previous seven,
were prepared, characterized and measured in furtherance of these goals.
**Experimental Procedure:**

**Sample Preparation:**

The preparation method employed has been proven effective to prepare other mixed magnetic insulating mixtures in this laboratory.\(^{4,6,7}\) We prepare the ternary mixtures from hydrated salts of the pure metal chlorides. We used Aldrich samples of CoCl\(_2\)\(\cdot\)6H\(_2\)O, MnCl\(_2\)\(\cdot\)4H\(_2\)O, and NiCl\(_2\)\(\cdot\)6H\(_2\)O. Since the salts are hygroscopic, we store these salts in closed containers sealed with laboratory film around the lids. After looking at the compositions of ternary samples previously studied, the permutation of compositions relating to 0.1, 0.3, and 0.6 best fill the remaining composition space we wish to survey.

Six grams of sample give us an adequate amount to study with the magnetometer and for possible future measurements of other kinds, so we attempt to prepare approximately that amount for each of the varying compositions. The metal chloride salts used to prepare these samples contain the same amount of chlorine as the desired compositions (two per unit) so no further considerations regarding the chlorine content are necessary. Ignoring the water content temporarily, we combine the salts so that the molar concentrations of the transition-metal give the desired ratios.
Table 1: Mass of the Metal Chloride Salts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass CoCl₂·6H₂O (MW= 237.93g)</th>
<th>Mass MnCl₂·4H₂O (MW= 197.91g) (g)</th>
<th>Mass NiCl₂·6H₂O (MW= 237.71g) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₀.₁Mn₀.₃Ni₀.₆Cl₂·2H₂O</td>
<td>0.978</td>
<td>2.44</td>
<td>5.829</td>
</tr>
<tr>
<td>Co₀.₁Mn₀.₆Ni₀.₃Cl₂·2H₂O</td>
<td>0.878</td>
<td>4.372</td>
<td>2.627</td>
</tr>
<tr>
<td>Co₀.₃Mn₀.₁Ni₀.₆Cl₂·2H₂O</td>
<td>2.591</td>
<td>0.728</td>
<td>5.170</td>
</tr>
<tr>
<td>Co₀.₃Mn₀.₆Ni₀.₁Cl₂·2H₂O</td>
<td>2.630</td>
<td>4.369</td>
<td>0.880</td>
</tr>
<tr>
<td>Co₀.₆Mn₀.₁Ni₀.₃Cl₂·2H₂O</td>
<td>5.182</td>
<td>0.723</td>
<td>2.590</td>
</tr>
<tr>
<td>Co₀.₆Mn₀.₃Ni₀.₁Cl₂·2H₂O</td>
<td>5.214</td>
<td>2.170</td>
<td>0.871</td>
</tr>
</tbody>
</table>

Sample Calculations for Co₀.₁Mn₀.₃Ni₀.₆Cl₂·2H₂O:

Formula Weight = 0.1 (58.93g) + 0.3 (54.94 g) + 0.6(58.70 g) + 2(35.45 g) + 2(18.00g)

= 146.90 g

\[6.0 \text{ g desired} \times \frac{1 \text{ mole } MCl_2 \cdot 2H_2O}{146.90 \text{ g}} = 0.0406 \text{ mole } MCl_2 \cdot 2H_2O \text{ desired}\]

\[.1 \times (.0409 \text{ mol Co}) \times \frac{237.93 \text{ g } CoCl_2 \cdot 6H_2O}{1 \text{ mol } Co} = .972 \text{ g } CoCl_2 \cdot 6H_2O \text{ desired}\]

\[.3 \times (.0409 \text{ mol Co}) \times \frac{197.91 \text{ g } MnCl_2 \cdot 4H_2O}{1 \text{ mol } Mn} = 2.425 \text{ g } MnCl_2 \cdot 4H_2O \text{ desired}\]

\[.6 \times (.0409 \text{ mol Co}) \times \frac{237.71 \text{ g } NiCl_2 \cdot 6H_2O}{1 \text{ mol } Ni} = 5.826 \text{ g } NiCl_2 \cdot 6H_2O \text{ desired}\]

At this point we place the transition metal chloride salts in clean and empty 250 mL Kimax beakers. To this, we add approximately 20 mL of deionized water to the powder and stir. The beakers are then covered with watch glasses to prevent accidental contamination from the environment. It has
been confirmed in previous studies (and will be examined later by X-ray diffraction) that the components mix completely and the resulting solution is homogeneous.⁴

Now that the samples contain the desired ratio of metal ions and chlorine, we attempt to achieve the desired hydration state. We use a heat treatment and place the samples in an oven at 80±2°C. Since rust is a potential contaminant from a dirty oven (though the oven ceiling was cleaned), we keep the samples covered by the watch glasses. To avoid water occlusions from developing, we break apart and crush the crystals into a powder repeatedly as the samples approach dryness. When the sample is thought to be at the correct hydration state, we quickly remove the powder, place the sample in a closed vial, and wrap with laboratory film (to rule out exposure to water in the external atmosphere) and place in a desiccator for storage. Then thermogravimetric analysis (TGA) is performed to confirm the hydration state. If the hydration state was less significantly less than two, we would place the sample back in a beaker, add 20 mL of deionized water, stir, and use a less rigorous heat treatment. If the sample had a hydration state significantly greater than two, we simply place the sample back in the oven for more treatment. The net, successful treatment for all samples is shown:

<table>
<thead>
<tr>
<th>Desired Sample</th>
<th>Temperature Range(°C)</th>
<th>Duration (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₀.₁Mn₀.₃Ni₀.₆Cl₂·₂H₂O</td>
<td>79-82</td>
<td>46</td>
</tr>
<tr>
<td>Co₀.₁Mn₀.₆Ni₀.₃Cl₂·₂H₂O</td>
<td>81-85</td>
<td>30.5</td>
</tr>
<tr>
<td>Co₀.₃Mn₀.₁Ni₀.₆Cl₂·₂H₂O</td>
<td>81-85</td>
<td>30</td>
</tr>
<tr>
<td>Co₀.₃Mn₀.₆Ni₀.₁Cl₂·₂H₂O</td>
<td>79-84</td>
<td>32</td>
</tr>
<tr>
<td>Co₀.₆Mn₀.₁Ni₀.₃Cl₂·₂H₂O</td>
<td>81-86</td>
<td>24.5</td>
</tr>
<tr>
<td>Co₀.₆Mn₀.₃Ni₀.₁Cl₂·₂H₂O</td>
<td>79-84</td>
<td>32</td>
</tr>
</tbody>
</table>
Thermogravimetric Analysis (TGA):

Thermogravimetric Analysis is the process by which a sample is carefully weighed while being subjected to a heat treatment in an inert environment. The change in mass can be followed as the temperature varies and will allow us to determine the mass loss and identify what molecule is being driven off of the sample and the composition by weight of that molecule in the original sample. In our case, we wish to calculate the hydration state, readily done as it is water which is driven off in the six compositions.

To do this, we will use a small amount of each sample (about 12 mg), making sure to minimize exposure time to the surrounding air, as the hygroscopic samples can continue to pick up water. This small portion is then placed on the pan in the TGA and weighed accurately. Starting from room temperature, the sample is then heated in an inert N₂ atmosphere at a rate of 5°C per minute until 300°C is reached. We can assume that this temperature range will only drive off the H₂O present in the sample (and not any other species because the metal chloride bonds are too strong). Thus the change in mass is purely the change in water content. A mass vs. temperature curve is created and if the observed change of mass is within 2% of the theoretical change in mass, corresponding to within an error in the of 0.005 in the actual to theoretical ratio of initial to final mass, we are satisfied. The curves for each of the six concentrations after their final successful heat treatment can be seen in figures 9 through 14. Table 3 summarizes the TGA results.
Table 3: Thermogravimetric Analysis after Final Successful Heat Treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>FW dihydrate complex (g)</th>
<th>FW anhydrous complex (g)</th>
<th>Theoretical (\frac{\text{initial mass}}{\text{final mass}})</th>
<th>Observe (\frac{\text{initial mass}}{\text{final mass}})</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Co}<em>{0.1}\text{Mn}</em>{0.3}\text{Ni}_{0.6}\text{Cl}_2)</td>
<td>146.86</td>
<td>110.86</td>
<td>0.781</td>
<td>0.784</td>
<td>0.003</td>
</tr>
<tr>
<td>(\text{Co}<em>{0.1}\text{Mn}</em>{0.6}\text{Ni}_{0.3}\text{Cl}_2)</td>
<td>163.37</td>
<td>127.37</td>
<td>0.780</td>
<td>0.776</td>
<td>0.004</td>
</tr>
<tr>
<td>(\text{Co}<em>{0.3}\text{Mn}</em>{1}\text{Ni}_{0.6}\text{Cl}_2)</td>
<td>165.29</td>
<td>129.29</td>
<td>0.782</td>
<td>0.780</td>
<td>0.002</td>
</tr>
<tr>
<td>(\text{Co}<em>{0.3}\text{Mn}</em>{0.6}\text{Ni}_{1}\text{Cl}_2)</td>
<td>165.36</td>
<td>129.36</td>
<td>0.780</td>
<td>0.775</td>
<td>0.005</td>
</tr>
<tr>
<td>(\text{Co}<em>{0.6}\text{Mn}</em>{1}\text{Ni}_{0.3}\text{Cl}_2)</td>
<td>163.41</td>
<td>127.41</td>
<td>0.782</td>
<td>0.782</td>
<td>0.001</td>
</tr>
<tr>
<td>(\text{Co}<em>{0.6}\text{Mn}</em>{0.3}\text{Ni}_{1}\text{Cl}_2)</td>
<td>164.61</td>
<td>128.61</td>
<td>0.781</td>
<td>0.781</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Sample Calculations for \(\text{Co}_{0.1}\text{Mn}_{0.3}\text{Ni}_{0.6}\text{Cl}_2\cdot2\text{H}_2\text{O}\):

