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Synthesis and Characterization of the Cobalt-Iron and Nickel-Iron Prussian Blue Analogues in a Silica Matrix

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SYNTHESIS AND CHARACTERIZATION OF THE COBALT-IRON AND
NICKEL-IRON PRUSSIAN BLUE ANALOGUES IN A SILICA MATRIX

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This dissertation is dedicated to my two daughters, Hannah Elizabeth and Lacy Olivia.
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ABSTRACT

There has been a considerable interest in the fabrication and characterization of molecular magnets. A complex that has garnered a great deal of attention is Prussian blue, Fe$^{III}_4$[Fe$^{II}$(CN)$_6$]$_3$, and its transition metal cyanide analogues. Molecular magnets of these Prussian blue complexes have been studied extensively, due to their interesting magnetic properties. For this research the sol gel process was used to fabricate some of these complexes in a silica matrix known as a xerogel. Specifically the two Prussian blue analogues that were studied are K$_x$Co$^{II}_y$[Fe$^{III}$(CN)$_6$]$_z$ and K$_x$Ni$^{II}_y$[Fe$^{III}$(CN)$_6$]$_z$.

These two analogues were incorporated into a transparent porous silica matrix using the sol-gel process. Transparent glasses containing the complexes were produced with total metal (Fe$^{III}$ and Co$^{II}$ or Ni$^{III}$) concentrations between 0.01 and 0.06; and between 0.01 and 0.1 mol % respectively. It was found that for the cobalt – iron xerogel samples nanoparticles on the order of 8 – 10 nm were formed. In the nickel – iron xerogel samples it was discovered that nanorods (15 nm by 40 nm) and nanodots (40 nm diameter) were formed during the sol gel process and are concentration dependent in that the lower concentrations were more likely to form the nanodots. It is believed that the particles for both types of Prussian blue analogues are formed by arresting the precipitation of the complexes when the gelation of the sol gel occurs.

The size of these particles allows for the samples to be magnetically characterized as superparamagnets. The blocking temperatures that are exhibited by these complexes are 10 and 15.5 Kelvin respectively for the cobalt and nickel – iron Prussian blue analogues. Both analogues showed frequency
dependence in the AC susceptibility measurements furthering the characterizaton as a superparamagnet.

The cobalt – iron xerogel samples displayed a previously determined photomagnetic effect that is attributable to the presence of cobalt (III) – iron (II) defect sites in the lattice of the complex. This photomagnetic effect is controlled by the introduction of anhydrous ammonia to the samples, which causes more defect sites to form. When more defect sites are present the photomagnetic effect is increased.
INTRODUCTION

Overview of the Sol-gel Process

The sol-gel process is a solution approach to the synthesis of semi metal and metal oxide glasses and ceramics. The process happens in two stages: the sol stage and the gel stage. A sol is a dispersion of colloidal particles in a liquid. A gel is an interconnected, rigid network with pores that are submicrometer in size and polymeric chains whose average length is greater than a micrometer. Materials that are made through this process transform from a sol into a gel through the formation of a macroscopic structure derived from aggregation of the smaller clusters. This formation occurs through the simultaneous hydrolysis and polycondensation of an organometallic precursor. The sol-gel process is of interest due to its inherent flexibility.

The sol-gel process that results in an amorphous silica glass (xerogel) generally involves the reaction of silicon tetraalkoxides with water in an alcoholic medium. The overall reaction is represented as reaction 1 where “R” is normally methyl or ethyl. The ultimate production of glass material by this route occurs in four primary stages: gelation, aging/drying, stabilization, and densification.

\[
\text{Si(OR)}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{ROH} \quad (1)
\]

in four primary stages: gelation, aging/drying, stabilization, and densification. The gelation step is composed of a series of hydrolysis (Reaction 2) and
condensation (Reactions 3 and 4) reactions in which the silicon alkoxide, in the presence of water, forms a continuous Si – O – Si bonded network.

\[
\begin{align*}
\text{Si(OR)}_4 & + \text{H}_2\text{O} \rightarrow \text{Si(OR)}_3(\text{OH}) + \text{ROH} \quad (2) \\
\text{Si(OR)}_3(\text{OH}) + \text{Si(OR)}_4 & \rightarrow (\text{OR})_3\text{Si-O-Si(OR)}_3 + \text{ROH} \quad (3) \\
2\text{Si(OR)}_3\text{OH} & \rightarrow (\text{OR})_3\text{Si-O-Si(OR)}_3 + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

When a sufficient amount of Si – O – Si bonds are made in a region, they begin to respond cooperatively as colloidal particles or a "sol". The size of these particles is mainly dependant upon the pH and the \( R \) ratio \( (R = [\text{H}_2\text{O}] / [\text{Si(OR)}_4]) \). A schematic overview of these processes is shown in Figure 1. Over time the colloidal particles and the condensed silica species start to connect and become a three-dimensional network (path A). When gelation occurs, the viscosity rapidly increases, and a solid sample is present in the shape of the mold. The onset of gelation is defined as the point at which the sol no longer flows. The "gel" that is formed is soft and contains incompletely reacted materials (SiOH and Si – O – Me functional groups), trapped alcohol, and water.

During the aging process (~ 3 months), further condensation reactions occur to form more Si – O – Si linkages. Localized solution and reprecipitation of the gel network continues which increases the width of interparticle necks, and in turn decreases the porosity. A large amount of shrinkage occurs and the concomitant evaporation of water and alcohol is also present (Figure 1, A2). As a result of the aging process the gel becomes much stronger. In the end, a hard piece of monolithic glass referred to as a xerogel is formed. The xerogel, while hard, is also highly porous. The transparent nature of these glasses makes them suitable for optical applications.

The next step is stabilization. At this point, the aged gels are dried at approximately 100 °C and then stabilized up to around 500 °C to remove any of the remaining organic materials and to further force the condensation process. Once stabilization has occurred, the pore structure can be closed (densification)
Figure 1. Schematic of the sol gel process.
at a temperature above 1500 ºC, which yields a glass that is indistinguishable from fused silica. Most of the samples used for the research presented here did not undergo either the stabilization or the densification steps.

Xerogels are unique due to their pore structure. These samples can act as a host matrix that can be used to entrap and stabilize reactive chemical species, while also allowing for the diffusion and reaction of small molecules. The inherent nature of these samples to be transparent, allows for them to be studied more easily with optical measurements. This transparency allows for spectra to be collected in transmission mode similar to solution measurements, while also keeping the structure of a solid. Working with solid samples, usually powders, normally requires using reflective techniques that are by nature much less sensitive.

The sol-gel process has other advantages as well. Its versatility is shown through the use of different precursors and the control of experimental conditions, such as the type and amount of solvent used, the water concentration ($R$ – value), catalyst concentrations and temperature. Acids can be use to catalyze the hydrolysis; which in turn, makes condensation the rate limiting step and leads to linear chains with very little cross linking evident in the final product. On the other hand, bases are used to catalyze condensation which leads to a final product with many cross linkages (Figure 2). Another advantage to the sol-gel process is the ability to make samples in a variety of shapes and sizes, which will fit the applications needed. They can also be made into thin films by either spin coating or dip-coating with the sol-gel solution (Figure 1, path B). These films can then be used to make optical, protective, dielectric and anti-reflective coatings.

The focus of most of the research done in our group centers around the ability to put different transition metals into the xerogel. There are two main ways to involve a metal in the sol-gel make up. The first and more involved method uses transition metal alkoxides, which can also undergo hydrolysis and condensation reactions as well. Hybrid xerogels are made with both metal and
Figure 2. Acid (a) and base (b) catalyzed sol gels.
silicon oxides and are made by the co-condensations of the two different oxides (Reaction 5). The second most common way to place transition metals into the

\[
\text{mSi(OR)}_4 + \text{nM(OR')}_4 + \frac{7}{2}(m+n) \text{H}_2\text{O} \rightarrow \left[\text{Si}_{m}\text{M}_{n}\text{O}_{(2m+2.5n)}\right] + 4m\text{ROH} + 4n\text{R'}\text{OH}
\]

sol gel matrix is to trap them in the inner pores of the gel. This placement is accomplished by having a metal ion or metal complex present in the original solution. When gelation has been accomplished the three dimensional silica network forms around the metal ions and the ions get trapped within the pores and as will be discussed later the pores are also instrumental in the shaping and size of these metal complexes. In both cases, the metals are still accessible via the pore network. When metals are embedded into xerogels, using either method, they can be used as catalysts, can undergo ligand substitution reactions (useful as sensors), or can display interesting magnetic properties.

**Molecular Magnets**

Humankind has benefited greatly from the discovery and exploitation of magnets and magnetism. This reliance on magnets is assured to expand as we move further into the 21st century. Magnets are found in a great many devices and are often taken for granted. These products have an impact on all parts of society and our economy. An example is that there are normally more than 20 magnets in an automobile. The global 1999 production of magnetic materials was valued at $30 billion, with annual growth projected at 10%. This field will only continue to grow in the future. As a direct consequence of the continued importance placed on magnets and magnetism, many materials-science laboratories worldwide are focusing on the development and the improvement of magnetic materials.

Molecule based magnets are a diverse and promising class of magnetic materials. They are expanding the common focus typically applied to magnetic
materials to a whole host of new properties. Some examples of these properties are low density, transparency, electrical insulation, and low temperature fabrication (detailed list in Table 1)\textsuperscript{10} that are unavailable in conventional metal / intermetallic and metal oxide magnets. They are also combining magnetic ordering with other properties such as photoresponsiveness. Essentially all of the properties associated with the conventional transition-metal and rare earth metal based magnets are also present in the molecule based magnets. The research into molecule based magnets offers a great many new processing techniques. Basically, the new magnets are made using an organic synthesis approach that is frequently used in pharmaceutical development, rather than the older means of high temperature metallurgical methods typically used to make magnets. The past decade has witnessed the discovery of several families of molecule based magnets.

Inorganic research in magnetism has recently centered on the use of transition metal coordination compounds for the synthesis of 1D, 2D, and 3D materials with both ferri- and ferromagnetic behavior.\textsuperscript{11, 12} The interest in 1D systems is connected to a number of features: the spin Peierls transition, the alternating spin chain, solitions, bound magnons, and the Haldane conjecture.\textsuperscript{13} The 2D systems are interesting for several reasons: for the study of 2D magnetic phase diagrams and the elicidation of magnetostructural correlations within and between layers. 3D Prussian blue analogs are playing a major role in the field of magnets that can order at high temperatures.\textsuperscript{14}

**Transition metal cyanide compounds:**

Magnets that are based on metal oxides have been important for hundreds of years. Chief among the examples are magnetite, Fe\textsubscript{3}O\textsubscript{4}, cobalt doped γ-Fe\textsubscript{2}O\textsubscript{3}, and CrO\textsubscript{2}. The oxide bridge between the two magnetic metal ions has filled p orbitals that provide the pathway for strong spin coupling.\textsuperscript{15} Although cyanide (C≡N') does so with an extra atom, it can bridge between two metal ions via its pair of empty antibonding orbitals and filled non-bonding orbitals. Before an understanding of their composition or structure had been
Table 1. Representative Attributes of Molecule-Based Magnets

<table>
<thead>
<tr>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Density</td>
</tr>
<tr>
<td>Mechanical flexibility</td>
</tr>
<tr>
<td>Low temperature processability</td>
</tr>
<tr>
<td>High strength</td>
</tr>
<tr>
<td>Modulation / tuning of properties by means of organic chemistry</td>
</tr>
<tr>
<td>Solubility</td>
</tr>
<tr>
<td>Low environmental contamination</td>
</tr>
<tr>
<td>Compatibility with polymer composites</td>
</tr>
<tr>
<td>Biocompatibility</td>
</tr>
<tr>
<td>High magnetic susceptibilities</td>
</tr>
<tr>
<td>High magnetizations</td>
</tr>
<tr>
<td>High remnant magnetizations</td>
</tr>
<tr>
<td>Low magnetic anisotropy</td>
</tr>
<tr>
<td>Transparency</td>
</tr>
<tr>
<td>Semiconducting and / or insulating dc electrical conductivity</td>
</tr>
</tbody>
</table>
observed, magnetic ordering had been noted at low temperatures for these types of compounds.\textsuperscript{16} The differing atoms at each end of the cyanide bridge have different binding affinities to metal ions. An example would be $[\text{Fe}^{II}(\text{CN})_6]^{2-}$ (ferrocyanide) with alkali metals as the counter ions can be easily made. The replacement of those cations with another transition metal creates insoluble materials such as $\text{Fe}^{III}_4[\text{Fe}^{II}(\text{CN})_6]_3$ other wise known as Prussian blue.

Transition metal cyanide chemistry has been around for quite some time. In 1704 a Berlin artist named Diesbach accidentally discovered Prussian blue. Mixing of the essentially colorless ions $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ with $[\text{Fe}(\text{CN})_6]^{4-}$ in water gives the insoluble blue precipitate.\textsuperscript{17} The extraordinary intensity and longevity of its color has led it to be used in industry as a pigment in paints, printing inks, and laundry dye. Its usefulness has been the driving force behind intense research efforts to get a better understanding of its properties. Work on this compound; establishing the chemical formula, oxidation states, and solid state structures; has been going on since the 1930’s.\textsuperscript{18} Prussian Blue is now recognized as the mixed valent complex iron (III) hexacyanoferrate: $(\text{Fe}^{III}_4[\text{Fe}^{II}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O} \ x = 14-16)$. The complex is identical to the material know as Turnbull’s Blue, which is formed during the mixing of $\text{Fe}^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$.\textsuperscript{19} The ability to get the same complex using a different set of starting materials puzzled researchers until it was found that an electron-transfer occurs between the ferrous ion and the ferric cyanide to give a compound that has the iron (II) at the center of the cyanides. The structure of Prussian blue was found to be cubic (isotropic) with iron (II) and iron (III) separations of approximately 5 Å.

The magnetic behavior of Prussian blue was investigated in 1928 by Davidson and Welo\textsuperscript{20} who reported a magnetic susceptibility of the complex at three temperatures between 200 and 300 °C. Over time many other papers were published touting the magnetic properties of Prussian blue, but in general these samples were for the most part impure. At this point the bonding in the compounds was not well understood. These studies did show that ferri- and manganicyanides exhibit ferromagnetic ordering below 20 Kelvin. Until the
structure of Prussian blue was known, it was difficult to appreciate where this behavior originated.

