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UMI
MAGNETIC PROPERTIES OF THIOGERMANATE OPEN-FRAMEWORK MATERIALS

by

Robert William James Scott

A thesis submitted in conformity with the requirements for the Degree of Master of Science in the Graduate Department of Chemistry, University of Toronto

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Magnetic Properties of Thiogermanate Open-Framework Materials
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Abstract

A history of thiogermanate materials leading to the development of novel open-framework frameworks is detailed. The materials under investigation have the chemical formula \( T_2MGe_4S_{10} \) where \( T \) is a templating cation, tetramethylammonium (TMA\(^+\)), Cs\(^+\) or Rb\(^+\) and \( M \) is a divalent transition metal cation, Fe(II), Mn(II) or Zn(II). The Ge\(_4S_{10}\)\(^+\) adamantanoid cluster can be isolated as a water-soluble precursor and subsequently reacted with metal salts at room temperature conditions. Raman spectroscopy, Thermal Gravimetric Analysis (TGA) and Powder X-ray Diffraction (PXRD) are used to verify the purity and structure of the materials obtained, and Rietveld refinement of PXRD data was successfully used to obtain the crystal structure of Cs\(_2\)MnGe\(_4\)S\(_{10}\)·xH\(_2\)O. The magnetic properties of the materials are examined utilizing Electron Paramagnetic Resonance (EPR), bulk susceptibility measurements, and Mössbauer spectroscopy. Susceptibility measurements indicate that these materials are nearly perfect paramagnets down to 2K, though the presence of weak antiferromagnetic interactions could exist.
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Chapter I - Introduction

1.1.0 On Zeolites and Open Frameworks

Open framework materials have been known for centuries, especially with their ability to absorb water - hence the term 'zeolite' was born to describe these natural three-dimensional aluminosilicate materials. The name zeolite signifies "boiling stone" and refers to the frothy mass that results when a zeolite is fused at high temperatures.\(^1\) In the late 1940's, researchers began synthesizing artificial zeolites under hydrothermal conditions in the laboratory, thus opening up the field for chemical exploration. It was found that many open-framework structures formed when templated by a molecular species, often cationic and neutral organics. By changing the nature of the templating species, it was found that the size and shape of the cages and channels leading to them could be controlled.

Silicate chemistry, based on tetrahedral \(\text{SiO}_4\) units yields many neutral three-dimensional frameworks. Upon utilizing \(\text{Al}^{\text{III}}\) or \(\text{Ga}^{\text{III}}\) to replace the \(\text{Si}^{\text{IV}}\) in certain sites, the framework becomes anionic and must be balanced by cationic species, often \(\text{Na}^+\), \(\text{K}^+\) and \(\text{Ca}^{2+}\) in natural materials. There is often room for many other molecules within the zeolite 'cages', and thus the host-guest properties of these materials have be exploited in many industrial applications, from their ability to absorb water from solutions, their ability to control shape and size selective catalysis, to their ability to function as molecular sieves.\(^2\)

It became apparent that the chemistry of these materials could be further expanded by concentrating on other substitutions of the building blocks - utilizing \(\text{Ge}^{\text{IV}}, \text{Sn}^{\text{IV}}\) and \(\text{Sb}^{\text{IV}}\) as replacements for \(\text{Si}^{\text{IV}}\) and sulfur, selenium, and tellerium as replacements for
oxygen. It is astounding to examine the vast diversity of structures found in today's literature, utilizing templates ranging from complex organics to simple alkali metals. Also, solvents with weaker polarity than water have been examined, opening up a whole new field of structures that were not stable in the presence of water. One of the advantages of exchanging sulfur and other elements for oxygen is the possibility of creating semiconducting open-framework materials, in which the conductivity of the material would be affected by guest molecules occluded in the structure. By creating an array of such materials differing only slightly in pore size and shape, it should be possible to discriminate between even small changes in molecular structures - hence a route towards the electronic nose.