\[
\text{FW of dihydrate} = 0.1 (58.93g) + 0.3 (54.94g) + 0.6(58.70g) + 2(35.45g) + 2(18.00g) \\
= 164.50 \text{ g}
\]

\[
\text{FW of anhydrous} = 0.1 (58.93g) + 0.3 (54.94g) + 0.6(58.70g) + 2(35.45g) \\
= 128.50 \text{ g}
\]

\[
Theoretical \text{ ratio} = \frac{128.50}{164.50} = 0.781
\]

\[
\text{Difference} = 0.784 - 0.781 = 0.003
\]
Figure 9: Thermogravimetric Analysis for Co$_3$Mn$_3$Ni$_6$
Figure 10: Thermogravimetric Analysis for $\text{Co}_{0.1}\text{Mn}_{0.6}\text{Ni}_{3}$
Figure 11: Thermogravimetric Analysis for Co$_3$Mn$_3$Ni$_1$
Figure 12: Thermogravimetric Analysis for Co$_3$Mn$_3$Ni$_6$
Figure 13: Thermogravimetric Analysis for $\text{Co}_6\text{Mn}_1\text{Ni}_3$
Figure 14: Thermogravimetric Analysis for Co$_3$Mn$_3$Ni$_1$
**X-Ray Diffraction Method:**

X-ray powder diffraction on solid substances is a useful characterization method. The following compositions for this system will be analyzed from a powder x-ray perspective: \( \text{Co}_{0.33}\text{Mn}_{0.33}\text{Ni}_{0.33} \), \( \text{Co}_{0.3}\text{Mn}_{0.6}\text{Ni}_{0.1} \), \( \text{Co}_{0.2}\text{Mn}_{0.4}\text{Ni}_{0.4} \), \( \text{Co}_{0.6}\text{Mn}_{0.2}\text{Ni}_{0.2} \), and \( \text{Co}_{0.6}\text{Mn}_{0.3}\text{Ni}_{0.1} \). The selections of these compositions were made to provide a survey over a moderate range of composition space, while still including samples which exhibit striking features in the low temperature susceptibility analysis. To do so, we expeditiously remove a portion of the sample, and immediately grind the sample down to fine powder with a pestle and mortar in a cool, dry room. When the sample has an appropriate consistency, a small amount of Paratone, an organic oil that will not react with our substances, is applied with a spatula and mixed entirely with the powder until a quite viscous slush is created. The film is then applied to a specific stage which can be mounted on the X-ray diffractometer instrument. Since the samples are hydroscopic, this entire process is done with great urgency so that the X-ray measurements are made on the correct hydration state. It is not unreasonable to expect the oil to protect the sample from moisture in the air, measurements are made in a fifteen minute set of scans which is enough to yield adequate data.

X-ray diffraction operates on the principle that electrons can diffract x-rays. By bombarding a single crystal with X-rays and measuring the diffraction angle and intensities, one can quantify the electron density and relative location of all atoms, thus identifying the crystal structure. However, with powder samples not in the cubic system, structure determination is not very feasible. Our goal here is merely estimation of homogeneity. The instrument will measure the spectrum from the powder-oil slush from a variety of angles and create three images of the spectrum. These images can then be manipulated using the APEX program to quantify the spectrum and compile a raw data file. The program EVA can convert this data file into a plot of the intensity versus twice the diffraction angle (2θ).
Magnetic Measurements:

With the confirmation of the desired water content, we now wish to study the magnetic behavior of the ternary magnetic system. We use a Princeton Applied Research Vibrating Sample Magnetometer and a Janis Research Cryostat. A simplification of this set up is depicted below.

The applied field induces a magnetization in the sample. The remanent field of the electromagnet is around 60 G. However, this small field itself is not adequate and an applied electric current through huge copper coils around the magnet pole pieces and induces a larger magnetic field. Mainly limited by the size of the electric current, it is possible for us to attain fields ranging from as small as 60G to nearly 16000G. We vary the field in two situations: 1.) as the temperature increases to ensure that a large enough magnetization is present in the sample and 2.) During magnetization hysteresis measurements. The temperature is regulated by the cryostat filled with liquid helium. Liquid helium serves as our coolant because of its low boiling temperature and its non-magnetic properties will not affect our measurements. Since liquid helium boils at 4.2K at atmospheric pressure, a filled cryostat would eventually equilibrate to this temperature. To attain temperatures greater than 4.2K, there exists an entire circuit devoted to heating the environment in the cryostat. Since power can be dissipated in an ohmic device in the form of heat, we will simply run a current through a resistor and allow it to heat helium gas that flows past the resistor to the sample. We can regulate the temperature by simply
controlling this current while supplying a constant supply of helium liquid converting to gas and flowing this gas past the sample. To attain temperatures lower than 4.2K, we will pump on the liquid helium in the cryostat to lower the vapor pressure and consequently the boiling point of the helium, and pull this colder gas out of the cryostat and past the sample. Our pump system is able to consistently achieve temperatures as low as 1.7K. It is of note that one problem with decreasing the temperature below the boiling point occurs at 2.174K. This is the location of helium’s lambda transition. At this temperature, helium is superfluid and it becomes difficult to maintain a steady temperature over this range with our method. Usually, there is a small gap in our low-temperature data at this temperature range, and we avoid collecting isotherm readings near this temperature due to this phenomenon.

The important raw information necessary for calculations is the thermometer voltage readings which will give the temperature of the sample, the net magnetic moment of the sample and the strength of the applied field. A magnetic probe rests next to the cryostat in between the poles of the magnet and measures the applied field. To measure the temperature of the sample under study, we use a Cernox resistance thermometer. Since resistance is a function of temperature, we can extrapolate the temperature of the sample by applying a small steady current and the measuring voltage drop across the resistance thermometer near the sample. It is important to note here that “thermal voltages” do occur. Temperature gradients and strain in the wires produce these voltages. In a fixed system, the thermal voltages do not change with current. Therefore, to remove this background thermal voltage, we simply reverse the current flow in circuit, and measure the voltage drop across the resistor in the other direction. The thermal voltage will maintain the same sign and magnitude, while the applied voltage will maintain its magnitude but reverse its sign. We record a volt reading in both directions. The correction to eliminate any thermal voltage is by simply the average of the magnitudes of these two voltages (the thermal voltage adds as much to the direction as it subtracts from the other). Later, using the averaged (or actual) magnitude of these voltages and measured current, we calculate
the resistance and interpolate the temperature by using a calibration table provided with the thermometer. Lastly, the magnetometer itself measures the magnetization in the sample. To do this, we invoke Faraday’s Law of electromagnetic induction which states that a changing magnetic flux induces a voltage in nearby circuit. The loudspeaker vibrates the sample which had in it an induced magnetic moment. This vibration causes a changing magnetic flux and consequently an induced voltage and current in “pick-up coils” near the sample. The magnetometer takes these readings from the pick-up coils and converts them into a magnetic moment measurement which we record.