In the Prussian Blue framework there are two main environments for the iron metal centers: $M^A$ and $M^B$ in the formula $M_x^A[M^B(CN)_6]^y$. The $M^A$ metals are coordinated to the nitrogen end of the cyanides, which are known as weak field ligands. The $M^B$ metal ions are coordinated to the carbon end of the cyanide which has a strong ligand field, making the ion low spin. The weak magnetic coupling which is observed in Prussian blue is due to the interaction of high-spin ferric centers though the intervening diamagnetic low spin ferrous centers. Ferromagnetic ordering of Prussian Blue at a Curie temperature of 5.5 Kelvin was found using Mössbauer investigations.\textsuperscript{21, 22} Mayoh and Day carried out an experiment to show the delocalization contribution to the ferromagnetism in Prussian Blue. They concluded that the ordering of the Fe (III) ions even though they are separated by long distances, showed that the intervening Fe (II) sites in the lattice played a part in the magnetic interaction.

The metal ion, its oxidation state, and consequently, its number of spins per site can be altered easily. The complexes formed using the Prussian blue framework, due to the bridging of the metal sites with the cyanide ligand, can exhibit strong magnetic coupling and magnetic ordering. Both ferromagnetic and ferrimagnetic behaviors have been observed, and many different complexes have been synthesized. Magnets with critical temperatures higher than room temperature have been made.\textsuperscript{23} Controllable photomagnets such as the one discussed in detail later, have also been fabricated. Binary and ternary solid solutions with unusual properties have been made. The critical temperature ($T_c$), saturation magnetization, and coercive fields, as well as color and size can be controlled by synthetic means and the specific metals chosen. The diversity of the physical properties evident in this particular class of materials makes them a strong candidate for more technological development and study. Some examples of the types of complexes that have been studied and are featured in my work can be found in Table 2. The critical temperatures range from around 5 Kelvin for
Table 2. Examples of Prussian blue analogues.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V[Cr(CN)$<em>6$]$</em>{0.86}$ • 2.8 H$_2$O</td>
<td>315</td>
</tr>
<tr>
<td>[Cr$<em>5$(CN)$</em>{12}$] • 10 H$_2$O</td>
<td>207</td>
</tr>
<tr>
<td>CsNiCr(CN)$_6$ • 2 H$_2$O</td>
<td>90</td>
</tr>
<tr>
<td>Mn(Mn(CN)$_6$)</td>
<td>48.7</td>
</tr>
<tr>
<td>Ni$_3$[Fe(CN)$_6$]$_2$</td>
<td>23.6</td>
</tr>
<tr>
<td>Co$_3$[Fe(CN)$_6$]$_2$</td>
<td>14</td>
</tr>
<tr>
<td>Fe$_4$[Fe(CN)$_6$]$_3$ • 14 H$_2$O</td>
<td>5.5</td>
</tr>
</tbody>
</table>
the actual Prussian blue complex to over room temperature for a vanadium – chromium complex.

Spin Glass vs. Superparamagnet

One of the key elements to understanding a great deal of this research is to understand some of the fundamental magnetics involved for the samples that are being studied. The most commonly used magnetic terms are diamagnetic and paramagnetic. Diamagnetic materials have no atomic magnetic moments because there are no uncompensated spins and have no magnetization in zero field. When a field is applied a small negative magnetization is induced on the atoms proportional to the applied field strength due to an extra torque applied to the electron, which results in an antiparallel alignment of the atomic orbital moment. In a paramagnetic material, the atoms have uncompensated spins and have a net magnetic moment. The spins however are randomly oriented throughout the sample due to thermal agitation, which gives zero magnetization. As a field is applied the spins tend to align along the field because the spin moment is larger than the orbital moment, which gives a net magnetization. Due to this alignment with the field the spins add to the field so that the magnetization is seen as positive. This magnetization increases with field strength as the spins become more ordered.

As the research moved away from these basic characterizations more complex systems emerged. One of the most commonly featured systems is a ferromagnet. Ferromagnets are materials in which there are uncompensated spins which are quantum mechanically coupled. Ferromagnetism is commonly thought of as a special case of paramagnetism. The uncompensated spins in individual atoms of a ferromagnet may couple either directly (direct exchange) or through an intermediate anion such as oxygen (super exchange). Ferromagnets have strong positive magnetic susceptibility. Unlike paramagnets, when a field is applied and then is removed, ferromagnets retain a component of the magnetization in the direction of the applied field. Because ferromagnetism
results from the interaction of atomic moments in materials, there is an exchange energy associated with the coupling of the spin moments. If thermal energy exceeds this spin coupling energy, then the coupling breaks down and the material behaves essentially as a paramagnet. This temperature is material dependant and is called the Curie temperature ($T_c$). Some special cases of ferromagnetism arise due to not all of the spins aligning in the same direction. Antiferromagnetism is when the uncompensated spins are coupled antiparallel to each other. One would think that this configuration would give rise to materials with no net magnetization, but that is not always the case. Antiferromagnets may have a net magnetization due to spin canting and lattice defects. Another special case is that of the ferrimagnet. In a ferrimagnet, neighboring spin lattices are antiparallel but are of unequal magnitude. These types of samples give rise to a relatively strong net magnetization when compared to antiferromagnets

For this research these somewhat basic characterizations are used, but the main determination comes down to two other complex magnetic cases: spin glasses and superparamagnets. During the process of working on this research the discussion has oftentimes turned to the difference between spin glasses and superparamagnets. In order to understand how these two different states of magnetism differ is often very difficult because they are very much alike in many of their measurable properties and many times respected scientists disagree or cannot come up with a consensus to answer the question. The properties of these states are highlighted in this dissertation.

A spin glass is a disordered material containing high degrees of magnetic frustration. The origin of this behavior can be linked to either a disordered structure or a disordered magnetic doping in an otherwise regular structure. One of the most important prerequisites of the spin glass is the randomness in either the position of the spins, or the signs of the neighboring couplings (ferro ($\uparrow\uparrow$) or antiferromagnetic ($\uparrow\downarrow$)). For a spin glass to be created disorder must be present, or the magnetic transition is just a standard ferromagnetic or antiferromagnetic type of long range ordering. Combining this randomness with the competing or mixed interactions causes frustration. Frustration refers to the inability of the
system to remain in a single lowest energy state (the ground state). Spin glasses have many ground states that are never explored on experimental time scales. The prerequisite of frustration is unique to the spin glass ground state, which is disordered, but still exhibits many interesting properties related to its cooperative nature.

This time dependence is what distinguishes spin glasses from other magnetic systems. Spin glass behavior is normally characterized using AC susceptibility. In a spin glass, magnetic spins experience interactions that are random with additional magnetic spins, which results in a state which is highly irreversible and metastable. The spin glass state is realized below the freezing temperature (The temperature where a second-order transition from a paramagnetic or ferromagnetic state to a spin-glass state in which spins from moment-bearing solute atoms become ordered randomly in a non-magnetic host). The system is seen as paramagnetic above the freezing temperature. The freezing temperature is determined in the AC by measuring the susceptibility versus temperature, which exhibits a cusp at the freezing temperature. The location of the cusp is dependent on the frequency of the AC susceptibility measurements, which is a feature not seen in conventional magnetic samples and give the basis for the determination of a spin glass system versus a superparamagnet discussed later. For DC measurements, beginning above the spin glass transition temperature, where the spin glass shows more typical magnetic behavior, which for this research is ferromagnetism, but could be other as well, if an external field is applied and the magnetization is plotted versus temperature the curve will follow along like a ferromagnet until the transition temperature is reached. At this point the magnetization becomes virtually constant and is the onset location of the spin glass phase. When the external field is removed, the spin glass has a rapid decrease in the magnitude of magnetization to a value called the remanent magnetization, and then a slow decay as the magnetization approaches zero. The decay is non-exponential and no single function can fit the curve of magnetization versus time adequately. The
slow decay is particular to a spin glass system. Experimental measurements on the order of days have shown continual changes.

If a similar experiment was performed on a ferromagnetic system, after the magnetic field was removed there would be a rapid change to the remanent value, but this value is a constant in time. For a paramagnetic system, when the field is removed the magnetization would immediately return to zero. In each of these cases, the change is very rapid and has an exponential decay with a small time constant.

If the spin glass is cooled below the transition temperature in zero field and then a field is applied there is a rapid increase in magnetization to a value, which is less than the field cooled magnetization. This increase is followed by a slow upward drift toward the field cooled value. For zero field cooled DC measurements a broad peak is seen, the maximum of this peak in the zero field cooled curve is determined by the strength of the field. As the field is decreased the maximum in the zero field cooled curve approaches the freezing temperature found for the lowest frequency used, which is expected for spin glass freezing.\textsuperscript{27}

A superparamagnet is made up of a family of magnetic clusters (domains), or fine particles. These clusters can be made up of any type of internal magnetic order (ferromagnetism, antiferromagnetism, or random). The clusters represented in a superparamagnet do not interact with each other which is a definite distinction from the spin glasses. Superparamagnetic relaxation is unique to magnetic nanoparticles.\textsuperscript{28, 29} It is directly associated with the magnetic anisotropy of the particles. In the single domain ferromagnetic or ferrimagnetic systems, the net moments in each particle become ordered and spontaneously magnetized when the temperature falls below the Curie magnetic transition temperature of the material. This spontaneous magnetization points the ordered magnetic moments for each particle to the same preferred direction. This preferred direction is known as the “easy axis” for magnetization. This axis is normally a certain crystallographic axis determined by the coupling between electron spin and its orbital angular momentum. These couplings at the atomic level generate anisotropy energy. The potential energy is at a minimum when the
nanoparticles align with the easy axis. This anisotropy serves as the energy barrier that prevents the change of magnetization direction. This anisotropy barrier is so small that thermal treatment and/or an external magnetic field can easily move the magnetic moments away from the easy axis. When this occurs the collective behavior of the magnetic nanoparticles is the same as a paramagnet. Magnetic order is still present in the nanoparticles with each particle behaving as a paramagnet with a giant moment. This is where the term superparamagnet originated. When this superparamagnetic state is achieved, the direction of magnetization for the nanoparticle rapidly fluctuates instead of aligning along a certain direction. The temperature at which the magnetic anisotropy energy barrier of the nanoparticle is overcome by thermal activation is defined as the blocking temperature. At this point the nanoparticle becomes superparamagnetically relaxed.\(^{30}\)

The magnetic properties of each of these types of samples tend to overlap substantially. Both types of samples show a peak in the DC magnetization versus temperature plots for the zero field cooled scans. Spin glasses and superparamagnets display open hysteresis loops for the magnetization versus field experiments. Sometimes it is very hard to distinguish between the two phenomena. When AC susceptibility measurements are performed on a sample with either spin glass qualities or superparamagnetic properties there is a frequency shift of the peak found for these behaviors in both magnitude (decreases with increase in frequency) and position along the temperature axis (increases with increase in frequency). In his book Mydosh\(^{27}\) proposes an equation that gives a quantitative measure of this frequency shift per frequency:

\[
K = \frac{\Delta T_f}{T_f} \frac{\Delta}{\omega}
\]

where \(K\) is the frequency shift, \(T_f\) refers to the temperature found at the maximum in \(\chi'\) and \(\omega\) is the frequency used. It has been found that spin glass materials have a frequency shift on the order of approximately 0.01 because for the most part even though frequency dependence is present the change in frequency
affects a spin glass sample very little. Superparamagnets on the other hand have a frequency shift that is about an order of magnitude higher than that of the spin glass ($K \geq 0.1$). This frequency shift for these particular types of samples is about the only way to distinguish the two magnetic species from each other.\textsuperscript{27}

**General Experimental**

**Superconducting Quantum Interference Device (SQUID):\textsuperscript{31}**

The magnetic property measurement system (MPMS) consists of several superconducting components. There is the superconducting magnet which is used to generate large magnetic fields. Next there is a superconducting detection coil which couples inductively to the sample to be measured. Then there is the SQUID itself which is attached to the detection coil. Lastly there is the superconducting magnetic shield that surrounds the SQUID.

The MPMS system uses a superconducting magnet wound in a solenoidal configuration. One of the important features of the magnet used is that it is constructed as a completely closed superconducting loop. This feature allows for the magnet to be charged to a specific current and then be operated in a persistent mode without using an external current source or power supply.

The detection coil is a single piece of superconducting wire wound in a set of three coils configured as a second-order gradiometer. The upper and bottom coils have a single turn clockwise. The center coil is made up of two turns which are wound counter-clockwise. The coils are found at the center of the superconducting magnet, but outside the sample chamber. They are positioned so that the magnetic field of the sample can couple inductively to the coils as the sample is moved through them. The gradiometer configuration is used to help reduce noise in the detection circuit that may occur as a result of the fluctuations in the magnetic field of the magnet.

The SQUID is the most sensitive magnetic field measuring device available. Even though the SQUID is the source of the instruments significant sensitivity, it actually does not directly detect the magnetic field from the sample.
What happens instead is that the sample moves through a system of superconducting detection coils which are connected to the SQUID with superconducting wires, which allows the current from the detection coils to couple inductively to the SQUID sensor. If the instrument is appropriately configured, the SQUID electronics produce an output voltage that is closely proportional to the current flowing in the SQUID input coil. At this point the thin film SQUID device which is found approximately 11 cm below the magnet inside the superconducting shield essentially functions as a tremendously responsive current-to-voltage converter.

When performing a measurement in the MPMS the sample is moved through the superconducting detection coils, which are located outside of the sample chamber and at the center of the magnet (Figure 3). When the sample moves through the coils, the magnetic moment of the sample induces an electric current in the detection coils. Since the detection coils, the connecting wires, and the SQUID input coil form a closed superconducting loop, any alteration of the magnetic flux in the detection coils produces a change in the persistent current in the whole detection circuit, which is proportional to the change in the magnetic flux. Because the SQUID functions as a linear current-to-voltage converter, the changes in current found in the detection coils produce similar variations in the SQUID output voltage. This change is proportional to the magnetic moment of the sample. If the system has been calibrated, measurements of the voltage variations form the SQUID detector as the sample is moved through the detection coils provide a highly accurate measurement of the sample’s magnetic moment.

Due to the extreme sensitivity of the SQUID to fluctuations in the magnetic field, the SQUID itself must be protected from normal shifts in the magnetic field of the laboratory and from the large magnetic fields that are produced by the superconducting magnet in the instrument itself. The requisite magnetic shielding is provided by a superconducting shield which provides a volume of relatively low magnetic field in which the SQUID and its coupling transformers are located. Basically the shield serves two purposes. 1) To shield the SQUID detector from
Figure 3. Schematic diagram of a Magnetic Property Measurement System.