It has been the role of the modern solid state chemist to find underlying patterns from the structures in these materials and dream up methods of creating similar structures with different building blocks - towards the rational synthesis of materials with desirable physical properties. Especially relevant are the host-guest interactions that can occur with absorption of molecules into the cages of these structures, leading to the possibility of chemical sensing. Near and Far IR, $^{133}$Cs NMR, $^{129}$Xe NMR and many other methods have been used to examine the host-guest chemistry within zeolite cages. One of the goals of this thesis is to examine the possibility of probing the host-guest chemistry of a class of microporous materials through magnetic measurements of the framework itself - utilizing Electron Paramagnetic Resonance spectroscopy (EPR), Mössbauer spectroscopy and bulk magnetization measurements.

A discussion of porous materials cannot be complete without a mention of the future of the field - the assembly of mesoporous materials. In 1992, Kresge et al. at Mobil synthesized a new form of aluminosilicate, MCM-41, that had pore diameters that could be tailored in the
range of 16 to 100 Å through the choice of templating surfactants, auxiliary organics and reaction conditions. The ability to remove the ammonium surfactants to free up the large pore volume in these materials gives them widespread chemical and catalytical applications. Since that time, the field of mesoporous materials has grown rapidly to include mesoporous structures of many inorganic oxides and sulfides, including many doped aluminosilicates, niobium oxide, tin sulfide, and just recently a thiogermanate mesostructure created by reacting amorphous GeS₂ with CTAB (cetyltrimethylammonium bromide) under hydrothermal conditions.

1.2.0 A History of the Thiogermanates

Sometimes a story has more than one beginning - things get lost and become discovered again. The history of science shows that one often walks in the same footsteps as those before, only to find paths that went previously undiscovered. Hence the irony of the word 're-search' - to look again at something that was examined once before.

To find a beginning to the study of germanium sulfide cluster compounds, one has to go all the way back to 1886 and the discovery of germanium itself, when Winkler found that germanium sulfide strangely did not precipitate from a weakly acidic solution containing germanium oxide and sulfide. He postulated, correctly, the existence of a soluble thiogermanate compound as an explanation of this unusual and unexpected behaviour. Later, in 1930, the first thiogermanates were isolated from solution by Schwarz and Giese, Na₆Ge₂S₇ and K₆Ge₂S₇. Willard and Zuehlke, in 1943, took it upon themselves to closely examine the reaction between solubilized germanium oxide and hydrogen sulfide gas. They
postulated the presence of a species, H$_2$Ge$_2$S$_5$ that reacted with a base like 5,6-benzoquinoline to precipitate a product that had the molar ratio B$_2$Ge$_2$S$_5$ where B was a base. They isolated the H$_2$Ge$_2$S$_5$ species, as well as its K$_2$Ge$_2$S$_5$ analogue, but mysteriously the work was never continued from that point. These reactions involve an incredible advance in the understanding of the chemistry behind thiogermanate complexes, especially in the sense that all preparations were done at room temperature with simple acid-base chemistry. All of the ensuing work done in the field has never captured the exquisite simplicity of this thiogermanate chemistry.

In the years to follow, many of the thiogermanate clusters in solution were characterized. The Russian group of Sevryukov et al. continued the work of Schwarz and Giese and identified species in solution consisting of Na$_4$GeS$_4$·(15 or 16)H$_2$O, Na$_2$GeS$_3$·(10 or 13)H$_2$O, and Na$_6$GeS$_7$·19H$_2$O based on elemental analysis. The structures for these thiogermanate clusters were characterized by several different groups. The French group, of Ribes and Maurin, studied the crystallography of the barium salts of the clusters and solved the crystal structure for the tetrahedral GeS$_4^{1+}$ species in Ba$_2$GeS$_4$ and later for the Sr and Ca salts as well.