We take the prepared compositions and quickly weigh to four or five significant figures approximately 0.13 g of one composition and pack it into a specifically designed nonmagnetic sample tube. The tube is quickly mounted on the sample rod, inserted in the cryostat and flushed with helium to preserve the sample’s hydration state. After the sample is cooled to the boiling point of liquid helium, the vibrating magnetometer must be saddled. This “saddling” places the sample in the optimal location to measure its magnetization and involves adjusting the sample position in all three directions of space. We then zero the magnet probe which measures the applied field. In order to ensure that a strong enough magnetization is being produced in the sample, we start at 100G and double the applied field until the magnetometer reads three digits on the lowest scale($10^{-3}$ emu). During the course of the run, as we gradually increase temperature, there is a tendency for the magnetic moment to decrease. If the magnetic moment drops below $100 \times 10^{-3}$ emu, we will double the applied field. Doubling the applied field tends to double the magnetization and thus preserve three significant figures in all our readings regardless of temperature.

Since liquid helium is a costly commodity, we try to orchestrate our runs efficiently and start with heating the sample instead of cooling which requires pumping and would quickly evaporate the coolant. The high temperature data (from approximately 30 K – 300K) should be almost linear and will
be fitted to the Curie-Weiss law. Since deviations from this law occur mainly at low temperatures, we initially make measurements every tenth of a degree to ensure that we observe all possible fluctuations. Gradually, as temperature increases, we space out the measurements. As mentioned above, the heating process is done by gradually increasing the current flowing through the heating resistor.

Next, we wish to investigate the low temperature behavior. The heater current is shut off and the sample is allowed to cool back down to the boiling point of liquid helium. By gradually exposing the system to a vacuum line and pumping down on the cryogenic, we can attain the lower temperatures, again making sure to take measurements frequently to observe all possible features. We combine decreasing temperature data with the previously measured increasing temperature data to assess the behavior of the system over the low temperature range (usually from 1.7K to 4.2 K and somewhat above).

Lastly, to collect the isotherm data, we simply control the temperature in a similar manner (using a heater current for temperatures above the boiling point and the pump for temperatures below). This requires constant feedback and strict control to maintain a small voltage range. We record the maximum and minimum voltage observed during the run and average this value to measure the temperature during the investigation. With temperature relatively constant, we increase the field from about 60 G to 15000 G, and then decrease back to the original low field over about an hour. By comparing the data of increasing field with the decreasing field, one can see if hysteresis is present. In between hysteresis data collection of two different temperature runs, any possible remaining magnetization in the sample from the previous high field application is removed by briefly raising the temperature, while in the small remanent field of the magnet.

In all situations, the above experimental apparatus and data collection involve or yield the following information: mass of the sample, current through the resistance thermometer, two voltages
through the resistance thermometer (one in each direction), applied magnetic field, and measured magnetic moment.
Voltage, Temperature and Moment Data Processing:

We first need to calculate the temperature at which the measurements were being made. First, any possible thermal voltages must be removed. This is done by simply averaging the magnitude of the voltages (forward and reverse).

\[ V_{\text{actual}} = \frac{|V_{\text{forward}}| + |V_{\text{reverse}}|}{2} \]  \hspace{1cm} (23)

Where \( V \) is the voltage in volts.

Next, Ohm’s law and the measured current through the thermometer resistor will yield the resistance.

\[ R = \frac{V_{\text{actual}}}{I} \]  \hspace{1cm} (24)

Where \( R \) is the resistance in ohms and \( I \) is the current in amps.

This resistance is substituted into a one of four fitting equations (depending on the measured voltage range) previously produced for this Cernox resistance thermometer to yield a temperature. These fitting equations can be seen on lines 55 to 99 of the Matlab code (Appendix).

With the temperature known, susceptibility must now be computed. Susceptibility is given by equation:

\[ \chi = \frac{M}{H} \]  \hspace{1cm} (25)

Where \( \chi \) is susceptibility in emu/G, \( M \) is magnetic moment in emu, and \( H \) is the applied field in G.

The inverse susceptibility is also calculated by simply taking the inverse of equation 3.
One correction made is for diamagnetic susceptibility. Diamagnetism is the tendency for a material to create a magnetic field in opposition to an applied field, thus changing the measured magnetic moment. According to Carlin, diamagnetic susceptibilities are largely additive (and temperature independent). So in order to correct for diamagnetism, we consult a published table of the individual components (Mn, Co, Ni, Cl, and H$_2$O) and simply use a mole fraction combination of these values to calculate the net diamagnetism for each composition. We then just adjust the magnetic moment reading for this correction.

A demagnetization correction is also applied to the data. Demagnetization is the reduction of magnetic induction due to the internal field of a system. The demagnetization is calculated from the known demagnetization values of the components, in a similar method to the diamagnetism correction. These corrections tend to be very small compared to the calculated magnetization and can be seen in Matlab lines 108 and 110 for demagnetization and diamagnetism respectively.

Another correction made to the magnetic susceptibility data is based upon the length expansion or length contraction of the apparatus with temperature. As stated before, the sample is saddled initially by adjusting the position. During the course of the measurement as temperature changes, the sample tube lengthens and contracts, changing the position ever so slightly. A previously determined correction for the sample tube expansion is applied.

With the temperature, susceptibility and inverse susceptibility now known at every point, valuable plots can be formed.
Data Analysis for Curie Weiss Plots:

The Curie Weiss law states the following:

\[ \chi = \frac{C}{T-\theta} \]  \hspace{1cm} (21)

Where \( \chi \) is susceptibility, \( T \) is temperature in K, and \( C \) and \( \theta \) are constants.

Close inspection shows that the inverse of the Curie Weiss law yields a more useful form.

\[ \chi^{-1} = \frac{1}{C} T - \frac{\theta}{C} \]  \hspace{1cm} (26)

A plot of the inverse of susceptibility versus temperature will create a line of slope \( 1/C \) and intercept of \( -\theta/C \), according to Curie Weiss law. We plot the inverse susceptibility versus temperature, fit the high temperature linear region (which is generally the 30-300K range) and determine the values of \( \theta \) and \( C \) from the slope and intercept. This allows us to comment on the net interaction characteristics of the system (ferromagnetic, antiferromagnetic, etc.). The linear fitting equations (lines 55 to 99 of Matlab) yields the uncertainty in the slope and intercept (\( \sigma_m \) and \( \sigma_b \) respectively). First the corresponding uncertainty in \( C \) is calculated by the following method:

\[ m = \frac{1}{C} \]  \hspace{1cm} (27)

Taking the partial derivative:

\[ \sigma_m = \frac{-1}{C^2} \delta C \]  \hspace{1cm} (28)

Solving for \( \delta C \) and recognizing that uncertainty is always positive yields.

\[ \delta C = |-C^2 (\sigma m)| \]  \hspace{1cm} (29)
Where $\delta_m$ is the uncertainty in the slope previously calculated and $C$ is the Curie constant previously calculated for that sample.

For the uncertainty in $\theta$, we use the following:

$$ b = \frac{-\theta}{c} $$  \hspace{1cm} (30)

Taking the partial derivative:

$$ \sigma_b = \frac{-\delta\theta + \delta C + \theta}{c^2} $$  \hspace{1cm} (31)

Solving for $\delta \theta$ and recognizing again that uncertainty is an absolute value:

$$ \delta \theta = \left| \frac{-\sigma_b C^2 + \delta C + \theta}{c} \right| $$  \hspace{1cm} (32)
Data Analysis for Magnetic Transition Plot:

We attempt to determine the presence and location of magnetic transitions in the samples. A plot of susceptibility versus temperature is the basis for this determination. The low temperature data (under 20K) usually show features such as maxima, minima, shoulders and inflection points. These features serve as the possible locations of magnetic transitions, although, theoretically, magnetic transitions occur at a temperature slightly lower than the maximum. We visually estimate the points that correspond to graphical features and carefully calculate the corresponding temperature. For samples containing multiple features, multiple identifications will be made. A three dimension plot of x, y, and transition temperature is constructed (x and y being the variables that describe transition metal composition). At this point, only the temperature of the most reliable feature apparent in the plots – typically a susceptibility maximum or well-formed shoulder- is employed
Data Analysis for Hysteresis Plots:

The low temperature behavior of the samples also usually shows hysteresis. That is, the magnetic moment of the sample is dependent on its history in the applied magnetic field. One isothermally increases the magnetic field from the remanent field (c.a. 60 G) to a field of 15.9 kG and then decreasing back to the permanent field again. At select applied field values we measure the magnetic moment of the sample under study. By plotting the magnetic moment versus field, we can detect any difference between increasing and decreasing fields. A hysteresis loop is seen graphically when the moment measured when coming from a higher field is different than the moment measured when coming from a decreasing field over a definite applied field range. These measurements are made for several different temperatures for each sample, chosen based upon the magnetic transition temperature and the size of any hysteresis, if present. Also, any non-linearity in the magnetic moment versus applied field is noted.