1. Sample Rod
2. Sample Rotator
3. Sample Transport
4. Probe Assembly
5. Helium Level Sensor
6. Superconducting Solenoid
7. Flow Impedance
8. SQUID Capsule with magnetic shield
9. Superconducting Pickup Coil
10. Dewar Isolation Cabinet
11. Dewar
12. Magnet Power Supply
13. Model 1802 Temperature Controller
14. Console Cabinet
15. Power Distribution Unit
16. Model 1822 MPMS Controller
17. Gas/Magnet Control unit
the magnetic field generated by the superconducting magnet. 2) To trap and stabilize the ambient laboratory magnetic field present when the SQUID and the superconducting shield are first cooled to liquid helium temperatures.

During a measurement the sample is attached to the end of a firm sample rod. The rod is inserted into the sample space through a special double seal which allows the rod to be moved by a mechanism found outside the chamber. The top of the rod is attached to a stepper-motor-controlled platform which is used to drive the sample through the detection coil in a series of discrete steps. When the position of the sample is changed a variation of the flux inside the detection coil occurs, which in turn alters the current in the superconducting circuit. During the measurement the sample is stopped at several positions in the overall scan length. At each of these stops the SQUID takes several readings and the voltage is collected and averaged. The complete scan can be taken a number of times and the signals averaged to reduce the signal-to-noise ratio.

There are a number of different experiments that can be done inside the SQUID. The three types of measurements taken for this work are temperature scans, hysteresis loops, and photomagnetic measurements. Each of these different measurements tells a different story about the magnetic make up of the complexes being studied.

**AC Magnetometry:**

AC magnetic measurements are where an AC field is applied to a sample and the resulting AC moment is measured. These types of measurements are an important tool for characterizing many different types of magnetic materials. AC measurements are very beneficial in describing and verifying the properties of spin glasses and superparamagnets. Due to the induced sample moment being time-dependant, AC measurements yield more information about magnetization dynamics than could be obtained using conventional DC measurements, where the sample moment remains constant during the time of the measurement.

In AC magnetic measurements, a small AC drive magnetic field is superimposed on the DC field, which causes a time-dependant moment in the
sample. The field of the time-dependant moment induces a current in the pick-up coils, which allows measurements to be taken without having to move the sample. The detection circuitry is normally configured to only detect within a narrow frequency band, usually at the fundamental frequency (the frequency of the AC drive field).

To understand what exactly is measured in AC Magnetometry, you need to first consider very low frequencies. These measurements are most like the DC measurements. For this case the sample’s moment follows the $M (H)$ curve that would be measured in DC Magnetometry. When the AC field is small, the induced AC moment is $M_{AC} = (dM/dH) \cdot H_{AC} \sin(\omega t)$ where $H_{AC}$ is driving frequency, and $\chi = (dM/dH)$ is the slope of the $M (H)$ curve, which is called the susceptibility. This quantity is the number of most interest in AC Magnetometry.

When the DC magnetic field is changed, different parts of the $M (H)$ curve become accessible; this will in turn give a different susceptibility. One of the advantages to AC measurements is that it is very sensitive to changes in the $M (H)$. Because the AC measurements are sensitive to the slope of the $M (H)$ curve and not the overall value involved, small magnetic shifts are detected even if the absolute moment is rather large.

When higher frequencies are looked at, the AC moment of the sample does not follow the DC magnetization curve due to the dynamic effects that are present in the sample. This reason is why AC susceptibility is often called dynamic susceptibility. In the case of higher frequency, the magnetization of the sample can lag behind that of the drive field, which is able to be detected by the magnetometer’s circuitry. This characteristic is why the AC susceptibility measurement yields two quantities: the magnitude of the susceptibility ($\chi$), and the phase shift ($\phi$), which is relative to the drive signal. On the other hand, one can consider the susceptibility as having two separate phases, an in-phase, “real”, component ($\chi'$), and an out-of-phase, or imaginary component ($\chi''$). At low frequencies where the AC measurements are most similar to the DC measurements, the real component $\chi'$ is just the slope of the $M (H)$ curve that is
discussed above. The imaginary component $\chi''$, indicates dissipative processes in the sample.

**Transmission Electron Microscopy (TEM):**

The transmission electron microscope is an analytical tool that allows detailed micro-structural examination with high-resolution and high-magnification imaging. It also enables the investigation of crystal structures, orientations and chemical compositions in phases, precipitates and contaminants through diffraction pattern, x-ray, and electron-energy analysis. Magnifications of up to 500,000x and detail resolution below 1 nm can be achieved often. Quantitative and qualitative elemental analysis can be provided from features smaller than 30 nm. For crystals with interplaner spacing greater than 0.12 nm, crystal structure, symmetry and orientation can be determined. A TEM is able to image the atomic arrangement of a single crystal. Structural examination of defect sites, including stacking faults, interstitial, precipitates and vacancies is possible.

The main benefit to using TEM is the ability to get atomic scale resolution. The shortcomings to using this technique are that it is expensive. It can be destructive to the sample. Some samples are sensitive to the electron beam which can cause them to lose crystallinity and mass. Sample preparation can also be time consuming.

TEM is an electron-optical microscope that uses electromagnetic lenses to focus and direct an electron beam. Data is accumulated from the beam after it passes through the sample. The reason for using an electron beam instead of a light beam is that electrons have a shorter wavelength than photons. Resolution and magnification of a microscope are related to the wavelength and the energy of the radiation. In general when a wavelength is shorter, one tends to get better resolution.

The source radiation is generated using an electron gun (Figure 4). The resulting beam of electrons is focused into a tight, coherent beam by multiple electromagnetic lenses and apertures. The lens system is designed to eliminate the loss electrons as well as to control and focus the electron beam. The
Figure 4. Schematic diagram of a transmission electron microscope.
corrected beam is focused on the sample. Various techniques are then used to collect data from the electrons that have passed through the sample. For example, image data can be collected by means of a fluorescent screen that is hit by the electron beam. The resulting image may be recorded on photographic film or with a CCD camera linked to a computer.

Preparation of the samples for TEM is as follows: The xerogel and bulk samples are both ground into a fine powder using a mortar and pestle. Once ground, a small amount of the samples are then placed in a clean vial. 200 proof ethanol is then added and the mixture is sonicated for 10 minutes. A 10 µL aliquot of the suspension is then deposited on to a 200 mesh copper grid with a carbon support film. This grid is then loaded into the instrument to be studied.

Another feature of the TEM that is advantageous is its ability to do electron diffraction measurements. Electron diffraction via the transmission electron microscope is a powerful tool for characterizing the structure of desired materials. These materials include perfect crystals and defect structures. Some of the advantages of electron diffraction studies over other methods (x-ray diffraction) is due to the very short wavelength (approximately 2 pm), the strong atomic scattering and the ability to study very small volumes of matter (approximately 10 nm$^3$). Once a sample of interest is found the electron beam can be used to get a diffraction pattern of the sample if the sample diffracts. Using this method the complex that you are taking pictures of can be verified to be the correct substance, by indexing the diffraction patterns obtained. For the research in this dissertation ring patterns were observed. Ring patterns are created when electron diffraction occurs simultaneously from many grains with different orientations relative to the incident electron beam. Analogous to x-ray powder diffraction, ring patterns, can be used to identify unknowns or characterize the crystallography of a material.

Once a diffraction pattern is obtained it has to be indexed to find out if the d-spacings match that of the sample being studied. Since two different instruments were used and the diffraction patterns were indexed in slightly different ways only one of these methods is going to be outlined in this section.
There are basically two steps to indexing the diffraction pattern once the pattern is found. The first step is to calculate the d-spacings of the complex to be studied based on the miller indices \((h, l, k)\). Miller indices may be used in any of three different ways: to designate a set of lattice planes, a member of a set, or the face of a macroscopic crystal parallel to the set designated.\(^{34}\) For this work calculations were done only up to the fourth order. Since both of the complexes to be studied were primitive there is no constraint on the \((h, l, k)\) numbers. Using the published values of the lattice constants \(a\) for these complexes the d-spacings were calculated using the following formula.

\[
d(h, l, k) = \frac{a}{\sqrt{h^2 + l^2 + k^2}}
\]

These d-spacings basically give you the PDF for the system being studied.

The second step is to actually interpret the diffraction pattern found on the TEM. To find the d-spacings from the diffraction pattern you can start with the Bragg equation where \(\lambda\) is the deBroglie wavelength of the electron from the electron beam used in the TEM.

\[
\lambda = 2d \sin \theta
\]

When \(\theta\) is very small, \(\sin \theta\), essentially becomes theta which leaves:

\[
\lambda = 2d \theta
\]

If \(H\) is considered the diameter of the ring on the image and \(L\) is the camera distance in the instrument:

\[
\tan 2\theta = \frac{(H / 2)}{L}
\]

For a small \(\theta\), the tangent of theta becomes just theta to give:
\[ \theta = \frac{1}{2} \left( \frac{H}{2} \right) / L \]

When these two equations are merged and rearranged the following equation emerges:

\[ d = \frac{\lambda L}{H / 2} = \frac{\lambda L}{\text{ring radius}} \]

The wavelength and camera length had been calculated for one of the instruments used and a constant was used to finally get d-spacings of the complexes studied.

\[ d = 369.5 \, \text{Å pixel} / (\text{ring radius in pixels}) \]

Once these d-spacings are extracted from the experimental data they are then compared to the spacings obtained in part one. If there are matching numbers it definitely strengthens the case for identifying the complexes based on the crystallographic data present. Being able to provide these matches goes a long way towards identifying the substance pictured.
CHAPTER 1

COBALT - IRON

Introduction

The cobalt (II) – iron (III) Prussian blue analogue has been previously studied and has been determined to be a spin glass in the bulk phase. This analogue has generated considerable interest because it has been shown to exhibit photomagnetism that can be controlled during the synthesis phase by the introduction of different cations. This chapter focuses on the fabrication of a new nanocomposite material containing $K_xCo^{II}_y[Fe^{III}(CN)_6]_z$, in a porous silica matrix. These new materials are made by a controlled multicomponent sol-gel synthesis in which the precipitation of the Prussian blue analogue is arrested at nanoscale dimensions by the gelation of the silica network. The resulting materials are homogeneous and optically transparent. They exhibit superparamagnetic behavior due to the formation of nanoparticles of the cobalt (II) – iron (III) complexes in the silica matrix. They are shown to have externally tunable photomagnetic behavior as well. It is believed that these new materials suggest a new approach for the utilization of the Prussian blue class of magnetic materials in advanced optical and magnetic applications.
Experimental

Fabrication:

**Xerogel Sample:** The 0.03 mol % Co$^{II}$/Fe$^{III}$ xerogel was made in the following manner: a solution of H$_2$O (4.6 mL), methanol (20.8 mL), and an aqueous solution of potassium ferricyanide (2.2 mM; 13.9 mL) was added dropwise to a solution containing tetramethylorthosilicate (30.3 mL), methanol (16.4 mL), and cobalt (II) nitrate hexahydrate (2.2 mM; 13.9 mL) in methanol. This mixture gives an overall metal concentration of 0.31 mM for each metal. After stirring 4 mL of the solution was placed into polystyrene cuvettes and capped for gelation. Once gelation occurred small holes were placed in the caps to allow for the aging and drying phases to occur. After the process is complete the xerogel has approximately 12% of the original volume with a final concentration of each metal being near 3 mM.

**Bulk Sample:** Bulk composites of the Co$^{II}$/Fe$^{III}$ Prussian blue complex were synthesized using a prep published by Hashimoto and co-workers.$^{35}$ An aqueous solution of cobalt (II) nitrate hexahydrate (10.0 mL; 0.83 M) was slowly added to a stirred aqueous solution of potassium ferricyanide (10.0 mL; 0.43 M). The resulting precipitate was vacuum filtered and washed with both methanol and diethyl ether.

**Characterization:**

**Electronic Spectroscopy:** UV/VIS data was collected on a Perkin Elmer Lambda 900 instrument. Scans were taken between 200 nm to 1500 nm with data collected every nanometer. Samples were run open to air in a quartz cell. The only exception was the UV/VIS spectra that were taken during the reaction with anhydrous ammonia. For this experiment an air tight attachment was used on the quartz cell to allow for the continuous flow of ammonia to the sample.
**Vibrational Spectroscopy**: IR data was collected on an Avatar 360 FT-IR at room temperature. A praying mantis diffuse reflectance attachment was used to look at the bulk powder samples.

**Transmission Electron Microscopy**: TEM images and electronic diffraction measurements were taken on a 300 kV Philips CM300-FEG microscope.

**X-Ray Fluorescence**: Elemental analysis was performed for the powdered bulk samples on an Oxford ED 2000.

**Magnetic Measurements**: DC magnetic measurements were taken on a superconducting quantum interference device (SQUID; Quantum Design MPMS XL-7). The zero field cooled and field cooled temperature scans were taken as follows: a fragment of the xerogel or a powdered sample of the bulk are secured at the end of a probe. Once the signal is centered the field is removed and the temperature is taken to a point well above the Curie temperature for the sample in question. After a waiting period the sample is then cooled to a temperature of 5 Kelvin absent a field (zero field cooled). After temperature equilibrium is reached a field of 100 Oe is turned on and DC measurements are begun. Measurements are taken at every 0.5 Kelvin up to 50 Kelvin. Then DC measurements are taken at the same temperature intervals on the way back down to 5 Kelvin (field cooled).

DC hysteresis measurements use the same sample set up. Once the desired temperature is reached (for the Co$^{II}$/Fe$^{III}$ samples 5 Kelvin and 13 Kelvin were used), a field of 50,000 Oe is turned on. DC measurements are taken at assigned Oersteds intervals down to -50,000 Oe and then cycled back using the same intervals back up to 50,000 Oe. Different intervals are used to maximize the data collected.

AC magnetic measurements were taken on a Quantum Design Physical Property measurement system (PPMS). Measurements were taken for a variety
of frequencies and fields. The type of experiment that was done was a temperature scan similar to that of the bulk but with different frequencies measured.