Krebs, Pohl, and Schiwy crystallized the germanium sulfide dimer, Na$_4$Ge$_2$S$_6$·14H$_2$O along with its tin analogue in 1970. They made the first characterized ‘tetramer’ Cs$_4$Ge$_3$S$_{10}$·4H$_2$O in 1971; the structures of the Ge$_2$S$_6^{1+}$ and Ge$_2$S$_{10}^{1+}$ clusters are shown in Figure 1.1. A noticeable shortening of the bond length for the terminal sulfurs is seen due to an increase in the \( \pi \)-character of these non-bridging bonds. The Ge-S-Ge angles in the tetramer species, Ge$_2$S$_{10}^{1+}$ are very close to the ideal tetrahedral angles at 108.9(2)$^\circ$ and
Figure 1.1
Structure of the Ge₄S₁₀⁺ and Ge₂S₆⁺ Clusters
Until this time, although the presence of a ‘Ge$_2$S$_2$’ species had been verified by a number of groups, no crystal structure had been obtained. The presence of stable, soluble thiogermanate clusters Ge$_2$S$_6^+$ and Ge$_3$S$_{10}^+$ was an unexpected thrill to inorganic chemists. Krebs et al. studied the chemistry and physical properties of these materials in detail, and also synthesized a larger cluster at low pH conditions, Ge$_8$S$_{19}^6$_. Much of the work is summarized nicely in an Angewandte Chemie review article published in 1983, along with a number of previously unpublished results. The mode of formation of thiogermanate cluster was hypothesized, as shown in Figure 1.2. GeS$_4^+$ species condense to give Ge$_2$S$_7^6$ species, which can further condense to give either the dimer or tetramer species. Figure 1.3 shows the effect of pH on the condensation and isolation of thiogermanate species. As the pH decreases, the formation of larger and larger building blocks is seen.

In the years that followed, the crystal structures of a number of salts of the tetramer, T$_4$Ge$_4$S$_{10}$ appeared in the literature ( T = weakly polarizing cations such as Tl$^+$, Na$^+$, and Cs$^+$), as well as the unique species Ba$_2$Ge$_4$S$_{19}$ which has Ba$^{2+}$ as a charge balancing cation. Tl$_4$Ge$_4$S$_{10}$ was made by molten salt methods, by melting Tl$_2$S and GeS$_2$ in a quartz tube at 500$^\circ$C while many of the others were synthesized by basic aqueous chemistry. All of these examples showed that a tetrameric thiogermanate species can be made with nearly any counter ion, and also that the chemical and physical properties of the Ge$_3$S$_{10}^+$ species are nearly independent of the cation.

Another beginning was to come - and it came in a field-opening patent by Bedard et al. in 1989. They found that a transition metal species, specifically M(II) where M = Mn, Fe, Co, Cu or Zn, reacts with germanium sulfide and a charge balancing organic cation in the
Figure 1.2
Mode of Formation of Thiogermanate Clusters$^{23}$

\[ \text{GeS}_6^{4-} \rightarrow \text{Ge}_2\text{S}_7^{6-} \rightarrow \text{GeS}_3^{2-} \]

\[ \text{Ge}_2\text{S}_6^{4-} \rightarrow \text{Ge}_4\text{S}_{10}^{4-} \]

\[ \{\text{Ge}_{10}\text{S}_{20}\} \rightarrow \text{Ge}_8\text{S}_{19}^{6-} \]
Figure 1.3
pH Dependence of Thiogermanate Clusters$^{23}$
presence of mineralizing and solubilizing agents to give a series of open-framework, porous materials that are templated by the cation. All the materials were made through a hydrothermal synthesis route - at temperatures from 120 to 150°C. The reaction was attempted on the basis that the short Ge-S terminal bonds could be viewed as sites of high reactivity, and therefore the whole cluster could be viewed as a single tetrahedral building block. Only one single crystal of the material labelled TMA-CoMnGS-2, 28 was obtained. It contained $M_{4.4}Ge_2S_6$ units linked together by $MS_3SH$ groups in a 'pinwheel' fashion. One of the interesting phases identified was labelled MGS-3, and it has been well characterized in the ensuing years. It was surprising, to say the least, that tetrameric building blocks would assemble to give a three-dimensional solid state material rather than an amorphous one. While the Bedard syntheses were a novel extension of the previous thiogermanate work, there was also a problem in that small amounts of GeO$_2$ and GeS$_2$ impurities were found in the samples, and was largely unavoidable given the harsh hydrothermal conditions at which they were made.