In certain cases, we further analyze the hysteresis loop by using polynomial equations to fit the increasing field and decreasing field data. We then integrate these equations over the extent of the hysteresis loop to calculate the total area. When hysteresis is present, we can imagine that energy from the previous, high field is being stored in the orientation of the sample. A significant time dependence in these readings was not noted in the studied system. To quantitatively measure this energy, we employ the Arrhenius equation used in kinetics:

\[ k = Ae^{-\left(\frac{E_a}{RT}\right)} \]  \hspace{1cm} (33)

Where \( k \) is the rate constant, \( E_a \) is the activation energy, \( A \) is a pre-exponential factor, \( R \) is the gas constant, and \( T \) is the absolute temperature. Taking the natural log yields:

\[ \ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \]  \hspace{1cm} (34)
In kinetics, one conducts multiple isothermal measures of the rate constant. A linear fit of the natural log of the rate constant versus $T^{-1}$ yields a slope of the activation energy over the gas constant. In our case, we can think of the activation energy as the energy necessary to relax from the magnetic orientation previously stored in the sample from the higher field on decreasing the field. The area of the hysteresis loop can be equated to the rate constant, $k$. In kinetics, $k$ is the number of collisions which result in a reaction per unit time. The area of the loop is a relative measure of the number of complexes that are “storing” the previous orientation from the higher field at that time. Thus a plot of the natural log of the area (in arbitrary units) versus the inverse of temperature will have a slope of $-\frac{E_a}{R}$ and an intercept of $\frac{1}{A}$. The opposite of the slope ($-\frac{E_a}{R}$) has units of temperature, and we can think of this as the temperature associated with the activation of hysteresis in the sample.
Results:

High temperature Data and Curie-Weiss fits:

Table 4 offers a summary of the Curie Weiss plots and their respective linear fits (on pp).

Table 4: Summary Table for High Temperature Curie-Weiss Fit

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>Y</th>
<th>T_{min} (K)</th>
<th>T_{max} (K)</th>
<th>m</th>
<th>b</th>
<th>σ_{m}</th>
<th>σ_{b}</th>
<th>C</th>
<th>Θ</th>
<th>δC</th>
<th>δΘ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co_{1/4}Mn_{3/4}Ni_{6}</td>
<td>.9</td>
<td>.6</td>
<td>30</td>
<td>200</td>
<td>0.3797</td>
<td>1.588</td>
<td>0.0017</td>
<td>0.150</td>
<td>2.634</td>
<td>-4.182</td>
<td>0.012</td>
<td>0.157</td>
</tr>
<tr>
<td>Co_{3/4}Mn_{1/4}Ni_{3}</td>
<td>.9</td>
<td>.3</td>
<td>30</td>
<td>145</td>
<td>0.2807</td>
<td>3.443</td>
<td>0.0018</td>
<td>0.133</td>
<td>3.563</td>
<td>-12.266</td>
<td>0.023</td>
<td>0.155</td>
</tr>
<tr>
<td>Co_{3/4}Mn_{1/4}Ni_{6}</td>
<td>.7</td>
<td>.6</td>
<td>30</td>
<td>300</td>
<td>0.4173</td>
<td>1.886</td>
<td>0.0017</td>
<td>0.251</td>
<td>2.396</td>
<td>-4.520</td>
<td>0.010</td>
<td>0.259</td>
</tr>
<tr>
<td>Co_{3/4}Mn_{1/4}Ni_{1}</td>
<td>.7</td>
<td>.1</td>
<td>30</td>
<td>300</td>
<td>0.2412</td>
<td>1.420</td>
<td>0.0037</td>
<td>0.573</td>
<td>4.146</td>
<td>-5.887</td>
<td>0.064</td>
<td>0.595</td>
</tr>
<tr>
<td>Co_{3/4}Mn_{1/4}Ni_{3}</td>
<td>.4</td>
<td>.3</td>
<td>30</td>
<td>285</td>
<td>0.3373</td>
<td>2.998</td>
<td>0.0015</td>
<td>0.249</td>
<td>2.965</td>
<td>-8.888</td>
<td>0.013</td>
<td>0.262</td>
</tr>
<tr>
<td>Co_{3/4}Mn_{1/4}Ni_{1}</td>
<td>.4</td>
<td>.1</td>
<td>30</td>
<td>300</td>
<td>0.2971</td>
<td>3.510</td>
<td>0.0011</td>
<td>0.136</td>
<td>3.366</td>
<td>-11.814</td>
<td>0.012</td>
<td>0.149</td>
</tr>
</tbody>
</table>

Note: In most cases one more figure than is genuinely significant is displayed.

Where x and y come from the notation: Co_{1-x}Mn_{x}Ni_{y} for the sample and define the composition. T_{min} and T_{max} are the lowest and highest temperature value point included in the linear fit equation respectively. The values m and b are the slope (in mol emu^{-1}K^{-1}) and y-intercept (in mol emu^{-1}) of the fit, respectively. C (K emu mol^{-1}) and Θ (K) are the Curie constants. The slope, y-intercept and the respective uncertainty calculations were made using linear least squares fitting method (lines 55 to 99 of the Matlab program in the appendix).
Sample Calculations for Co$_{0.1}$Mn$_{0.3}$Ni$_{0.6}$:

**Best Fit Equation:** $y = 0.3797x + 1.588$, $\sigma_m = 0.0017$, $\sigma_b = 0.150$

\[
C = \frac{1}{m} = \frac{1}{0.3797} = 2.634 \text{ K emu/mol}
\]

\[
\theta = -\frac{b}{C} = -\frac{1.588}{2.634} = -4.182 \text{ K}
\]

\[
\delta C = |-C^2 (\sigma m)| = |-(2.634)^2 (.0017)| = .012 \text{ K emu/mol}
\]

\[
\delta \theta = \left| -\frac{\sigma_b \cdot C^2 + \delta C \cdot \theta}{C} \right| = \left| -\frac{(.150) \cdot (2.634)^2 + (.012) \cdot (-4.182)}{(2.634)} \right| = 0.157 \text{ K}
\]

One can compare the values of $C$ and $\theta$ to those we expect if no new interactions existed in the samples by simply finding the weighted sum of those constants from the pure metal chloride complexes (previously studied here). It is reasonable to expect our measured $C$ values to be close to the linear combination of the pure components because $C$ is dependent on a single ion property as the Curie Law assumed non-interacting ions (at least on a per spin basis). It is less reasonable for $\theta$ as theta is dependent on all interactions present and new interactions that will exist in the mixture of unlike ions. The values for the pure components were calculated in this laboratory through Curie-Weiss fits on the pure components:
Table 5: Curie-Weiss Constants of Pure Components Measured Previously in this Laboratory

<table>
<thead>
<tr>
<th>Complex</th>
<th>C</th>
<th>Θ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl₂·2H₂O</td>
<td>4.460</td>
<td>-14.5</td>
</tr>
<tr>
<td>NiCl₂·2H₂O</td>
<td>1.273</td>
<td>11.2</td>
</tr>
<tr>
<td>CoCl₂·2H₂O</td>
<td>3.035</td>
<td>-7.5</td>
</tr>
</tbody>
</table>

The pure values were then used to calculate the expected constants for our mixtures. The expected and measured constants are shown for comparison in Table 6.

Table 6: Comparison of Expected and Measured Curie-Weiss Constants

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (Expected)</th>
<th>C (Actual)</th>
<th>Θ (Expected) (K)</th>
<th>Θ (Actual) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₁Mn₃Ni₆</td>
<td>2.405</td>
<td>2.634</td>
<td>1.62</td>
<td>-4.18</td>
</tr>
<tr>
<td>Co₁Mn₆Ni₃</td>
<td>3.361</td>
<td>3.563</td>
<td>-6.09</td>
<td>-12.27</td>
</tr>
<tr>
<td>Co₃Mn₁Ni₆</td>
<td>2.120</td>
<td>2.396</td>
<td>3.02</td>
<td>-4.52</td>
</tr>
<tr>
<td>Co₅Mn₄Ni₁</td>
<td>3.714</td>
<td>4.146</td>
<td>-9.83</td>
<td>-5.89</td>
</tr>
<tr>
<td>Co₆Mn₁Ni₃</td>
<td>2.649</td>
<td>2.965</td>
<td>-2.59</td>
<td>-8.89</td>
</tr>
<tr>
<td>Co₆Mn₃Ni₁</td>
<td>3.286</td>
<td>3.366</td>
<td>-7.73</td>
<td>-11.81</td>
</tr>
</tbody>
</table>