**Photomagnetism:** The photomagnetism experiments were done using a fiber optic SQUID probe and a 200 watt mercury-xenon Oriel arc lamp. The light ($\lambda \geq 550$ nm) was focused into a fiber optic cable attached to the fiber optic SQUID probe. A fragment of the xerogel sample was placed at the end of the SQUID probe and centered in the instrument. All photomagnetic measurements were taken at a field of 500 Oe and at a temperature of 5 Kelvin. After baseline magnetism was achieved the light was directed down the probe as DC measurements were continually being taken. Irradiation continued for 45 minutes. Once the irradiation was stopped, DC measurements continued until thermal equilibrium was achieved at the sample and the magnetic measurements stabilized. A variation of this experiment was done where irradiation alternated between $\lambda \geq 550$ nm and $\lambda = 448 \pm 50$ nm taking a DC measurement after 20 minutes of each irradiation.

The photomagnetism measurements taken as a function of exposure to ammonia were done as previously stated. The xerogel sample to be used had its photomagnetism measured before the introduction of ammonia. The sample was removed from the SQUID and placed in an air tight vessel and flushed with argon gas. Gaseous anhydrous ammonia is taken up with an air tight syringe (10 $\mu$L) and injected into the vessel with the sample. After the appropriate exposure time has lapsed the argon gas is used to flush out the ammonia. The sample is then placed back into the fiber optic probe and the photomagnetic measurements are run again. This dosing process is repeated on the same sample until all the desired data is collected.
Results and Discussion

General Characterization:

I was able to make homogeneous silica xerogels containing the cyanide bridged cobalt (II) – iron (III) metal centers by the incorporation of both of the transition metal components during the solution phase of the synthesis. To be able to obtain these homogeneous materials reproducibly, the conditions had to be optimized for the amount of water and the concentration and molar ratio of cobalt (II) to ferricyanide. This optimization was done by following previously developed procedures in our lab.\textsuperscript{36, 37} In the optimized procedure a molar ratio of 5:1 (mol TMOS: mol H\textsubscript{2}O) was used and a 1:1 ratio of the two metals was used. When other molar ratios were used the samples did not come out as clean and as homogeneous as they did when the 1:1 ratio was employed. When mixing occurs the solution turns a deep purple color, which suggests that the formation of the mixed-valence Prussian blue analogue is achieved. It was initially thought that concentrations only up to 0.03 mol % total metal to silicon could be formed. It was found, though that the highest concentration to be formed was 0.06 mol % total metal to silicon (Fe + Co / Si). When concentration much higher than the 0.06 % were attempted the cobalt – iron Prussian blue complex precipitated out of solution as the bulk phase. For concentrations up to the 0.06 % samples the solution remained transparent through gelation, aging, and drying, and ultimately yielded a homogeneous optically transparent xerogel (Figure 5, inset) with nanoparticles of the Prussian blue complex embedded within the silica matrix.

The electronic spectrum of this xerogel (Figure 5) is qualitatively similar to that of the bulk materials. A broad intervalence charge transfer band is located in the visible region between 450 and 650 nm. There is also a sharp higher energy peak at around 400 nm. This broad band has been assigned by Hashimoto to the d-d transitions of the Co\textsuperscript{II} (high-spin) and the sharper peak at 400 nm is assigned to the ligand-to-metal charge transfer (LMCT) band of [Fe\textsuperscript{III}(CN)\textsubscript{6}]\textsuperscript{3-}, which are said to be just the superposition of the spectra of the two individual species.\textsuperscript{38} While the assignment of the LMCT band seems correct, the assignment of the
Figure 5. The optical absorption spectrum of 0.03 mol % cobalt (II) – iron (III) xerogel (inset) shows an intervalence charge transfer band in the range of 450 – 650 nm with a maximum at 452 nm.
broad band as a d-d transition of the cobalt (II) species appears to be somewhat dubious. Based solely on the extinction coefficients previously determined for these types of species it does not seem plausible for the broad band to be a d-d transition. The extinction coefficient for the LMCT band in the [Fe$^{III}$\,(CN)$_{6}$]$^{3-}$ species is approximately 1100.\textsuperscript{39} The d-d transition for a cobalt (II) hexamine, which is a good approximation for a nitrogen bound cyanide ligand, has an extinction coefficient of approximately eight.\textsuperscript{40} The spectrum from which Hashimoto\textsuperscript{38} makes his assignments shows that the two peaks are of approximately equal absorbance. Using the stoichiometry of the complex they are studying Co:Fe is 1.5:1 and the extinction coefficients it doesn’t make sense for these two peaks to be equal or even close in magnitude. Even with a distortion in symmetry due to some sites being occupied by water, one would not expect the extinction coefficient to be raised significantly to account for the equal absorbance. It is our belief that this broad peak is an intervalence band. The band can be attributed to the metal-metal charge transfer band from iron (II) to cobalt (III) (low spin). This feature is present due to the cobalt (III) – iron (II) defect sites present in the lattice, which also give rise to the photomagnetism discussed later. These materials are considered a class II type of mixed valence compound\textsuperscript{38} under the classification of Robin and Day.\textsuperscript{41} This classification means that an electron is mainly trapped on the iron, but is partially delocalized on the cobalt. The maximum of the intervalence band lies at 452 nm (22,124 cm$^{-1}$) which is blue shifted by approximately 2,900 cm$^{-1}$ from that of the bulk materials. This shift is in part due to the size of the particles found in the xerogel complex in contrast to that of the bulk. The difference in size between the xerogel particles and the bulk phase particles is at least one order of magnitude. This phenomenom is called quantisation and arises due to the size of the nanoparticles being comparable to the de Broglie wavelength of its charge carriers (electrons). Due to the spatial confinement of the charge carriers, the edge of the valence and conduction bands split into discrete, quantized, electronic levels. These electronic levels are similar to those found in atoms and molecules. The spacing of the electronic levels and the bandgap will increase.
with a decreasing particle size. The increase in bandgap can be observed experimentally by the blue-shift in the absorption spectrum (ie. the shift mentioned above). A larger bandgap means that more energy is required to excite an electron from the valence band to the conduction band and consequently the light of a higher frequency and a lower wavelength would be absorbed. 42, 43

From previous studies, infrared measurements taken at 12 Kelvin in the region from 2000 to 2200 cm\(^{-1}\) give a good estimation of the make up of the cobalt – iron Prussian blue analogue. Three peaks have been observed: a strong peak at 2162 cm\(^{-1}\), a weaker peak at 2116 cm\(^{-1}\), and a shoulder at 2097 cm\(^{-1}\). 35 The cyanide stretch for Co\(^{II}\)\([\text{Fe}^{III}(\text{CN})_6]_2\) occurs at 2160 cm\(^{-1}\) and is observed at 2085 cm\(^{-1}\) for the Co\(^{II}\)\([\text{Fe}^{II}(\text{CN})_6]\) complex. 44 The peak seen at 2116 cm\(^{-1}\) appears when K\(^+\) is introduced into the compounds. It is believed that the peak at 2162 cm\(^{-1}\) comes from the stretching of cyanide in Fe\(^{III}\)–CN–Co\(^{II}\) linkages at positions where no K\(^+\) ion is present in the interstitial sites. The peak at 2116 cm\(^{-1}\) is assigned to the stretching of cyanide groups that surround K\(^+\) ion sites. The somewhat low frequency of the cyanide stretch (2116 cm\(^{-1}\)) is indicative that the oxidation states of the metals in the Fe–CN–Co complex that tend to exhibit this lower frequency are iron (II)–cobalt (III). The small shoulder found at 2097 cm\(^{-1}\) is most likely due to the cyanide stretch of Fe\(^{II}\)–CN–Co\(^{II}\) moieties, but it has not been fully investigated. 35 This data was further investigated using Mössbauer spectroscopy and using different cations (sodium and potassium) to shift between the two most common species. When the Mössbauer results are combined with the infrared data it was felt that these assignments were valid. 45 Our infrared data of the bulk composites seem to support the information put forth in these previous studies. Essentially the same infrared spectrum at room temperature was also attained for this research (Figure 6). It is however debatable whether these scans show exactly what was seen previously or the three modes found for the cyanide ligand that has been noted for octahedral complexes. It seems that based on results to be discussed in the next chapter that our infrared data is looking at the three modes present for the cyanide and
Figure 6. Infrared spectrum taken of the $K^xCo^{II}_y[Fe^{III}(CN)_6]_z$ bulk phase sample synthesized under the same conditions of stoichiometry and concentrations found in the silca composite samples.
not the different species being exhibited in the same spectra. For the simple octahedral potassium ferricyanide compounds the following cyanide stretching frequencies: 2135 cm\(^{-1}\) (\(A\_1g\)), 2130 cm\(^{-1}\) (\(E_g\)), and 2118 cm\(^{-1}\) (\(T\_1u\)).\(^{46}\) When cyanide is used as a bridging ligand the \(\nu(C\equiv N)\) shifts to higher frequency due to the addition of the nitrogen bound metal ion perturbing the system.\(^{47}\) The logic for it being these three modes would seem to be valid since the concentration of the Fe\(^{II}\) – CN – Co\(^{III}\) defect sites are probably very low and not detectable under our conditions. The concentration of the metals in the silica matrix is too low to be able to examine them in the IR.

Previous research was done on the bulk phase of these types of Prussian blue analogues in the area of powder X-ray diffraction. The compounds crystallize in the face-centered cubic lattice with the space group \(F42m\) (\(T\_d^2\)) (Figure 7).\(^{48}\) The diffractogram for the complex most resembling the system present in the xerogel exhibited intense peaks.\(^{49}\) The lattice can be described as a cubic close-packed array of two different anions: carbon and nitrogen, which create the cyanide bridging ligand with the metal ions located in the interstitial positions in the array. Along the cube edge there is the following sequence of atoms: Fe-C≡N-Co-N≡C-Fe. The value that was found for the lattice constant (a), was found to be 10.296 ± 0.006 Å.\(^{48}\) This value was used to verify the electron diffraction pattern found when using the transmission electron microscope.

Support for a superparamagnetetic origin of the magnetic properties and an explanation for the blue shift in the electronic spectrum is provided by the observation of K\(_x\)Co\(^{II}\)\(y\)[Fe\(^{III}\)(CN)\(_6\)]\(_z\) nanoparticles in the silica matrix. These particles can be observed directly by transmission electron microscopy. The electron microscope reveals domains that are approximately 8 to 10 nm in size (Figure 8). These domains are distributed throughout the amorphous matrix.

The strong diffraction of these domains verifies that they have crystalline properties. The quantitative analysis of the diffraction pattern obtained for these xerogel materials (Figure 8, inset), which was described in the general experimental section, yields a set of d-spacings identical to those of the bulk cobalt (II) – iron (III) phases. Due to these matching, the nanoparticles formed,
Figure 7. Unit cell of the cobalt – iron Prussian Blue analog. Interstitial K\(^+\) ions, water molecules, and defects sites have been left out for clarity. Depending on stoichiometry a certain number of Fe sites are vacant.\(^{50}\)
Figure 8. Transmission electron microscopy image of a powdered cobalt (II) – iron (III) xerogel showing nanoparticle crystalline structures with a size of 8 – 10 nm (inset: indexed diffraction pattern of the nanoparticles shown).
can be unambiguously assigned to the mixed valence compound (Table 3). Powder x-ray diffraction of these nanocomposite materials is not possible due to the very low concentration of the actually Prussian blue complex in the silica matrix.

Since the synthesis of these materials is carried out by mixing solutions of the different components together to form the homogeneous sol-gel solution, the formation of these nanoparticles must occur spontaneously during one of the phases in the sol-gel process. Given the large formation constants for Prussian blue analogues, the existence of nanoparticles in the matrix (as opposed to bulk phase separated regions within the glass) strongly suggests that gelation of the silica matrix effectively arrests the precipitation of the \( \text{K}_x\text{Co}^{II}\text{y}[\text{Fe}^{III}(\text{CN})_6]\text{z} \) and is able to sequester the particles of the complex. This explanation is probably one of the reasons high concentrations of these materials in a xerogel are very hard to make. It is believed that this is the first time that nanoparticles of these types of materials have been generated in this particular way. With one exception, Prussian blue complexes have not been produced as nanoparticles, and, to the best of our knowledge there have been no reports of their systematic incorporation in to composite structures. In the one exception Mann\textsuperscript{51} synthesized the hydrophobic nanoparticles of crystalline cobalt hexacyanoferrate using water- in-oil emulsions. These nanoparticles were well defined and uniform in size within the range of 12 – 22 nm. Their size distribution depended on the concentration of the encapsulating agents.

Given that many of the magnetic properties of this and other Prussian blue analogues are dependent on the exact composition of the complex, including the amount of alkali metal present in the lattice, x-ray fluorescence measurements were undertaken to hopefully ascertain the composition of our materials. In the case of the nanocomposite materials reported here, the total amount of the metals is so low that an accurate determination of the amount of \( \text{K}^+ \) ions present in the lattice of the nanoparticles (rather than the gross amount present in the material as a whole) proved impossible by conventional techniques. Instead, bulk \( \text{K}_x\text{Co}^{II}\text{y}[\text{Fe}^{III}(\text{CN})_6]\text{z} \) was synthesized under the same conditions of stoichiometry.
Table 3. Matching d-spacings from the electron diffraction data of a 0.03 mol % Co / Fe xerogel sample.

<table>
<thead>
<tr>
<th>Ring</th>
<th>d-spacings from diffraction pattern (Å)</th>
<th>Calculated d-spacings (Å)</th>
<th>h l k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1</td>
<td>2.21</td>
<td>2.30</td>
<td>4 2 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.10</td>
<td>4 2 2</td>
</tr>
<tr>
<td>Line 2</td>
<td>1.88</td>
<td>1.82</td>
<td>4 4 0</td>
</tr>
<tr>
<td>Line 3</td>
<td>1.63</td>
<td>1.63</td>
<td>6 2 0</td>
</tr>
<tr>
<td>Line 4</td>
<td>1.36</td>
<td>1.38</td>
<td>6 4 2</td>
</tr>
<tr>
<td>Line 5</td>
<td>1.16</td>
<td>1.15</td>
<td>8 4 0</td>
</tr>
</tbody>
</table>
and concentrations and was found from, X-ray fluorescence and FTIR measurements, to have the formula $K_{0.27}Co^{II}_{1.33}[Fe^{III}(CN)_6]$. This formula is close to that of the materials studied by Hashimoto, but it cannot be asserted that this composition is retained in the nanoparticles made during the sol-gel process. The presumed presence of the potassium ion becomes important when explaining the photomagnetic effects of the complex.