Not long afterwards, in 1994, Yaghi et al. published the first paper for the synthesis of TMA$_2$MnGe$_4$S$_{10}$ 29. Powder X-ray diffraction data confirmed this was identical to the TMA-MnGS-3 structure of the Bedard synthesis. The system crystallizes in the tetragonal space group $I\overline{4}$, with $a=9.513(1)$ Å and $c=14.281(2)$ Å. Figure 1.4 shows the structure of the framework, omitting the TMA$^+$ charge balancing cations for clarity. There are two cations present in every 'cage'. What makes the synthesis even more intriguing was the methodology that was used in producing the single crystals. Borrowing from the work of Krebs and others in the field, a tetrameric species, TMA$_4$Ge$_4$S$_{10}$ was prepared under hydrothermal conditions at
Figure 1.4
Structure of TMA$_2$MnGe$_4$S$_{10}$ Framework
(TMAs omitted for clarity)
a very high yield. This water soluble species was then reacted at room temperature with an excess of Mn(CH₃COO)₂·4H₂O to give the final product. The ability to conduct the reaction in two steps, one to produce a precursor, and the second to react the purified tetramer species with the corresponding metal salt represented a paradigm shift in the field. The purity of the reagents and final products could now be easily controlled, and more importantly, the growth of the framework species could be slowed down by choosing the appropriate transition metal salt in order to produce fewer nucleation sites and larger crystals. Indeed, the ability to use diffusion growth techniques and selective complexing, mineralizing, and transporting agents aids in the structural characterization of this novel group of open-framework materials. The same synthesis has been successfully used to grow crystals for the TMA₂MGe₄S₁₀ for M = Fe(II)³⁰, Co(II)³¹, Cd(II)³¹ and Zn(II)³¹ as well as for Cs₂FeGe₄S₁₀·xH₂O.³⁰ Transition metal dimer species were synthesized unexpectedly in TMA₂M₂Ge₄S₁₀ for M = Ag(I)³², Cu(I)³², Au(I)³³ and Hg(I).³³ A representation of the structure of the dimer framework is found in Figure 1.5. It crystallizes in the same I 4 tetragonal space group as the T₂MGe₄S₁₀ species. While the S-Ge-S angles remain close to the tetrahedral ideal, larger deviations are seen for the S-M-S bonds, which gives the framework a large degree of flexibility. This allows the system to incorporate many different linking species (M and M₂) and many different templating cations (TMA, Cs).

While the extremely mild tetramer synthesis is an excellent method of producing many members of the T₂MGe₄S₁₀ or T₂M₂Ge₄S₁₀ family, hydrothermal preparations allow for many other structures to be built from the basic building blocks. Parise et al. have prepared a number of interesting structures that contain the Ge₄S₁₀⁻ cluster but do not follow the T₂MGe₄S₁₀ building arrangement. They include a ((CH₃CH₂)₄N)₂Cu₂Ge₄S₁₀ phase that does
Figure 1.5
Structure of $\text{TMA}_2\text{M}_2\text{Ge}_4\text{S}_{10}$
not contain Cu(I)-Cu(I) bonding, but rather S-Cu(I)-S bonding.\textsuperscript{34} It is likely that the increased size of the templating cationic amine changes the Cu-Cu distance from a bonding value of 2.409 Å in the TMA phase\textsuperscript{32} to a non-bonding distance of 6.947 Å in the TEA phase. Yet another Cu structure was found which was isomorphous with the Bedard TMA-CuGS-2 structure and has the formula (TMA)\textsubscript{6}[(Cu\textsubscript{0.44}Ge\textsubscript{0.56}S\textsubscript{2.23})\textsubscript{4}(Ge\textsubscript{4}Se\textsubscript{6})\textsubscript{3}]\textsuperscript{35}. It also contains Ge\textsubscript{4}S\textsubscript{10}\textsuperscript{4-} building blocks, but in a ‘pinwheel’ arrangement resembling that of the Bedard Co-Mn structure.