As predicted, the expected and the actual values of C agree definitely better than do those values of Θ. One notes a tendency for C (expected) to be somewhat less than C (actual). Also, although the Θ for the high Nickel components is predicted to be positive (predicting ferromagnetic behavior) it is actually negative (antiferromagnetic behavior). Thus, the distribution of interactions in the mixture is strongly modified by the new interaction between the unlike ions.
Figure 16: Curie Weiss Fit for $\text{Co}_{1-x}\text{Mn}_y\text{Ni}_{x-y}\text{Cl}_2\cdot2\text{H}_2\text{O}$

$\chi^{-1}$ (mol/emul) vs. $T$ (K)

Co$_{1-x}$Mn$_y$Ni$_{x-y}$Cl$_2$·2H$_2$O

$x = 0.90$  $y = 0.30$

Powder Data

30K - 200K Fit

$y = 0.3797x + 1.588$

$\sigma_m = 0.0017$

$\sigma_b = 0.150$
Figure 17: Curie Weiss Fit for Co$_{1-x}$Mn$_x$Ni$_y$Cl$_2$·2H$_2$O

Co$_{1-x}$Mn$_x$Ni$_{y}$Cl$_2$·2H$_2$O

$x = .90$  $y = .60$

Powder Data

30K - 145K Fit

$y = 0.2807x + 3.443$

$\sigma_m = 0.0018$

$\sigma_b = 0.133$
Figure 18: Curie Weiss Fit for Co$_{3}$Mn$_{1}$Ni$_{6}$

Co$_{1-x}$Mn$_{y}$Ni$_{x-y}$Cl$_2$·2H$_2$O

x = .70  y = .10

Powder Data

30-K-300K Fit

y = 0.4173x + 1.886

σ$_m$=0.0017

σ$_b$=0.251
Figure 19: Curie Weiss Fit for Co$_{3}$Mn$_{y}$Ni$_{1-y}$

$$\chi^{-1} (\text{mol/emu})$$

$$T (\text{K})$$

$$\text{Co}_{1-x}\text{Mn}_{y}\text{Ni}_{x-y}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$$

$$x = 0.70 \quad y = 0.60$$

Powder Data

$$y = 0.2412x + 1.4199$$

$$\sigma_m = 0.0037$$

$$\sigma_b = 0.573$$
Figure 20: Curie Weiss Fit for Co$_{0.6}$Mn$_{0.1}$Ni$_{0.3}$

$\text{Co}_{1-x}\text{Mn}_y\text{Ni}_{x-y}\text{Cl}_2\cdot2\text{H}_2\text{O}$

$x = 0.40 \quad y = 0.10$

Powder Data

30K - 285K Fit

$y = 0.3373x + 2.998$

$\sigma_m = 0.0015$

$\sigma_b = 0.249$
Figure 21: Curie Weiss Fit for Co$_{0.4}$Mn$_{0.3}$Ni$_{0.3}$

\[ y = 0.2791x + 3.510 \]
\[ \sigma_m = 0.0011 \]
\[ \sigma_b = 0.136 \]

Co$_{1-x}$Mn$_y$Ni$_{x-y}$Cl$_2$·2H$_2$O

Powder Data
Low Temperature Behavior:
For the low temperature data we plotted susceptibility versus temperature. Figures 22 through 27 are those plots. Below is a summary of that information.

Table 7: Summary of Low Temperature Behavior

<table>
<thead>
<tr>
<th>Name</th>
<th>X</th>
<th>Y</th>
<th>T1 (K)</th>
<th>T2 (K)</th>
<th>T3 (K)</th>
<th>T4 (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co&lt;sub&gt;0.1&lt;/sub&gt;Mn&lt;sub&gt;3&lt;/sub&gt;Ni&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.9</td>
<td>0.3</td>
<td>5.4</td>
<td>Shoulder</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.1&lt;/sub&gt;Mn&lt;sub&gt;6&lt;/sub&gt;Ni&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.9</td>
<td>0.6</td>
<td>3.8</td>
<td>Shoulder</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.3&lt;/sub&gt;Mn&lt;sub&gt;1&lt;/sub&gt;Ni&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.7</td>
<td>0.1</td>
<td>7.8</td>
<td>Maximum</td>
<td>2.7</td>
<td>Minimum</td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.3&lt;/sub&gt;Mn&lt;sub&gt;6&lt;/sub&gt;Ni&lt;sub&gt;1&lt;/sub&gt;</td>
<td>0.7</td>
<td>0.6</td>
<td>3.8</td>
<td>Shoulder</td>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.4&lt;/sub&gt;Mn&lt;sub&gt;1&lt;/sub&gt;Ni&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.4</td>
<td>0.1</td>
<td>7.4</td>
<td>Maximum</td>
<td>2.3</td>
<td>Minimum</td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.6&lt;/sub&gt;Mn&lt;sub&gt;3&lt;/sub&gt;Ni&lt;sub&gt;1&lt;/sub&gt;</td>
<td>0.4</td>
<td>0.3</td>
<td>12.0</td>
<td>Maximum</td>
<td>5.2</td>
<td>Minimum</td>
</tr>
<tr>
<td>Co&lt;sub&gt;0.9&lt;/sub&gt;Mn&lt;sub&gt;3&lt;/sub&gt;Ni&lt;sub&gt;6&lt;/sub&gt;</td>
<td>0.9</td>
<td>0.6</td>
<td>3.7</td>
<td>Shoulder</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>* Co&lt;sub&gt;0.2&lt;/sub&gt;Mn&lt;sub&gt;4&lt;/sub&gt;Ni&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.8</td>
<td>0.4</td>
<td>2.6</td>
<td>Shoulder</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>* Co&lt;sub&gt;0.2&lt;/sub&gt;Mn&lt;sub&gt;8&lt;/sub&gt;Ni&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.8</td>
<td>0.2</td>
<td>6.8</td>
<td>Maximum</td>
<td>4.8</td>
<td>Minimum</td>
</tr>
<tr>
<td>*Co&lt;sub&gt;0.4&lt;/sub&gt;Mn&lt;sub&gt;4&lt;/sub&gt;Ni&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.6</td>
<td>0.2</td>
<td>8.0</td>
<td>Shoulder</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>* Co&lt;sub&gt;0.3&lt;/sub&gt;Mn&lt;sub&gt;3&lt;/sub&gt;Ni&lt;sub&gt;33&lt;/sub&gt;</td>
<td>0.67</td>
<td>0.33</td>
<td>4.9</td>
<td>Maximum</td>
<td>2.4</td>
<td>Minimum</td>
</tr>
<tr>
<td>*C.4M.2N.2</td>
<td>0.6</td>
<td>0.2</td>
<td>6.5</td>
<td>Maximum</td>
<td>2.3</td>
<td>Minimum</td>
</tr>
<tr>
<td>*C.6M.2N.2</td>
<td>0.4</td>
<td>0.2</td>
<td>5.5</td>
<td>Maximum</td>
<td>2.9</td>
<td>Minimum</td>
</tr>
<tr>
<td>*Mn</td>
<td>1</td>
<td>1</td>
<td>7.2</td>
<td>Maximum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Co</td>
<td>0</td>
<td>0</td>
<td>17.5</td>
<td>Maximum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Ni</td>
<td>1</td>
<td>0</td>
<td>8</td>
<td>Maximum</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Those samples that have the designation of * are compositions run by previous researchers in this laboratory. These samples are used in the three dimensional plot so that a larger portion of composition space is shown and the global behavior of the system can be better seen.

Simple visual inspection of the plots shows that the low temperature behavior of the samples is not a simple weighted combination of the pure components. Maxima in susceptibility versus temperature do not generally occur near where such appear for the pure components, as one would expect by linear combination. This fact shows that there is a more complex set of interactions present in the mixed system than in the pure components.

Some of the figures appear to show some features rather near 4.2K with a sudden break or jump in the data. This fictitious feature is caused by the experimental method and associated random shifts in instrument reading occurring an hour or more apart. Liquid helium has an atmospheric boiling point at 4.2K. As mentioned above, we started at this temperature and heated to 300K, then let the system equilibrate back at 4.2K before cooling again by lowering the pressure. Sometimes, the measured magnetic moment at 4.2 K before heating the sample did not match extremely well with the magnetic moment at 4.2 K after. However, the plots are greatly enlarged making this discontinuity seem much exaggerated. The discrepancies associated with the discontinuities are only on the order of a few percent or less.