**Magnetic Characterization:**

The magnetic properties of the cobalt (II) – iron (III) Prussian blue analogue have been studied in great detail. One of the first to look into these properties was Juszczyk. His goal was to design molecular ferromagnets. They decided to build a three-dimensional covalent bonding network between first row transition metals, using cyanide superexchange bridges as the linkages to presumably mediate intra- as well as interplaner magnetic couplings in these systems. The formula of the complex he studied was $Co_3[Fe(CN)_6]_2 \cdot H_2O$. For this complex a substantial departure from Curie-Weiss behavior was evident below 50 Kelvin. It was seen that below 15 Kelvin the magnetization saturates in the way characteristic of a ferromagnet. He found the critical Curie temperature ($T_c$) for the onset of long-range ferromagnetic ordering to be 14 Kelvin. The magnetization against applied field for the $Co_3[Fe(CN)_6]_2 \cdot H_2O$ complex exhibits a hysteresis loop that can be characteristic of ferromagnetic behavior.

Others such as Hashimoto and Verdaguer, found the cobalt (II) – iron (III) Prussian blue analogue to have similar magnetic properties. Most of the work centered on the photomagnetic features of this particular Prussian blue analogue. Further research in to the basic magnetic properties was not really explored. This seems to be a common theme in the study of the whole line of Prussian blue analogues. Most researchers when looking at the Moment vs. Temperature studies fail to look at zero field cooled data. Another omission is that of any AC susceptibilities being studied.

These earlier studies imply that this system exhibits long range ferromagnetic ordering below the well defined critical temperature of $T_c = 16$
Kelvin. Miller et al's\textsuperscript{52, 53} results show that these complexes (K_{0.16}Co[Fe(CN)]_{6}0.72 \cdot 4.4 \text{H}_2\text{O}) behave in a way that is characteristic of a cluster glass. There is no true long range order present in these complexes and the glassiness has a great effect on the dynamics of the magnetic ordering. In phase linear AC susceptibility measurements were taken and the complex showed a frequency dependent broad peak. The peak height decreases and the location of the peak shifts to higher temperatures with increasing frequency. This particular behavior is indicative of the slow relaxation processes that are found in glassy materials and the freezing into a non-equilibrium state at the frequency dependant temperature $T_p$. Using the equation mentioned earlier it is found that the relative shift in $T_p$ per decade of frequency is found to be approximately 0.01, which is a value that is characteristic of canonical spin glasses.\textsuperscript{27}

The DC magnetization data shows that the long moment of the sample below 16 Kelvin rises rapidly as the temperature is decreased. At lower temperatures the $M_{ZFC}$ deviates from the $M_{FC}$. This type of behavior indicates a history dependence of the magnetization processes. The bifurcation point (the temperature at which the $M_{FC}$ and $M_{ZFC}$ curves merge) was shifted to lower temperatures as the magnetic field used for the measurements was increased. The difference between $M_{FC}(T)$ and $M_{ZFC}(T)$, which indicates strong irreversibility; and the fact that the bifurcation point was shifted to lower temperatures with the field increases makes the case for describing these complexes as having glassy behavior.\textsuperscript{54} In normal spin glasses $M_{FC}$ for the temperatures below the bifurcation point is almost flat, but in Miller's data the magnetization continued to rise. It was reported that such behavior has been seen previously in cluster glass materials.\textsuperscript{55} This rise in magnetization that happened around 16 Kelvin might be associated with the occurrence of finite range antiferromagnetic coupling, which forms clusters around the pseudocritical temperature $T_c$. The peak that was seen in the AC scans might be attributed to the freezing of clusters as $T$ is taken below $T_c$. In the DC data the freezing was indicated by the strong deviation of the $M_{FC}$ and $M_{ZFC}$ curves.
As discussed earlier, it had long been thought that bulk samples of the Prussian blue analogue $\text{M}_x\text{Co}^{II}\text{y}[\text{Fe}^{III}(\text{CN})_6]_z$ (M = alkali-metal cation) were basically ferromagnets, shown by the field cooled magnetization curves, with a Curie temperature of 14 Kelvin. It was then discovered that this complex also showed a blocking behavior in the zero field cooled magnetization. This blocking behavior has been attributed to spin glass properties, which are said to arise from defects in the lattice of the complex. Specifically the bulk complexes are denoted as cluster glasses. AC susceptibility was also used and a distinct frequency dependence was found in the bulk materials and using Mydosh’s equation the data fit with this new characterization of the $\text{M}_x\text{Co}^{II}\text{y}[\text{Fe}^{III}(\text{CN})_6]_z$ as a spin glass.\textsuperscript{27}

When this complex was made within the sol gel matrix it was not known what the magnetic properties would end up being. Since the samples had to be made in such low concentrations one might expect that a dilute dispersion of the $\text{K}_x\text{Co}^{II}\text{y}[\text{Fe}^{III}(\text{CN})_6]_z$ complex in a xerogel would only exhibit simple paramagnetic behavior. This expectation however was not the case. The field cooled and zero field cooled magnetization curves as a function of temperature for the 0.03 mol % $\text{K}_x\text{Co}^{II}\text{y}[\text{Fe}^{III}(\text{CN})_6]_z$ xerogel (Figure 9) indicated a much more complex behavior similar to that of the spin glass properties seen by Miller.\textsuperscript{52} The field cooled magnetization curve basically mirrors that of the bulk phase samples studied earlier and shows the increase that indicates ferromagnetism, except that the Curie temperature is lower at approximately 13 Kelvin. The zero field cooled magnetization curve shows a well defined broad peak that is centered at approximately 10 Kelvin. This peak is associated with the superparamagnetic blocking temperature of the nanoparticles in the silica matrix. The blocking behavior is determined by the magnetic anisotropy of the particles and their size. The broadness of the peak is normally due to the particle size distribution. Above this blocking temperature the zero field cooled and field cooled magnetization curves merge and become coincident. This type of behavior has been noted to be characteristic of the blocking behavior in a superparamagnet system of small, single-domain particles or, as it has been described in the bulk phase samples of
Figure 9. Field cooled (FC) and zero field cooled (ZFC) DC magnetization versus time curves at $H = 100 \text{ Oe}$ for a 0.03 mol % cobalt (II) – iron (III) xerogel.
the complex the glass transition in a spin glass.\textsuperscript{56} There is however a difference in the behavior of the magnetism versus temperature plots for the zero field and field cooled cases when talking about superparamagnetism and spin glass systems. For the xerogel system the two curves are distinguishable at temperatures much higher than the temperature where the zero field cooled curve shows a maximum and the field cooled curve continues to increase after that temperature. Whereas for spin glasses the curves are still rather close together at that point.

Measurement of the magnetization as a function of field strength at 5 Kelvin, which is below the blocking temperature (Figure 10, A) reveals open hysteretic behavior that reaches a magnitude of $7.08 \times 10^3$ EMU mol$^{-1}$ at 5 kOe. The coercive field was measured to be approximately 0.41kOe. From room temperature down to the blocking temperature no hysteresis is observed (Figure 10, B). These observations are also characteristic of both a superparamagnet and a spin glass. When the hysteresis loops are measured under both field cooled and zero field cooled conditions at 5 Kelvin (Figure 10, A) the loops are identical and are symmetric about the center. This feature is one of the defining characteristics of superparamagnetism.\textsuperscript{56, 57} In contrast, although the hysteresis loop of a spin glass at temperatures well below its glass transition temperature is still seen to be symmetric about the center when the system is cooled in a zero field environment, when the system is cooled in the presence of a field the hysteresis loop has been seen to be displaced from the origin in the direction opposite to that of the external field used when the system was cooled. It can be suggested that in the nanoparticle system set up by the xerogel that this property is possibly superimposed by the inherent spin glass characteristics of the bulk.

These conclusions are also consistent with the AC susceptibility data (Figure 11). The in-phase linear susceptibility data shows a broad peak that is frequency dependant in that the placement of the peak on the temperature scale increases with an increase in frequency. The peak height also decreases with the increasing frequency, which is indicative of a slow relaxation process that is found in both spin glasses and superparamagnets. One of the ways to
Figure 10. A) Field cooled (●) and zero field cooled (○) hysteresis loops of a 0.03 mol % cobalt (II) – iron (III) xerogel at T = 5 Kelvin and B) hysteresis loop at T = 13
Figure 11. Frequency dependence of AC susceptibility measurements taken at 100 (●), 1,000 (○), 5,000 (■), and 10,000 (□) Hz for a 0.03 mol % cobalt (II) – iron (III) xerogel.
distinguish between these two types of magnetism is to look at how the peaks shift with regard to a change in frequency in the AC. The degree of shift helps determine if a sample is a spin glass or if it is a superparamagnet. A quantitative measure of the frequency shift (K) is obtained by looking at the equation that was discussed earlier and was proposed by Mydosh\textsuperscript{27}, where $T_f$ is the freezing temperature for the samples and is defined as the maximum in the ac susceptibility, $\chi'$, and $\omega$ is the frequency. As mentioned before the bulk sample of these materials characterized as a cluster glass by Miller had a K value of approximately 0.01.\textsuperscript{52} Using bulk samples made with Hashimoto’s prep the K values that were obtained are on the order of 0.045 (Table 4). This number falls into the range typical of a spin glass system. For the nanocomposite system the values were approximately 0.17. Spin glasses normally give K numbers that are on the order of 0.01 and superparamagnets give values higher that 0.1. Our nanocomposite sample is probably on the border due to it having some spin glass properties as well as also being a superparamagnet. According to Mydosh\textsuperscript{27} this frequency shift offers a good criterion for distinguishing spin glasses from spin glass like materials from a superparamagnet.

\textbf{Photomagnetism:}

One of the more interesting characteristics of the Co\textsuperscript{II}[Fe\textsuperscript{III}(CN)\textsubscript{6}] complex is that it displays photomagnetism, which was originally reported by Hashimoto.\textsuperscript{35} The basic phenomenon is that at temperatures lower than 150 Kelvin red-light illumination ($\lambda \approx 600$ nm) causes a net increase in the magnetization of the bulk material. Their research focused on a bulk sample with the formula $K_{0.2}Co_{1.4}[Fe(CN)\textsubscript{6}] \cdot 6.9H\textsubscript{2}O$. When they irradiated the sample at 5 Kelvin, the magnetization at 5 gauss increased quickly and then gradually saturated after several tens of minutes. This enhancement lasted for a period of several days at 5 Kelvin. The magnetic enhancement relaxed to the initial state when the
Table 4. Frequency shifts of $T_f$ for the two different cobalt-iron Prussian blue systems studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency ($\omega$, Hz)</th>
<th>Freezing Temperature ($T_f$, K)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 mol % Co/Fe sol gel</td>
<td>1,000</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>0.03 mol % Co/Fe sol gel</td>
<td>10,000</td>
<td>6.3</td>
<td>0.17</td>
</tr>
<tr>
<td>Co/Fe bulk phase</td>
<td>100</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>Co/Fe bulk phase</td>
<td>1,000</td>
<td>9.2</td>
<td>0.045</td>
</tr>
</tbody>
</table>
temperature of the sample was raised over 150 Kelvin, indicating that the magnetization can be induced by the photon mode, but can also be restored almost to its original level by thermal treatment. Using infrared spectroscopy it had been determined that after red-light illumination the intensity of the peak at 2116 cm$^{-1}$ decreased substantially and the peak at 2162 cm$^{-1}$ increased. After illumination was complete the strong peak at 2162 cm$^{-1}$ and the small shoulder at 2097 cm$^{-1}$ remained. These results show that the Fe$^{II}$ – CN – Co$^{III}$ moieties are responsible for the photoinduced effects. The electronic spectrum also changed due to the irradiation. The absorbance around 550 nm decreased and the peak around 400 nm increased after red-light illumination.\textsuperscript{35}

Based on the infrared data it was concluded that the oxidation states of both iron and cobalt change from Fe$^{II}$ – CN – Co$^{III}$ to Fe$^{III}$ – CN – Co$^{II}$ through red-light illumination. Generally Co$^{II}$ and Co$^{III}$ are coordinated octahedrally by nitrogen and have high spin ($t^5_{2g}e^2_g$, $S = 3/2$) for the Co$^{II}$ and low spin ($t^6_{2g}$, $S = 0$) for the Co$^{III}$. For the iron metal centers, Fe$^{III}$ is found as low spin ($t^5_{2g}$, $S = 1/2$) and Fe$^{II}$ is low spin ($t^6_{2g}$, $S = 0$). The contribution of the state of Fe$^{II}$ – CN – Co$^{III}$ is reduced, and after red-light illumination the state of Fe$^{III}$ – CN – Co$^{II}$ is increased. The increase brought on by the contribution of more of the paramagnetic components Fe$^{III}$ and Co$^{II}$ leads to the enhancement of the magnetization value. In addition the pathways that are disrupted by having the diamagnetic species Fe$^{II}$ and Co$^{III}$ in the lattice before illumination are reestablished due to the red-light illumination. The $T_c$ value is then raised because there is an increase in the number of magnetic neighbors\textsuperscript{35, 52, 58, 59, 60} In Hashimoto’s work the $T_c$ was raised from 16 to 19 Kelvin. The magnetization of the sample was raised for the entire temperature range below the new $T_c$.

Other than time and thermal treatments it was found that if they carefully tuned the wavelength of incident light the enhancement that comes from illuminating with red-light can be negated through blue light irradiation ($\lambda \approx 450$ nm). The magnetization that was decreased with blue light could then be enhanced again by using the red light. The cycle can then be repeated. IR spectra showed that the stretch located at 2097 cm$^{-1}$ increased and decreased
repeatedly with the alternating blue and red light respectively. This stretch is associated with the Fe$^{II}$ – CN – Co$^{II}$ pair which is found in very small quantities.

Once it was understood that the amount of Fe$^{II}$ – CN – Co$^{III}$ pairs drove the enhancement of the magnetization after red-light illumination, the next step was to try and control the amount of Fe$^{II}$ – CN – Co$^{III}$ available for transformation in the samples. Much of this control was centered on using differing amounts and types of cations to drive the formation of the Fe$^{II}$ – CN – Co$^{III}$ defect sites. During the synthesis of the cobalt – iron Prussian Blue analogues substitution of the hexaaqua complex [Co$^{II}$$(\text{H}_2\text{O})_6$]$^{2+}$ by [Fe$^{III}$$(\text{CN})_6$]$^{3-}$ occurs. This substitution leads to a progressive increase in the cobalt’s ligand field as the oxygen atoms from the water are replaced with the nitrogen atoms found on the cyanide. Once there are an adequate number of nitrogen atoms surrounding the cobalt ion, the cobalt becomes low spin due to the large ligand field splitting and its ability to reduce is greatly enhanced. At this point a chemically induced electron transfer leads to a more stable Fe$^{II}$ – CN – Co$^{III}$ pair. To be able to increase the number of diamagnetic pairs responsible for the photomagnetic effect, one has to increase the number of nitrogen atoms that surround the cobalt ion.