A trend in many of the compositions is a slight up-turn near or slightly above 2.0K where the susceptibility rapidly increases with small decreases in temperature. Another trend in many samples is a turn over near or below 2.0K where the susceptibility levels off or does not increase nearly as dramatically with small decreases in temperature.
The only samples that display two maxima or shoulders are very similar in composition: \( \text{Co}_0.6\text{Mn}_2\text{Ni}_{1.2} \) and \( \text{Co}_0.6\text{Mn}_{1.1}\text{Ni}_{1.3} \), yet despite the close composition, the graphs themselves are markedly different in which feature is more pronounced (the higher temperature or the lower temperature one).
Figure 22: Low Temperature Susceptibility for \( \text{Co}_{1-x}\text{Mn}_y\text{Ni}_{x-y}\text{Cl}_2\cdot\text{2H}_2\text{O} \)

\[ x = .90 \quad y = .30 \]

Powder Data
Figure 23: Low Temperature Susceptibility for Co_{0.9}Mn_{0.6}Ni_{0.3}Cl_{2}·2H_{2}O

\[
\chi_{(\text{emu/mol})}
\]

\[
T (\text{K})
\]

Co_{1-x}Mn_{y}Ni_{x-y}Cl_{2}·2H_{2}O

x = 0.90  y = 0.60

Powder Data
Figure 24: Low Temperature Susceptibility for $\text{Co}_{0.70}\text{Mn}_{0.10}\text{Ni}_{0.10}$

$\chi_{\text{emu/mol}}$ vs $T$ (K)

$\text{Co}_{1-x}\text{Mn}_y\text{Ni}_{x-y}\text{Cl}_2\cdot2\text{H}_2\text{O}$

$x = 0.70 \quad y = 0.10$

Powder Data
Figure 25: Low Temperature Susceptibility for \( \text{Co}_{x} \text{Mn}_{y} \text{Ni}_{x-y} \text{Cl}_{2} \cdot 2\text{H}_{2}\text{O} \),

\( x = .70 \quad y = .60 \)

Powder Data
Figure 26: Low Temperature Susceptibility for $\text{Co}_x\text{Mn}_{0.1}\text{Ni}_{0.3}$

$\text{Co}_{1-x}\text{Mn}_y\text{Ni}_{x-y}\text{Cl}_2\cdot2\text{H}_2\text{O}$

$x = .40 \quad y = .10$

Powder Data
Figure 27: Low Temperature Susceptibility for Co$_{0.6}$Mn$_{0.3}$Ni$_{0.1}$

\[ \chi \text{ (emu/mol)} \]

\[ T \text{ (K)} \]

Co$_{1-x}$Mn$_y$Ni$_{x-y}$Cl$_2$·2H$_2$O

\[ x = 0.40 \quad y = 0.30 \]

Powder Data
The data from Table 4 are shown in the following three dimensional plots of $T(x,y)$. The plots all contain the same information, but show the data from a different perspective of phase space.

Figure 28: $T_1(x,y)$ for Co$_{1-x}$Mn$_x$Ni$_y$ System from high Nickel Perspective
Figure 29: $T_1(x,y)$ for $\text{Co}_{x}Mn_{x-1}\text{Ni}_{y}$ System from High Cobalt Perspective
Figure 30: $T_1(x,y)$ for $Co_{1-x}Mn_xNi_y$ System from High Manganese Perspective
The temperature plotted was the location of the maximum (if present) or shoulder (if maximum not present) in the susceptibility versus temperature plots. In the case of Co_{0.6}Mn_{1.1}Ni_{3.3} and Co_{0.6}Mn_{3.3}Ni_{4.3}, which both had two of these features, we chose to use the more prominent feature (the 7.4 maximum and 14.1 maximum respectively)
**Hysteresis Results:**

We plot the magnetic moment versus applied field strength for each of samples at a variety of temperatures. Those plots can be seen in figures 31, 32, 33, 34, 35, and 36. Table 8 is a summary of the plots.

**Table 8: Summary of Hysteresis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Shape</th>
<th>Strength of Hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$<em>{1.1}$Mn$</em>{3.6}$Ni$_{0.3}$</td>
<td>1.84</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td>X = 0.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y = 0.30</td>
<td>2.78</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>4.27</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>7.935</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td>Co$<em>{3.1}$Mn$</em>{6.6}$Ni$_{3}$</td>
<td>1.84</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td>X = 0.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y = 0.60</td>
<td>2.78</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td>Co$<em>{3.6}$Mn$</em>{1.1}$Ni$_{6}$</td>
<td>1.84</td>
<td>Slight Upwards Curve</td>
<td>Moderate</td>
</tr>
<tr>
<td>X = 0.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y = 0.10</td>
<td>2.78</td>
<td>Slight Upwards Curve</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>Slight Upwards Curve</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td>9.65</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td>Co$<em>{3.6}$Mn$</em>{6.6}$Ni$_{1}$</td>
<td>1.84</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td>X = 0.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y = 0.60</td>
<td>2.78</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>3.41</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>4.23</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>5.87</td>
<td>Almost Linear</td>
<td>Negligible</td>
</tr>
</tbody>
</table>
Table 9: Summary of Hysteresis (Continued)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Shape</th>
<th>Strength of Hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₀Mn₁Ni₃ X = 0.40</td>
<td>1.84</td>
<td>Upwards Curve</td>
<td>Strong</td>
</tr>
<tr>
<td></td>
<td>2.43</td>
<td>Upwards Curve</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td>3.20</td>
<td>Upwards Curve</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td>4.21</td>
<td>Upwards Curve</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td>5.53</td>
<td>Slight Upwards Curve</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>7.91</td>
<td>Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>8.17</td>
<td>Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td>Co₀Mn₃Ni₁ Y = 0.30</td>
<td>1.84</td>
<td>Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>4.22</td>
<td>Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>8.98</td>
<td>Linear</td>
<td>Negligible</td>
</tr>
<tr>
<td></td>
<td>15.12</td>
<td>Linear</td>
<td>Negligible</td>
</tr>
</tbody>
</table>
Figure 31: $M$ vs. $H$ for $\text{Co}_{1-x}\text{Mn}_x\text{Ni}_y\text{Cl}_2\cdot\text{H}_2\text{O}$ Isotherms. For visual clarity, the magnetization values between consecutive runs were increased by 300 emu/mol.
Figure 32: M vs. H for $\text{Co}_{1-x}\text{Mn}_x\text{Ni}_{y}\text{Cl}_2\cdot\text{H}_2\text{O}$ Isotherms For visual clarity, the magnetization values between consecutive runs were increased by 300 emu/mol.

For $x = 0.90$ and $y = 0.30$,

$\text{Co}_{1-x}\text{Mn}_x\text{Ni}_y\text{Cl}_2\cdot\text{H}_2\text{O}$

Powder Data

- $1.841$ K
- $2.779$ K
- $4.230$ K
Figure 33: $M$ vs. $H$ for $\text{Co}_{3-x}\text{Mn}_x\text{Ni}_{1.6}$ isotherms. For visual clarity, the magnetization values between consecutive runs were increased by 200 emu/mol.

$\text{Co}_{1-x}\text{Mn}_{x-y}\text{Ni}_y\text{Cl}_2\cdot\text{H}_2\text{O}$

$x = 0.70 \quad y = 0.60$

**Powder Data**

- $1.840 \text{ K}$
- $2.780 \text{ K}$
- $4.223 \text{ K}$
- $9.652 \text{ K}$
Figure 34: M vs. H for $\text{Co}_{3}\text{Mn}_{x}\text{Ni}_{1-x}$ isotherms. For visual clarity, the magnetization values between consecutive runs were increased by 300 emu/mol.
Figure 35: $M$ vs. $H$ for $\text{Co}_{0.6}\text{Mn}_{0.1}\text{Ni}_{0.3}$ isotherms. For visual clarity, the magnetization values between consecutive runs were increased by 100, 300, 500, 600, 700, 1000 emu/mol, respectively.
Figure 36: M vs. H for $\text{Co}_{x}\text{Mn}_{y}\text{Ni}_{1-x}$ Isotherms. For visual clarity, the magnetization values between consecutive runs were increased by 200, 300, 600 emu/mol respectively.
The $\text{Co}_{3.3}\text{Mn}_{1.1}\text{Ni}_{0.6}$ sample shows measurable hysteresis but does not lend itself to further analysis. The 2.78 K isotherm oddly shows more hysteresis than the 1.84 K isotherm at the only the 15 kG field. This unusual reading, along with the fact that there were only three isotherms that showed hysteresis, makes further quantitative analysis too difficult without further investigation.

In the case of the strongest hysteresis, $\text{Co}_{6.6}\text{Mn}_{1.1}\text{Ni}_{0.3}$, we further analyze the data by fitting the increasing field data and decreasing field data with polynomial fits. We then integrate the difference of the increasing field fit and the decreasing field fit equation over the hysteresis loop to determine the size of the hysteresis loop or intersection. Those plots and the corresponding fits can be seen in figure 37-41. Below is a summary of results.

**Table 10: Area versus Temperature for $\text{C6M1N3}$**

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>Area (kG emu/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84</td>
<td>183.3</td>
</tr>
<tr>
<td>2.43</td>
<td>115.8</td>
</tr>
<tr>
<td>3.20</td>
<td>65.4</td>
</tr>
<tr>
<td>4.21</td>
<td>33.0</td>
</tr>
<tr>
<td>5.53</td>
<td>29.9</td>
</tr>
<tr>
<td>7.10</td>
<td>20.4</td>
</tr>
</tbody>
</table>
Figure 37: Hysteresis Loop for $\text{Co}_{0.6}\text{Mn}_{0.1}\text{Ni}_{0.3}$ at 1.84 K

$M$ vs. $H$ for $\text{Co}_{0.60}\text{Mn}_{0.10}\text{Ni}_{0.30}\cdot\text{2H}_2\text{O}$ at 1.841K

$y = 0.0022x^6 - 0.1061x^5 + 1.865x^4 - 13.971x^3 + 44.524x^2 + 59.035x + 11.861$

$y = -0.001x^6 + 0.0365x^5 - 0.4481x^4 + 2.3147x^3 - 4.7282x^2 + 109.59x + 1.5837$
Figure 38: Hysteresis Loop for $\text{Co}_{0.60}\text{Mn}_{0.10}\text{Ni}_{0.30}\cdot2\text{H}_2\text{O}$ at 2.43 K

$M$ vs. $H$ for $\text{Co}_{0.60}\text{Mn}_{0.10}\text{Ni}_{0.30}\cdot2\text{H}_2\text{O}$ at 2.426 K

$y = -0.0004x^6 + 0.0074x^5 + 0.0574x^4 - 1.5617x^3 + 8.0637x^2 + 96.64x + 3.7995$

$y = 0.0005x^6 - 0.0381x^5 + 0.8553x^4 - 7.3793x^3 + 25.495x^2 + 81.185x + 4.6323$
Figure 39: Hysteresis Loop for Co$_{0.60}$Mn$_{0.10}$Ni$_{0.30}$$\cdot$2H$_2$O at 3.201 K
Figure 40: Hysteresis Loop for $\text{Co}_{0.60}\text{Mn}_{0.10}\text{Ni}_{0.30}\cdot\text{2H}_2\text{O}$ at 5.53 K

$M\text{ vs. } H$ for $\text{Co}_{0.60}\text{Mn}_{0.10}\text{Ni}_{0.30}\cdot\text{2H}_2\text{O}$ at 5.532K

$y = 0.0007x^6 - 0.0309x^5 + 0.5142x^4 - 3.5066x^3 + 10.681x^2 + 111.98x + 2.015$

$y = 0.0008x^6 - 0.0376x^5 + 0.6125x^4 - 4.1131x^3 + 12.235x^2 + 111.12x + 2.7727$
Figure 41: Hysteresis Loop for Co$_{60}$Mn$_{10}$Ni$_{30}$•2H$_2$O at 7.096 K

$y = 0.0003x^6 - 0.0142x^5 + 0.2461x^4 - 1.8088x^3 + 5.1521x^2 + 151.08x + 0.1732$

$y = 0.0004x^6 - 0.0179x^5 + 0.2625x^4 - 1.5268x^3 + 2.7425x^2 + 155.27x + 0.3582$
We then construct a plot of the natural log of the area versus the inverse temperature according to the Arrhenius equation.

Figure 42 is a depiction of this plot. The data are not exactly linear, but the best fit curve represents a reasonable fit. We find that the slope is 5.56 K. Multiplying by the gas constant, this corresponds to the activation energy of 46.2 J mol\(^{-1}\).
Figure 42: Arrhenius Plot for Co$_{0.6}$Mn$_{0.1}$Ni$_{0.3}$ Isotherms

\[
y = 5.56x - 4.59
\]
X-Ray Diffraction Results:

X-ray diffraction measurements were performed on an instrument designed for crystals, but can operate in powder mode. The data are not of high enough quality to allow detailed structural analysis of the system.

The X-ray diffractograms are shown in figures 43 through 48. The signal peaks were labeled by the EVA program and their corresponding 2θ values are listed in the diffractograms. For our purposes, a qualitative analysis is all that is necessary so more calculations were not performed. When looking at the diffractograms, one should note the relative size, location, and number of peaks.
Figure 43: X-Ray Diffractogram for $C_1M_6N_3$
Figure 44: X-Ray Diffractogram for C2M4N4
Figure 45: X-Ray Diffractogram for C$_{33}$N$_{33}$M$_{33}$
Figure 46: X-Ray Diffractogram for C₆M₁N₃
Figure 47: X-Ray Diffractogram for C₆M₂N₂
Figure 48: X-Ray Diffractogram for C₆M₃N₁
Discussion

Interpretation of X-Ray Diffractograms:

The diffractograms show a large amount of background signal. Fluorescence, which can be attributed to some of the metal ions (as at least cobalt is known to fluoresce), could be the cause of the background signal. However, there is no clear variation in background with cobalt content.

Secondly, and most important to our study, the diffractograms themselves are remarkably similar. The relative intensity of some of the peaks does differ with composition; however, the number and actual location of the peaks themselves is relatively constant. The most noticeable consistent feature is the three large peaks that occur when 2θ is in the range 15° to 20°. Many other, if less prominent, peaks also are observed to occur at very similar angles in the six patterns. This similarity in the location and number of peaks is consistent with the assumption that our samples are homogeneous. Were the samples heterogeneous, there would be more than one type of unit cell in the powder. The diffractogram would be a simply weighted combination of the individual unit cells. Also, if the system lent itself to being inhomogeneous, the diffractograms from different compositions would be drastically different as the types of individual unit cells would be vastly different from composition to composition. This result is not startling, and is expected from previous measurements on related systems. Moreover, the magnetic susceptibility data above, particularly at low temperature (< 20K) provide strong evidence for absence of individual pure components, and some evidence as well for fairly homogeneous mixing.

The diffractograms were also compared to the 2θ values from the previously studied pure components and nothing was found that would suggest non-homogeneous mixing.
High Temperature Behavior and Curie-Weiss Fits:

The high temperature behavior agreed with the Curie-Weiss theory in that over the 30K to 300K high temperature range the susceptibility generally varied linearly with temperature. The respective linear fits were successful. The calculated Curie constants (C) from the fits were slightly less, but still generally agreed with the expected constant attained from the mole fraction combination of the pure components. All the samples had a negative calculated Weiss constant (θ), a sign of antiferromagnetic behavior. This was not expected in the high Nickel (x-y = 0.6) components as the mole fraction θ value was positive (ferromagnetic behavior). The calculated θ values themselves also differed greatly from expectations (not even the order of compositions from least to greatest θ value matched), so clearly complicated interaction between the unlike ions is present not reflected in the individual component θ values.
Low Temperature Plots:

The most immediate and striking observation of the low temperature $\chi^{-1}$ v. T plots is the remarkable differences between relatively similar compositions. These differences between samples (and between the mixed system and the pure components themselves) result from interactions not easily predicted or modeled. The $\chi(T)$ features disagree strongly with the pure components.

Despite the differences, almost all samples exhibit an up-turn near or slightly above 2.0 K. The majority display an additional feature of a turn-over at temperatures near or slightly less than 2.0 K. This could indicate a universal feature in all compositions below the temperature range capable of being measured by our instrument. Previous studies of the pure components noted a similar up-turn in samples containing manganese. An explanation is the presence of impurities. $\text{MnCl}_2\cdot4\text{H}_2\text{O}$ orders antiferromagnetically at $1.6$ K with a relatively large susceptibility (around 1 emu/mol). So the trend of up turns approaching 1.6 K might be a sign of this impurity.\(^7\)

Many listed features can be attributed to magnetic transitions. These transitions can be sought and confirmed elsewhere by measuring the heat capacity of the sample over the low temperature range. One should see the heat capacity behave similar to $\chi^{-1}$ over the same temperature range.

The three dimensional plot of $T(x,y)$ depicts the main (maximum) high temperature feature attributed to a magnetic transition. Yet, it is clear that the survey of composition space is not presently complete. The study only surveys approximately two-thirds of composition space ($0.8 \times 0.8 = .64$). Future preparations beyond this survey can further complete the plot.
Hysteresis:

The majority of the samples did not demonstrate significant hysteresis, and none of the samples demonstrated hysteresis above 10 K. The plots were also generally linear with some plots showing a slight upward curvature in magnetization as the applied field increased. After careful inspection of both the hysteresis and low temperature behavior, one can see that the samples with the largest deviations from linearity or hysteresis loop correlate to those samples with the most prominent features in the low temperature $\chi^{-1}$ vs. $T$ plot. This is to be expected as the stronger the magnetic transition, the greater the energy difference between different ordered states, and the greater chance that hysteresis will be observed.