Michel Verdaguer was the first to use cations to try and control the photomagnetic effect.$^{49, 61}$ By introducing various quantities of alkali cations in to the structure, they synthesized three different cobalt – iron Prussian Blue analogues in which the environment around the cobalt ion varies from an average of four nitrogens and two oxygen atoms CoN$_4$O$_2$ in the idealized structure A$^{II}_4$B$^{III}_4$(CN)$_6$$_{8/3}$ (Complex 1), to six nitrogen atoms CoN$_6$ in the compact structure C$^{I}_4A^{II}_4$B$^{III}_4$(CN)$_6$$_4$ (C$^{I}$ = alkali cation, Complex 3). An intermediate complex was also studied that had on average five nitrogen atoms and 1 oxygen atom around the cobalt (Complex 2). Complex 1 was made with only the small amount of potassium present from the potassium ferricyanide. Complexes 2 and 3 were made by adding in rubidium and cesium nitrate respectively to the mixture of cobalt nitrate hexahydrate and potassium ferricyanide. The insertion percentage of the alkali cation tends to increase with the size of the cation. Through infrared spectroscopy it was found that complex 1 is made up of cobalt
atoms with the oxidation state of 2+ and iron atoms with an oxidation state of 3+. Very little to no electron transfer occurs during the synthesis of this complex, so there are practically no Fe$^{II}$ – CN – Co$^{III}$ pairs. The IR spectrum of complex 2 indicates that the majority of the cobalt atoms are found to be in the 3+ oxidation state with a few being in the 2+ state. The iron in complex 2 is almost exclusively in the 2+ oxidation state. The electron transfer that is induced by the increasing of the ligand field around cobalt during the synthesis is said to be total. The IR spectrum of complex 3 denotes that practically all of the cobalt – iron pairs are Fe$^{II}$ – CN – Co$^{III}$.

These three samples were then tested to see what if any photomagnetic effects were present. Complex 1 is ferromagnetic before irradiation and the magnetization was not effected by the irradiation. This result is not surprising seeing as complex one is made up of Fe$^{III}$ – CN – Co$^{II}$ magnetic pairs. Complex 2 is in essence diamagnetic before irradiation. The complex is built mainly of Fe$^{II}$ – CN – Co$^{III}$ pairs that have both metals being low spin d$^6$. After irradiation the magnetism was enhanced by a factor of approximately ten. The temperature scan after irradiation resembles that of complex 1 (the magnitude of the magnetization of complex 2 at 5 Kelvin was about 50% of complex 1’s), but the $T_c$ was raised to ~ 21 Kelvin. Complex 3, which is also diamagnetic before irradiation, showed only a very small photoinduced effect (the magnitude of the magnetization of complex 3 at 5 Kelvin was about 0.25% of complex 1’s).

Based on these results it was concluded by Verdaguer that a sufficient number of the diamagnetic Fe$^{II}$ – CN – Co$^{III}$ pairs must be present for the photoinduced effect to be observed. This is why complex 1 showed no effect, because it is made up mainly of the paramagnetic Fe$^{III}$ – CN – Co$^{II}$ pairs. Complex 2 exhibited the photoinduced effect due to the abundance of the Fe$^{II}$ – CN – Co$^{III}$ pairs. The irradiation of complex 3 showed very little photoinduced effect. The result seemed to disappear when too many diamagnetic pairs were present. To explain this phenomenon, Verdaguer offers the following hypothesis. The photoinduced electron transfer involves a change in the cobalt oxidation state from low spin Co$^{III}$, with no electron inhabiting the antibonding e$_g^*$ orbitals,
to either a low or high spin Co$^{II}$ with either one or two electrons respectively in the $e_g^*$ orbitals. This electron transfer should then be accompanied by an increase in bond lengths in the coordination sphere of the cobalt by 0.15 to 0.20 Å according to published values for cobalt complexes.\textsuperscript{62} For the system to be able to absorb the fluctuation in the Co – N bond length and the related increase of the cell parameters, the network must be flexible. The iron vacancies around the cobalt are normally filled with water molecules that are loosely hydrogen bound to other waters and can behave as a relaxation point in the matrix. In complex 3 however all of cobalt’s coordination sites are filled and there are no relaxation points, which make the framework much more rigid, so that during the irradiation process the excited state never reaches its equilibrium distance and relaxes immediately.

This photomagnetic effect was examined for our newly established system in the xerogel. In the nanocomposite system there is an analogous photomagnetic effect when the glass is irradiated at 5 Kelvin, and 500 Oersteds; with $\lambda \geq 550$ nm (Figure 12). The sample was irradiated for a period of approximately 50 minutes. At the beginning a sharp increase in the magnetization occurs. After the initial enhancement the level of magnetization levels off until the irradiation is over. This enhancement of magnetization is once again due to the electron transfer from the iron metal center in the Fe$^{II}$ – CN – Co$^{III}$ defect sites to the cobalt metal center causing a change to the paramagnetic Fe$^{III}$ – CN – Co$^{II}$ pair. When the irradiation is complete there is a final increase in magnetization. While the sample is being irradiated it is also being slightly warmed as well (magnitude of warming not able to be seen on the instrument). Due to this warming the magnetization is somewhat suppressed. Since these samples are field cooled the magnetization lies on the ferromagnetic part of the temperature scan at 5 Kelvin. Basically the warming causes the sample to see its magnetization back down that curve slightly, but once the source of heat is taken away (the lamp) the magnetization increases to the point where it would have been all along. As seen in Hashimoto’s samples our nanocomposite system also demonstrates a loss of magnetization when irradiated with blue light ($\lambda = 448$ nm).
Figure 12. Photomagnetic effect at $\lambda \geq 550$ nm, H = 500 Oe, and T = 5 K.
When the sample is then irradiated with red light ($\lambda \geq 550$ nm) an increase is seen. This process can be repeated a number of times. This phenomenon is probably attributed to the blue light irradiation which causes an increase in the amount of the defect Fe$^{II}$ – CN – Co$^{III}$ diamagnetic pairs. The red light irradiation causes a conversion back to the Fe$^{III}$ – CN – Co$^{II}$ paramagnetic pairs. Not much is known about how this is accomplished. In Hashimoto’s observations of this effect it was noted that the cyanide stretch which they assigned to the Fe$^{II}$ – CN – Co$^{II}$ stretch was increased due to the blue light irradiation. It would seem that the irradiation was producing more of these pairs which, doesn’t seem feasible since there would have to be an oxidation occurring elsewhere in the lattice for this reduction to be occurring. No evidence has been found to suggest that this oxidation occurs. It is more feasible to speculate that basically the blue light irradiation is driving the same electron transfer that occurs when there is an increase in the ligand field splitting of the cobalt that was discussed previously. This electron transfer would cause a decrease in the magnetization due to the formation of more diamagnetic pairs. This photochemically driven electron transfer has not been studied much further than just showing the effect on the magnetization. Other than just showing that the xerogel materials also exhibit this effect, it was not studied further. The basic effect of being able to control the magnitude of the magnetization by alternating different wavelengths of light was the only real point to be made.

The next avenue that was explored dealt with trying to control the photomagnetic effect. Just as Verdaguer used different cations to increase the ligand-field strength around the cobalt metal centers, driving the electron transfer from the cobalt to the iron to generate more Fe$^{II}$ – CN – Co$^{III}$ defect sites this research focused on ligand substitution. Due to the porous nature of the silica matrix one is able to do ligand substitution around the cobalt metal center. This substitution of the cobalt centers by ammine and other high-field ligands can be accomplished cleanly and in a highly controlled manner. By using ligands that cause a greater ligand field splitting it was the aim of this research to drive the electron transfer and create more of the Fe$^{II}$ – CN – Co$^{III}$ defect sites responsible
Figure 13. Magnetization changes induced by altering blue (corresponds to the decreases in magnetization) and red (corresponds to the increases in illumination) light illumination of a 0.03 mol % cobalt (II) – iron (III) xerogel sample.
for the photomagnetic effect. As shown in Figure 14, flowing ammonia over the composite results in continuous spectral changes that are highly isobestic. The broad intervalence band seen between 450 and 650 nm is replaced by a single peak at 470 nm. This peak is characteristic of hexamine cobalt (III) centers. What this suggests is that diamagnetic Fe$^{II}$ – CN – Co$^{III}$ defect sites have been created when ammonia is substituted on to the cobalt metal centers. This effect is similar to what is seen when a bulk complex of Na$_x$Co$^{II}_y$[Fe$^{III}$(CN)$_6$]$_z$ is immersed in a saturated solution of potassium ions at high temperatures.$^{50}$ A cation exchange occurs between the sodium and the potassium. This exchange leads to an electron transfer from the cobalt to the iron to give the Fe$^{II}$ – CN – Co$^{III}$ pair. When this reaction takes place the intervalence band at approximately 550 nm increases and the peak at 400 nm disappears, which is in agreement with what had been seen using the ammonia ligand exchange. More diamagnetic defect sites are created in each circumstance.

Measurement of the magnetization of the composite as a function of ammine doping shows a steady decrease in the magnetization overall, and the materials become diamagnetic at the highest levels of ammonia doping. The changes in the magnitude of the photomagnetic effect as a function of the amount of exposure time to ammine doping is shown in Figure 15. Using extremely small exposure increments the change in magnetization due to the photomagnetic effect increases to a maximum of 9.4 % above that of the doped but non irradiated composite. Originally the photomagnetic effect denotes about a 7.6 % increase in the magnetization of an undoped sample. Above this threshold the photomagnetic effect decreases. At higher degrees of ligand substitution the photomagnetic effect vanishes altogether. This change is consistent with the observations that were made on the bulk samples by Verdaguer when the sample was comprised exclusively of the diamagnetic Fe$^{II}$ – CN – Co$^{III}$ pairs, which exhibited a severely diminished capacity to undergo the photomagnetic change. As noted earlier this change to the photomagnetic effect was explained as arising from an increased rigidity in the lattice as the number of Fe$^{II}$ – CN – Co$^{III}$ pairs is increased. This rigidity will no longer accommodate the
Figure 14. A series of optical absorption spectra taken every 30 minutes while anhydrous ammonia flowed over a 0.03 mol % cobalt (II) – iron (III) xerogel.
bond-length increases that accompany the electron transfer of the Fe$^{II}$ – CN – Co$^{III}$ to the metastable state. Although this rigidity effect may also be happening in the nanocomposites, high degrees of ammine substitution on the cobalt may ultimately result in the disruption of the cyanide bridge between the iron and the cobalt. This disruption would result in the deactivation of the electron transfer pathway, which in turn would also degrade the photomagnetic effect.$^{63}$

Figure 15. Percentage increase in magnetization of NH$_3$ – substituted 0.03 mol % cobalt (II) – iron (III) xerogels as a function of NH$_3$ exposure time (10 µL doses).
CHAPTER 2

NICKEL - IRON

Introduction

The nickel (II) – iron (III) Prussian blue analogue is the much less studied cousin to the cobalt (II) – iron (III) analogue. The absence of the photomagnetic effect makes this analogue less desirable to study. For our work it was the next logical step in the production of these new nanoparticles within the silica matrix. The nickel (II) – iron (III) complexes have the next highest Curie temperature for the Prussian blue analogs. It was once again assumed that this complex is basically another ferromagnetic Prussian blue analogue. This research focused on the fabrication of these new nanocomposite materials containing $K_xNi^{II}_y[Fe^{III}(CN)_6]_z$ in a porous silica matrix. Using the same methodology described in the previous chapter the precipitation was arrested for these materials giving what can be described as nanorods of the complex. These particular xerogel samples better demonstrate the effect that the gelation of the silica network has on the formation of the nanostructures involved. Magnetically, they exhibit superparamagnetic behavior in the sol gel samples and show spin glass behavior in the bulk phase samples. Once again the sequestering of nanostructures suggests a fresh approach for the utilization of the Prussian blue class of magnetic materials and using the sol-gel method in nanoparticle formation.
Experimental

Fabrication:

**Xerogel Sample:** The 0.1% Ni$^{II}$/Fe$^{III}$ xerogel was made in the following manner: a solution of methanol (20.8 mL) and an aqueous solution of potassium ferricyanide (5.5 mM; 18.6 mL) was added dropwise to a solution containing tetramethylorthosilicate (30.3 mL), methanol (11.4 mL), and nickel (II) nitrate hexahydrate (5.5 mM; 18.6 mL) in methanol. This mixture gives an overall metal concentration of 1.0 mM for each metal. After stirring 4mL of the solution was placed into polystyrene cuvettes and capped for gelation. Once gelation occurred small holes were placed in the caps to allow for the aging and drying phases to occur. After the process is complete the xerogel has approximately 12% of the original volume with a final concentration of each metal being near 10 mM.

**Bulk Sample:** Bulk composites of the Ni$^{II}$/Fe$^{III}$ Prussian blue complex were synthesized in the following manner: an aqueous solution of nickel (II) nitrate hexahydrate (25.0 mL; 0.30 M) was slowly added to a stirred aqueous solution of potassium ferricyanide (25.0 mL; 0.20 M). The resulting precipitate was vacuum filtered and washed with water, methanol and diethyl ether.

Characterization:

**Electronic Spectroscopy:** UV/VIS data was collected on a Perkin Elmer Lamda 900 instrument. Scans were taken between 200 nm to 1500 nm with data collected every nanometer. The sample was open to air and was scanned in a quartz cell. Bulk samples were measured using a diffuse reflectance attachment.
**Vibrational Spectroscopy:** IR data was collected on an Avatar 360 FT-IR at room temperature. A praying mantis diffuse reflectance attachment was used to look at the bulk powder samples.

**Transmission Electron Microscopy:** TEM images and electronic diffraction measurements were taken on a 200 kV JEOL-2010 microscope.

**X-Ray Fluorescence:** Elemental analysis was performed for the powdered bulk samples on an Oxford ED 2000.

**Magnetic Measurements:** DC magnetic measurements were taken on a superconducting quantum interference device (SQUID; Quantum Design MPMS XL-7). AC magnetic measurements were taken on a Quantum Design Physical Property measurement system (PPMS). All measurements follow the cobalt – iron experimental section.

**Results and Discussion**

**General Characterization:**

Homogeneous silica xerogels containing the nickel (II) –iron (III) Prussian blue analogue were manufactured by incorporating both of the metal center components during the solution phase of the sol-gel process. As mentioned in the previous chapter conditions such as the water to silicon ratio had to be optimized as well as the ratio of the two metals. Once again the water to silicon ratio was 5:1 and the metals were mixed at a 1:1 concentration ratio. Other metal ratios were tested, but did not give the homogeneous materials desired or precipitation of the Prussian blue complex occurred. The 1:1 metal ratio was found to be the most advantageous. When mixing occurs for the xerogel samples there is not a discernable color change from that of the yellow color characteristic of the ferricyanide. When mixing occurs at much larger concentrations, like when the bulk samples are made, there is an immediate precipitation of a brown solid.
One is able to make xerogel samples with higher concentrations using this analogue as compared to the cobalt – iron samples. The highest concentration regularly obtained was 0.1 mol % total metal to silicon. These samples retained their transparency throughout the gelation, aging and drying sol-gel phases, yielding a homogeneous optically transparent xerogel with nanoparticles of the $K_xNi^{II_y}[Fe^{III_z}(CN)_6]_z$ Prussian blue complex embedded within the silica glass. Powders of the bulk phase sample were obtained for characterization and comparison.

The electronic spectrum of the xerogel samples is similar to that of the bulk phase samples. In the xerogel samples two distinct peaks are present for all the concentrations of metal in the xerogel (Figure 16). In looking at these three different concentrations, the peak intensity is practically the only difference in each of the spectrums. There is a broad peak found at approximately 406 nm (24,631 cm$^{-1}$) for the 0.05 mol % xerogel sample and a little bit sharper peak found at approximately 300 nm (33,467 cm$^{-1}$). These two bands can more than likely be assigned to the ligand to metal charge transfer bands seen for the ferricyanide complex because one would not expect to see an intervalence band for this particular Prussian blue analogue. In a ferricyanide xerogel sample of similar concentration three bands are present, 23,800, 33,000, and 38,460 cm$^{-1}$. These bands have been assigned as LMCT bands from the cyanide to the iron and have extinction coefficients of 493, 1338, and 1157 respectively. The spectrum of a nickel xerogel also exhibits two bands in a similar pattern to the mixed valence species, but the extinction coefficients for these bands are approximately two orders of magnitude smaller, once again using the hexamine as an approximation for the nitrogen bound cyanides. Even given that the nickel in the complex is of lower symmetry thus increasing these coefficients it does not seem that the bands for the complex are the nickel bands. It would stand to reason that the bands present are due to the LMCT bands seen for the ferricyanide sample. The bands at 23,800 and 33,000 cm$^{-1}$ are shifted to higher energy in the nickel – iron xerogel samples, which is probably due to the distortion brought on by the attached nickel to the nitrogen end of the cyanide.
Figure 16. The optical absorption spectra of a 0.01 (—), 0.025 (—), and 0.05 (—) mol % nickel (II) – iron (III) xerogel.
The third band at 38,460 cm\(^{-1}\) has most likely been shifted into the higher energy shoulder seen in the spectrum of the mixed valence complex. Just as in the cobalt – iron xerogel samples the broad peak found for these samples is blue shifted from the peak found in the bulk phase samples. For the 0.05 mol % samples the peak is blue shifted by about 707 cm\(^{-1}\) from the bulk phase samples. Once again it is believed that this shift in the electronic spectrum is due to the size of the particles found in the xerogel as compared to those found in the bulk samples.

Infrared spectroscopy experiments were performed on the nickel – iron bulk complex. The spectrum showed three peaks in the area where one would expect the cyanide stretches to appear (Figure 17). The assignment of these particular peaks is the three vibrational modes found for a cyanide stretch on an octahedral species (\(A_{1g}, E_g, \text{ and } T_{1u}\)).\(^{47}\) As discussed earlier the location of these modes is shifted to higher energy when the cyanide is used as a bridging ligand as it is for these complexes. As stated in the previous chapter it is believed that these stretches that appear in our spectrum are from the three vibrational modes found for cyanide ligands and not from the specific oxidational isomers of the Prussian blue complexes. The fact that there are three stretches for the nickel – iron samples helps to back up that theory. The nickel – iron Prussian blue analogue exhibits only one set of oxidation states the \(\text{Ni}^{\text{II}} – \text{NC} – \text{Fe}^{\text{III}}\) pair. Since no other oxidation pairs are present and there still are three peaks it can at least be hypothesized that the three peaks seen in the infrared spectrum for the cobalt – iron analogue is also only the three modes found for cyanide ligands perturbed from their normal location due to the cyanide being used as a bridging ligand. It would make sense that for both analogues that all that are being found are these three modes and not peaks denoting other oxidation state pairs. The xerogel samples have limited metal concentrations and meaningful infrared data was not collected.

Support for both the blue shift in the electronic spectrum and the superparamagnetism found in the magnetics data is observed once again by the detection of nanoparticles in the xerogel samples of the nickel – iron Prussian
Figure 17. Infrared spectrum taken of the K₉Ni₃[Fe(CN)₆]₂ bulk phase sample synthesized under the same conditions of stoichiometry and concentrations found in the silica composite samples.
blue analogues. Transmission electron microscopy was performed on the composite nickel – iron samples to reveal these types of particles. In examining the 0.1 mol % xerogel sample under the microscope instances of nanostructure formation were located. Figure 18 shows one of the nanorods that were formed for this concentration. This particular nanorod is measured to be approximately 13 nm by 35 nm. The average size found was about 15 nm wide by about 40 nm long. Enough examples of these types of rods were found to say that they were not a random anomaly. The “curve” seen at the end of the nanorod is actually a series of angled straight sections (Figure 19). To further test that theory, a second group of samples were made under strictly clean conditions to be examined with the microscope. It was found that these new samples also had nanorods formed. When the 0.05 mol % nickel – iron xerogel samples were studied nano structures were also discovered. In these particular samples it was found that there was a mix of both nanorods as shown for the higher concentration samples and nanodots (Figure 20) formed. The nanodots were never seen in the higher concentration samples. Qualitatively it was observed that there were more of the nanodots formed that the nanorods for the 0.05 mol % xerogels. There also seemed to be on the whole much fewer structures available to be studied in the lower concentration samples which would make sense. A statistical study was not done to corroborate either of these observations. Once again the samples were remade and the new samples exhibited those same features. The nanodots that were formed had an average diameter of approximately 40 nm. Just like was determined for the cobalt – iron nanoparticles found, these particular nanoformations are said to have formed from an arrested precipitation of the sol-gel solution. As the nickel – iron Prussian blue complex is starting to precipitate out of solution it becomes trapped by the simultaneous gelling of the silica network surrounding the complexes. Due to the high formation constants of this and most of the Prussian blue analogues it can be safely assumed that the existence of these nanostructures (instead of bulk phase separated regions within the xerogel) once again promotes the idea of arrested precipitation. The silica network is what locks in the nanoscale size of
Figure 18. Transmission electron microscopy image of a powdered 0.1 mol % nickel (II) – iron (III) xerogel showing a nanorod crystalline structure.
Figure 19. Close-up picture of the “curve” that is formed at the end of the nanorod that is present in the 0.1 mol % nickel – iron xerogel samples.
Figure 20. Transmission electron microscopy image of a powdered 0.05 mol % nickel - iron xerogel showing nanoparticle crystalline circles with a diameter of approximately 40 nm.
the particles and keeps them separated from each other. Now the exact structures that are formed are a little bit different. One would think that only the silica network might dictate the structure of the nanoformations. It would seem from the empirical evidence that which structure will form is concentration dependant. It would appear that when there is more material to be formed the nanorods are the preferred structure. When the concentration is a bit lower (in this case half of the original samples) it can be concluded that the nanodots are the favored structure. Some nanorods do however form in the 0.05 mol % samples. The conclusion that is being asserted is that when there is more material around to form the complexes the larger nanorod formations are what will be formed during the arrested precipitation. When less materials is available to form the complexes the nanodot structure is all that can be formed before the silica network closes off access to more of the metals to form the larger rods. While examining these materials with the microscope electron diffraction pictures of the materials were also taken. The strong diffraction of these nanoformations verifies the crystalline properties that they have.

X-ray diffraction of the bulk nickel – iron cyanide complexes had been previously studied.$^{48, 66}$ In these studies it was found that the profiles for these complexes correspond to a sodium chloride type structure, which essentially the same structure found for the cobalt – iron analogue. The complexes crystallize in the face centered cubic lattice with the space group $F43m$. All the diffraction peaks were rather broad and both the diffraction angles and the intensities were fairly independent of the metal mixing ratios. This result would suggest that the lattice constants and the average crystallite sizes vary very little with changes to the mixing ratios. They were however affected to a certain degree. The lattice parameter decreased with an increase in the molar mixing ratio of the metals. It was found that the samples made with low mixing ratios were soluble and contained potassium ions in the lattice, while the samples with high mixing ratios were found to be insoluble and contained little to no potassium ions within the lattice. From these results it was concluded that the lattice parameter depended on the potassium ion content within the structure. Unlike the lattice constant the
average crystallite size increased in small increments with the increase in the molar mixing ratios of the metals. The mixing ratio of the bulk phase samples and the xerogel samples that were synthesized was 1:1. The lattice parameter previously determined was 1.0232 nm with an average crystallite size of 11.3 nm (Juszczyk obtained a number of 1.0229 nm). The numbers from both studies are essentially the same. In looking at actual Prussian blue when the mixing ratio is one the lattice constant is 1.027 nm and the average crystallite size is 9.77 nm. When comparing the values for the nickel – iron cyanide complex with Prussian blue it can be seen that the lattice sizes are comparable, but the average crystallite size is a little bigger for the nickel – iron cyanide complexes. Powder X-ray diffraction of the xerogels samples was not possible due having such a low concentration of metals present in the samples. Although more metal was present for these samples than the cobalt – iron samples, it was still not possible to extract that data.

To verify that the structures that were found using the TEM were indeed formations of the nickel – iron Prussian blue complex the electron diffraction patterns that were found were indexed (Figure 21). Using the information provided in the x-ray diffraction study referenced above we were able to take the electron diffraction from the xerogel samples and index the ring patterns that were found. Measurements were taken from various electron diffraction patterns of the nanostructures found in the xerogel samples. From these measurements the d-spacings of the rings were calculated. The d-spacings for various Miller indices up to the fourth order were calculated using the lattice parameters found in previously reported research. The d-spacings taken from the actually diffraction patterns matched the d-spacings calculated from the lattice parameters (Table 5). Four almost perfect matches were acquired using this method. Due to these matching, the nanostructures that were formed can be unambiguously assigned to the nickel – iron mixed valence compound.

As explained in the previous chapter, many of the magnetic properties of this and other Prussian blue analogues are dependent on the exact composition of the complex, which includes the amount of alkali metal present in the lattice.
Figure 21. Indexed diffraction pattern of a nanorod found in the 0.1 mol % nickel – iron xerogel sample.
Table 5. Matching d-spacings from the electron diffraction data of a 0.1 mol % nickel - iron xerogel sample.

<table>
<thead>
<tr>
<th>Ring</th>
<th>d-spacings from diffraction pattern (Å)</th>
<th>Calculated d-spacings (Å)</th>
<th>H I k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1</td>
<td>4.15</td>
<td>4.17</td>
<td>2 1 1</td>
</tr>
<tr>
<td>Line 2</td>
<td>3.39</td>
<td>3.40</td>
<td>2 2 1</td>
</tr>
<tr>
<td>Line 3</td>
<td>2.40</td>
<td>2.41</td>
<td>3 3 0</td>
</tr>
<tr>
<td>Line 4</td>
<td>1.97</td>
<td>1.97</td>
<td>3 3 3</td>
</tr>
</tbody>
</table>
Because of this dependence, x-ray fluorescence measurements were undertaken to hopefully verify the composition of our materials. In the case of the nanocomposite materials reported here, once again the total amount of the metals is so low that an accurate determination of the amount of $K^+$ ions present in the lattice of the nanoparticles (rather than the gross amount present in the material as a whole) was not possible using traditional techniques. The synthesized bulk $K_xNi^{II}_y[Fe^{III}(CN)_6]_z$ samples were used instead. These samples were synthesized under the same stoichiometric conditions as the xerogel samples. X-ray fluorescence and FTIR measurements were done, to give the following formula $K_{0.2}Co^{II}_{1.9}[Fe^{III}(CN)_6]$. We assume that this formula is the same as what is found in the xerogels but we cannot assert concretely that this composition is retained in the nanoparticles made during the sol-gel process.

**Magnetic Characterization:**

As stated earlier the magnetic properties of nickel (II) – iron (III) Prussian blue analogue have not been studied to the degree that those of the cobalt – iron analogue have been researched. The main reason is the apparent lack of photomagnetism present in these analogues. The iron (III) will continue to be in the low spin $d^5$ configuration ($t^5_{2g}$, $S = \frac{1}{2}$) due to the high ligand field splitting on the carbon bound cyanide ligand. The nickel (II) is a $d^8$ metal center which is not distinguishable as either high spin or low spin ($t^6_{2g}e^2_{g}$, $S = 1$). There does not appear to be any reason for defect sites to form analogous to the cobalt – iron system. The nickel metal center is fairly stable in its +2 oxidation state and increasing the ligand field splitting by either adding in alkali cations like Verdaguer\textsuperscript{49} or using a high field ligand such as ammonia as previously described, would not drive the electron transfer present in the cobalt – iron complexes to create defect sites that are photochemically activated. The ferromagnetism that is used to describe these systems results from the $t^5_{2g}$, $S = \frac{1}{2}$ for the low spin iron and the $t^6_{2g}e^2_{g}$, $S = 1$ from the nickel to give magnetic orbitals that overlap with orthogonal orbitals on the cyanide bridge, which favor the maximum total spin in accordance with Hund’s rule.
Some studies however have been done on this particular analogue. One of the first studies was once again done by Juszczyk. In the paper where he describes the cobalt – iron analogue he also looks into the magnetic properties present for the nickel – iron bulk system. This complex showed that it also had a substantial departure from Curie-Weiss behavior around 50 Kelvin and below 15 Kelvin the magnetization saturates in such a way as to be described as a ferromagnet. He found that the Curie temperature of the $\text{Ni}_3[\text{Fe(CN)}_6]_2$ bulk samples to be 23.6 Kelvin. The magnetization against applied field for the $\text{Ni}_3[\text{Fe(CN)}_6]_2$ complex exhibited a hysteresis loop that can be characteristic of a ferromagnetic material. At 4.4 Kelvin the hysteresis loop had a coercive field of 2570 Oersteds and a well defined remanence. The coercive field for this system was found to be much larger than that of the cobalt – iron complex.