The sample that displays the most prominent hysteresis, $\text{Co}_0.6\text{Mn}_{1.1}\text{Ni}_{3.4}$, lent itself to further analysis. The hysteresis loops can be approximated by two sets of polynomial fits. Integrating the fits over the extent of the loop will yield a net area for each isotherm. Plotting the natural log of the inverse of the area versus the inverse temperature in accordance with the Arrhenius equation yields a linear plot. Fitting this plot, one can estimate the activation energy for this hysteresis at 46.2 J mol$^{-1}$ or an absolute temperature of 5.56 K. This is a plausible activation energy magnitude for domain wall motion in such a material.
**Conclusion:**

X-ray evidence points to sample homogeneity. The high temperature paramagnetic properties (and Curie-Weiss constants) are approximately consistent with relative composition and mean field expectations based on pure components, but imply new interactions in the mixture. The variety of structure in the low temperature susceptibility plots points to a likely range of magnetic behaviors on mixing. For certain compositions, especially $\text{Co}_{0.6}\text{Mn}_{0.3}\text{Ni}_{0.1}$, hysteresis in the magnetization versus field isotherms is more prominent. Finally a prospective $T(x,y)$ magnetic phase diagram has been partially determined. Many more compositions need to be prepared and measured in the future to complete the phase diagram and accumulate more information on the global behavior of the material as a function of composition.
Appendix:

Matlab Program Code for Processing Voltage, Temperature and Moment Data:

```matlab
clf;clear;
[C,C2]= xlsread('M05N95-X3.xlsx','Sheet1');

% chi plot
xmin=0;
xmax=35;
ymin=0;
ymax=10;

% chi plot
XMIN=1.5;
XMAX=20;
YMIN=.14;
YMAX=.18;

% ICHI Fit
TMIN=70;
TMAX=270;

mass = C(1,7);
mwt = C(1,8);
dmg = C(1,9);
sample=C2(2,6);
DIA =C(1,10);

ncount = length(C);

for i = 1:ncount
h(i)    = C(i,1);
amp(i)  = C(i,2);
v1(i)   = C(i,3);
v2(i)   = C(i,4);
m(i)    = C(i,5);
end

N = mass/mwt;
BKGD=0.00008;

MX=1;
X = [6.06150 -1.632 2.89825 ];

ICHIM=90.0;
CHIMAX=2.0;
PTMAX=80.0;
```
XTMAX=10.0;

for i = 1:ncount
    vavg(i)=(v1(i)+v2(i))/2;
    vavg(i)= vavg(i)/1.255;
    R(i) = vavg(i)/amp(i);
    if (R(i) > 53.8285) && (R(i) < 51181.)
        % CALCULATE TEMPERATURES ACCORDING TO THE FOLLOWING RESISTANCE-
        % DEPENDENT FUNCTIONS:
        A(i)=log10(R(i));
        if (R(i) > 1236.0)
            ZU=4.90664609931;
            ZL=3.03324781184;
            ZT=((A(i)-ZL)-(ZU-A(i)))/(ZU-ZL);
            ZR=acos(ZT);
            T(i) = 5.486640-6.314608*cos(ZR)+2.814680*cos(2.*ZR)...  
                 -1.034632*cos(3.*ZR)+0.314345*cos(4.*ZR)...  
                 -0.075795*cos(5.*ZR)+0.012433*cos(6.*ZR);
        end % if (R(i) > 1236.0 )
    end
    if ((R(i) > 217.6) && (R(i) < 1236.1))
        ZU=3.16177633747;
        ZL=2.28467635798;
        ZT=((A(i)-ZL)-(ZU-A(i)))/(ZU-ZL);
        if (ZT > 1.0)
            break;
        end
        ZR=acos(ZT);
        T(i) = 41.699271-37.497202*cos(ZR)+9.133259*cos(2.0*ZR)...  
            1.462062*cos(3.0*ZR)+0.192268*cos(4.0*ZR)...  
            -0.015378*cos(5.0*ZR)-0.004029*cos(6.0*ZR);
    end % if ((R(i) > 217.6) && (R(i) < 1236.1))
    if ((R(i) > 53.83) && (R(i) < 217.6))
        ZU=2.39549800796;
        ZL=1.72477955668;
        ZT=((A(i)-ZL)-(ZU-A(i)))/(ZU-ZL);
        ZR=acos(ZT);
        T(i) = 174.683699-125.913745*cos(ZR) + 24.564951*cos(2.0*ZR)...  
            3.969682*cos(3.0*ZR)+0.780722*cos(4.0*ZR)...  
            -0.165184*cos(5.0*ZR)+0.030028*cos(6.0*ZR);
    end % if ((R(i) > 53.83) && (R(i) < 217.6))
end % for i = 1: ncount

for i = 1:ncount
    MCORR(i)  = m(i) - BKGD;
    MCORRH(i) = MCORR(i)/h(i);
    CHI(i)    = MCORRH(i)/N;
    CHI(i)    = CHI(i)/(1.0-dmg*CHI(i));
    % CORRECTION FOR DIAMAGNETISM
CHI(i) = CHI(i)-DIA;
% THIS IS A VVTIP CORRECTION
% HIGH TEMPERATURE CORRECTION
if T(i) > 60
    CHI(i)=CHI(i)*(1.+0.00025*(T(i)-60.0));
end
ICH(i) = 1./CHI(i);

SX=0;
SY=0;
SXX=0;
SYY=0;
SXY=0;

mcount=ncount;
for i = 1:ncount
    if T(i) < TMAX && T(i) > TMIN
        SX= SX+T(i);
        SY= SY+ICH(i);
        SXX= SXX+T(i)^2;
        SYY= SYY+ICH(i)^2;
        SXY= SXY+(ICH(i)*T(i));
    else mcount=mcount-1;
    end
end

D= (mcount*SXX)-(SX)^2;
B= (SXX*SY-SX*SXY)/D;
M= (mcount*SXY-SX*SY)/D;
SIGB= (abs((SXX*(SYY-M*SXY-B*SY)))/((mcount-2)*D))^,.5;
SIGM=(mcount/SXX)^.5*SIGB;

x=0:300;
y=M*x+B;
d = { 'T' 'CHI' 'ICH' 'H' 'I' 'V1' 'V2' 'Vavg' 'M' 'Mass' 'MWT' 'DMG'};
e= { 'm', 'b', ' ', 'std. dev m', 'std. dev b'};
xlsxwrite('M05N95-X3.xlsx', d,'Output','A1')
xlsxwrite('M05N95-X3.xlsx', T,'Output','A2')
xlsxwrite('M05N95-X3.xlsx', CHI,'Output','B2')
xlsxwrite('M05N95-X3.xlsx', ICHI,'Output','C2')
xlsxwrite('M05N95-X3.xlsx', h,'Output','D2')
xlsxwrite('M05N95-X3.xlsx', amp,'Output','E2')
xlsxwrite('M05N95-X3.xlsx', vl,'Output','F2')
xlsxwrite('M05N95-X3.xlsx', v2,'Output','G2')
xlsxwrite('M05N95-X3.xlsx', vavg,'Output','H2')
xlsxwrite('M05N95-X3.xlsx', m,'Output','I2')
xlsxwrite('M05N95-X3.xlsx', mass,'Output','J2')
xlsxwrite('M05N95-X3.xlsx', mwt,'Output','K2')
xlsxwrite('M05N95-X3.xlsx', dmg,'Output','L2')
Xhat = zeros(size(X));
figure(1);
plot(T, ICHI,'rO',x,y);xlabel('T');ylabel('1/\chi');title(sample);

m= num2str(M);
b= num2str(B);
SIGM =num2str(SIGM);
SIGB =num2str(SIGB);
TMIN= num2str(TMIN);
TMAX= num2str(TMAX);

Equation = ['y=' m 'x +' b];
text(200,10,Equation)

Std = ['\sigma' ' fontsize{6} m' ' fontsize{10} = ' SIGM ' ' '\sigma'
' ' fontsize{6} b' ' fontsize{10}=' SIGB];
text(150,5,Std)
FIT = ['fit from ' TMIN ' to ' TMAX];
text(200,15,FIT)

axis([xmin xmax ymin ymax]);

figure(2);
plot(T, CHI,'rO');xlabel('T');ylabel('\chi');title(sample);
axis([XMIN XMAX YMIN YMAX]);
annotation(figure1,'textbox',[0.2258 0.2028 0.2537 0.1855],'String','Co_1-x
Mn_y Ni_x-y',...'
'FitBoxToText','off');
References