One of the only other studies performed on the nickel – iron Prussian blue analogue, was conducted by Talham et al. In their study they assemble two – dimensional cyanide bridged nickel (II) – iron (III) square grid networks at the air – water interface and transfer these networks as isolated monolayer, isolated bilayer, and multiple bilayer films via the Langmuir – Blodgett technique resulted in novel low – dimensional systems. The effect of dimensionality on magnetic behavior in the molecule – based materials can be observed. Each of the different layering samples were studied for their research. The multiple bilayer films (150 cycles of dipping) are the results that will be discussed here because it would seem that those would have the closest resemblance to the true bulk phase. This particular sample had alternating regions of organic to organic and inorganic to inorganic bilayers present. DC magnetic measurements were taken on the samples. For the magnetization versus temperature studies both field cooled and zero field cooled scan were taken. The field cooled curves showed a rapid rise in the magnetization at temperatures lower than 10 Kelvin, gradually leveling off after 5 Kelvin. This behavior is characteristic of ferromagnetic exchange which has been noted earlier. The field cooled magnetic response was said to be anisotropic. In the zero field cooled scan a broad peak appears that is similar to the ones seen for the cobalt – iron analogues. The overall scan
intensity is diminished when the measurements are taken with the films perpendicular to the field than when they are parallel. Hysteresis measurements were also undertaken to give open hysteresis loops with a large remnant magnetization when the films are aligned parallel to the field and a much smaller one when they are perpendicular. The coercive field was also found to be anisotropic for both orientations.

What set this research apart from Juszsczyk’s experiments is that the zero field cooled measurements were taken, but also that AC Magnetometry measurements were looked at as well. The AC data at low temperatures shows a distinct frequency dependant peak that shifts similar to those found in the cobalt – iron system. Once again the intensity of the parallel samples is about one order of magnitude higher than that of the perpendicular. If these measurements had not been undertaken it would have been similarly concluded that these films were indeed just ferromagnets which has been the prevailing wisdom in many cases. The frequency dependent AC magnetization fights that simplistic conclusion to reveal a more complex description. Since frequency dependence is seen for both spin glasses and superparamagnets the frequency dependence ratio brought forth by Mydosh and described earlier was calculated for these films. The value obtained for the sample dipped 150 times was found to be 0.04 which is well within the range of a spin glass. This behavior was interpreted to be characteristic of spin glass type ordering of ferromagnetic domains to form a cluster glass similar to the conclusions Miller drew about the cobalt – iron bulk phase samples described earlier. This spin glass behavior stems from the spin frustration which arises from a combination of structural disorder, the presence of dilute diamagnetic iron (II) impurities and the competing exchange anisotropies between the in plane and interplaner coupling. All of the samples showed highly anisotropic magnetic behaviors.

For both the bulk phase samples and the xerogel composite samples of the nickel – iron Prussian blue analogue it was not possible to take measurements similar to the ones undertaken by Talham. The arrangement of the structures found in our samples is fairly erratic and not organized as they
were in the films they produced. No such distinction can be made on our particular complexes.

When this complex was fabricated it was hypothesized that the magnetic behavior of the nickel–iron complex would be similar to that of the cobalt–iron complexes. The low concentrations of these samples were not worrisome this time around based on the results that were obtained with the cobalt–iron samples. The xerogel samples were examined using both field cooled and zero field cooled magnetization versus temperature DC experiments (Figure 22). Just like its cobalt–iron counterpart the nickel–iron Prussian blue complex when distributed in a silica matrix exhibits a more complex behavior than just being a ferromagnet. For the field cooled magnetization temperature curve the sample shows basic ferromagnetic behavior similar to what had been seen previously.48 The curve at high temperatures is flat and then when the critical temperature is reached the magnitude of magnetization increases sharply and then eventually begins to level off in typical ferromagnetic fashion. Once again the interesting aspect of these materials shows up in the zero field cooled temperature curve. For these samples just like the cobalt–iron xerogels a broad peak is observed as the temperature is increased. The curve then becomes coincident with the field cooled measurements. The blocking temperature found for this sample is 15.5 Kelvin for the 0.05 mol % sample. This value did not vary significantly for the three different metal concentrations used (0.01 %, 0.05 %, and 0.1 %). The only significant difference between the different concentrations was the predicted magnitude of magnetization follows the concentration trend. The blocking behavior depicted by this peak is determined by the magnetic anisotropy found for these types of samples. The broadness of the peak is due to the particle size distribution. As noted in the previous chapter one of the ways to determine a superparamagnet from a spin glass system is how the two curves split. For this sample the zero field curve and the field cooled curve remain separate at temperatures significantly higher than the blocking temperature. This feature is indicative of a superparamagnet.56
Figure 22. Field cooled (FC) and zero field cooled (ZFC) DC magnetization versus time curves at $H = 100$ Oe for a 0.05 mol % nickel (II) – iron (III) xerogel.
Measurements of the magnetization as a function of field strength were studied at different temperatures. The measurement made at 5 Kelvin (Figure 23), which is well below the blocking temperature, shows an open hysteresis loop. The coercive field for the 0.05 mol % sample is 1.18 kOe. From room temperature down to the blocking temperature no hysteresis is observed. For a measurement taken at a temperature over the blocking temperature (20 Kelvin) no coercive field is detected (Figure 23). These observations are characteristic of both a superparamagnetic system as well as a spin glass.

Since the bulk phase of the complex had not been thoroughly studied the same experimental parameters were applied to it as was done to the xerogel samples. It was expected that this research would get similar results to what was achieved in the cobalt – iron bulk samples by Miller.\textsuperscript{52} The field cooled and zero field cooled magnetization curves for the bulk sample gave a similar picture to that of a spin glass and not just being a simple ferromagnet as was suggested by Juszczyk.\textsuperscript{48} The two temperature sweeps for the bulk phase sample of $\text{K}_x\text{Ni}^{\text{III}}_y[\text{Fe}^{\text{III}}(\text{CN})_6]_z$ show the much more complex behavior seen in a spin glass (Figure 24). The field cooled curve basically mirrors the previously obtained temperature sweep study and shows the increase in magnetization that has been linked to the ferromagnetism of the samples. The Curie temperature that was obtained for our bulk samples was approximately 25 Kelvin which is a little higher than the previous study. The zero field cooled curve once again showed a broad peak that is normally linked to either the blocking behavior of a superparamagnet or to the freezing temperature of a spin glass. This peak is centered at approximately 21 Kelvin. This temperature is much higher than what was seen in the xerogel nanocomposite materials. This difference is most likely due to the nanocomposite samples being a superparamagnet and the bulk sample being a spin glass. The two curves become coincident above the freezing temperature. As described earlier, for a spin glass the two curves almost immediately become coincident as they go to higher temperatures past the freezing temperature indicated by the maximum of the zero field cooled curve, which distinguishes it from a superparamagnet. Other than the placement of the broad peak at a much
Figure 23. Hysteresis loops for the 0.05 mol % Ni$^{II}$/Fe$^{III}$ xerogel sample at 5 (—) and 20 Kelvin (—).
Figure 24. Field cooled (FC) and zero field cooled (ZFC) DC magnetization versus time curves at $H = 100$ Oe for a bulk composite of nickel (II) – iron (III).
higher temperature than that of the composite glass and the curves becoming coincident much sooner past the blocking feature the temperature scans for both types of complexes are very similar. The magnetic intensity is obviously different, but that is a mere factor of concentration.

Measurements of the magnetization as a function of field strength at 5 Kelvin, which is below the supposed freezing temperature shows an open hysteresis loop (Figure 25). The coercive field of 2.08 kOe, is similar to that of the previous studies and is found to be about double that found for the nanocomposite samples meaning that it takes more energy to have a reversal of magnetization in the bulk samples when compared to the xerogel samples. As the temperature increases to the freezing temperature the hysteresis loop closes off. The magnetization versus field strength measurements taken at 20 Kelvin show that the loop has been practically closed due to the temperature being near the freezing temperature of the sample. The coercive field has dropped to 31.7 Oersteds. This closure is characteristic of both a spin glass and a superparamagnet. A hysteresis measurement taken at 30 Kelvin, well above the freezing temperature shows a completely closed curve (not in figure).

Again it really comes down to the AC magnetometry to truly distinguish whether the samples studied are either a spin glass or a superparamagnet. The in-phase linear magnetic susceptibility for both the bulk samples and the nanocomposite samples exhibit a broad peak that is frequency dependant in the location of the maximum of the susceptibility in regards to temperature (Figures 26 and 27). As was seen for the cobalt – iron samples the peak height also decreases for both samples with increasing frequency, which is indicative of the slow relaxation process found in both spin glasses and superparamagnets. For these samples the frequency shift (K) noted by Mydosh\textsuperscript{27} once again is important. The bulk samples prepared have a K value of approximately 0.015 (Table 6). This number falls into the range that is typical of spin glasses and is similar to the number obtained by Talham\textsuperscript{67} for the layered samples made, which was 0.04. The nanocomposite samples have a K value of approximately 0.112,
which falls into the value range for a superparamagnet. Mydosh feels that these frequency shift values are sufficient to characterize these types of systems.\textsuperscript{27}

It is however possible in the nanoparticle samples that like the cobalt–iron samples that the superparamagnetic features are superimposed by the inherent spin glass behavior of the bulk materials. As shown earlier the fact that nanoparticles are formed helps reason that in the xerogel samples superparamagnetism is present due to the separation of the domains by the silica network in these dilute nanocomposite samples.

Figure 24. Hysteresis loops for the bulk composite of nickel (II) – iron (III) at 5 (—) and 20 Kelvin (—).
Figure 25. Frequency dependence of the AC susceptibility for a 0.1 mol % xerogel sample of the nickel (II) – iron (III) Prussian blue analog: 100 (●), 3,000 (○), and 10,000 Hz (▲).
Figure 27. Frequency dependence of the AC susceptibility for the bulk sample of the nickel – iron Prussian blue analog: 100 (—), 1,000 (—), 5,000 (—), and 10,000 Hz (—).
Table 6. Frequency shifts of $T_f$ for the two different nickel – iron Prussian blue systems studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency ($\omega$, Hz)</th>
<th>Freezing Temperature ($T_f$, K)</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mol % Ni/Fe sol gel</td>
<td>100</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>0.1 mol % Ni/Fe sol gel</td>
<td>10,000</td>
<td>11.1</td>
<td>0.112</td>
</tr>
<tr>
<td>Ni/Fe bulk phase</td>
<td>100</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>Ni/Fe bulk phase</td>
<td>10,000</td>
<td>21.6</td>
<td>0.015</td>
</tr>
</tbody>
</table>
CONCLUSION

Prussian blue and its analogues have been extensively studied over the years. It has been found that some of these analogues have interesting magnetic properties such as Curie temperatures over room temperature and photomagnetism. For the most part these complexes have been studied in the bulk phase as powders. Others such as Talham have made layered structures of the analogues to study their properties. This research succeeded in placing two of these analogues \( (K_x\text{Co}^{II}_y[Fe^{III}(CN)_6]_z \text{ and } K_x\text{Ni}^{II}_y[Fe^{III}(CN)_6]_z) \) into a silica matrix using the sol-gel process to form homogeneous and optically transparent materials.

By using a solution phase synthesis technique this research was able to fabricate nanoparticles of both of the analogues studied. In the higher concentration nickel (II) – iron (III) samples nanorods on the order of 15 nm by 40 nm were formed during the gelation of the silica matrix. In lower concentration samples of the same complex it was discovered that nanodots were formed with an average diameter of 40 nm. It is believed that these nanoparticles as well as the nanoparticles formed in the cobalt (II) – iron (III) samples are formed by the arrested precipitation of the species during the gelation phase of the sol-gel process. The gelation of the silica network traps the particles as they precipitate and controls their size and shape.

The nanoparticle formation leads to more complex magnetic properties in both of the analogues studied. It was expected that the bulk would exhibit ferromagnetic behavior in the xerogel samples, but what was discovered is that the xerogel samples of the Prussian blue analogues exhibit superparamagnetic properties. Miller had concluded previously that the cobalt (II) – iron (III) bulk
complexes were in fact spin glasses and not simple ferromagnets, but no one had examined the nickel (II) – iron (III) complexes for similar properties. It was found that the bulk phase of this sample also displayed spin glass properties. Both the superparamagnetic and spin glass behaviors were seen in the DC magnetization studies performed. A distinct peak was observed in the zero field cooled magnetization vs. temperature experiments that denotes either a spin glass or a superparamagnet. Further studies of magnetization vs. field strength exhibited hysteresis curves that are characteristic of both a spin glass and a superparamagnet. AC magnetization measurements were performed and allowed us to distinguish between the two magnetic phenomena by examining the shift in temperature the magnetization peak showed due to changing frequencies. The xerogel samples are concluded to be superparamagnets based on the AC data as well as their nanoparticle size. The bulk phase sample of the nickel (II) – iron (III) analogue is a spin glass.

One of the most interesting properties of the cobalt (II) – iron (III) Prussian blue analogues is its photomagnetism which is due to the presence of cobalt (III) – iron (II) defect sites that are converted back to the cobalt (II) – iron (III) pairs with irradiation, that had been previously studied. This photomagnetism within our cobalt – iron xerogel samples was able to be recreated. The next step is to control the magnitude of the photomagnetic effect. Others such as Verdaguer have changed the alkali cation to produce more cobalt (III) – iron (II) defect sites within the lattice. Using their method there is only control during the synthesis of the complex. The photomagnetic effect was able to be controlled externally after the synthesis by flowing anhydrous ammonia over the sample creating more defect sites, which in turn increases the photomagnetic effect.

Future work in this field would have to include trying to incorporate other Prussian blue analogues into the silica matrix and examining their properties. There would be great interest in being able to feature an analogue with a room temperature Curie temperature. Another project could focus on making thin films of these previously studied Prussian blue analogues.
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