1,4-diazabicyclo[2,2,2]octane, or DABCO, has also been used to make two new structures, labelled SB1 and SB2 (SB=Stony Brook, NY). The SB2 structure, (DABCO-H\textsuperscript{+})(H\textsubscript{2}O)(H\textsubscript{2}O)AgGe\textsubscript{4}S\textsubscript{10}\textsuperscript{36} contains three-coordinate silver connected to Ge\textsubscript{4}S\textsubscript{10} building blocks, while the SB2 structure, (DABCO-2H\textsuperscript{+})MnGe\textsubscript{4}S\textsubscript{10}•3H\textsubscript{2}O\textsuperscript{37} contains 4 and 8 membered rings based on tetrahedral units. The SB1 structure was analogous to that of Zeolite Li-A(BW). The S-Mn-S angles show a very large tetrahedral distortion (128.5(2)°) for the 4-rings and a slightly smaller distortion for the 8-rings (98.7(1)°).

While concentrating on the history of thiogermanate compounds, intriguing frameworks have also been made using selenido- and telluridogermanate chemistry. Tetramers for the T\textsubscript{4}Ge\textsubscript{4}Se\textsubscript{10} species have been synthesized for which T = Na\textsuperscript{38}, K\textsuperscript{39}, Cs\textsuperscript{40}, Rb\textsuperscript{41} and Tl\textsuperscript{42}. The Cs and Rb selenido-tetramers were made by methanothermal synthesis at 190°C with some chemisorbed methanol groups found in the structure. The Sheldrick group also made an unique selenidogermanate dimer containing Se-Se bonds, Ge\textsubscript{2}Se\textsubscript{4}\textsuperscript{+},\textsuperscript{40} as well as some selenium and tellurium GeSe\textsubscript{4}\textsuperscript{+} and GeTe\textsubscript{4}\textsuperscript{4-} species.\textsuperscript{41} The tetramer for T = TMA has also been synthesized hydrothermally from the elements.\textsuperscript{43} The tetrameric telluridogermanate
has also been synthesized by fusion of the elements to give $K_4Ge_4Te_{10}$ and its tetraethylammonium salt, $(Et_4N)_4Ge_4Te_{10}$ by reaction of the potassium tetramer with a tetraethylammonium salt dissolved in ethylenediamine. More recently, the framework compounds $T_2MnGe_4Se_{10}$ and $T_2AgGe_4S_{10}$ have been obtained from hydrothermal syntheses with the elements (for $T = Cs, Rb$), and both crystallize in the same $I \bar{4}$ space group as the original thiogermanate frameworks. Also $TMA_2MGe_4Se_{10}$ structures for $M = Mn, Fe, Co, Zn$ have been recently synthesized.

Other synthetic methods for creating thiogermanate clusters have appeared in the literature. The electrochemical synthesis of $[NEt_4]_2[enH]_2[Ge_2Se_6]$ and $[NEt_4]_4[Sn_4Se_{10}]$ ($NEt_4 = $ tetraethylammonium, $enH = $ protonated ethylenediamine) have been reported by Park et al. using cathodes made of of $Ge_2Se_3$ and $Sn_2Se_3$ respectively with nickel as the sacrificial anode. A saturated solution of $NEt_4Br$ in ethylenediamine was added to the cell, and a current of 300 $\mu$A was applied to the electrochemical cell. It was also found that $GeS_2$ dissolved in ammonia at low temperatures can give the corresponding ammonium dimers and tetramers.

While the field for both the thio and selenidogermanates shows plenty of promise, so far they have failed to produce a truly 'porous' material, in which the template can be removed. The cationic nature of the templates is troublesome in that they are needed for charge balancing of the anionic framework. However, it may be possible to remove the template partially without collapsing the structure, or perhaps more plausibly, to ion-exchange large templates with smaller cations to free up pore volume. One of the lessons learned from a thorough examination of these open-framework germanium sulfide structures is that they cannot be viewed as rigid bodies but rather quite flexible ones - they expand and
contract to fill the available space. While this flexibility allows for a large number of novel structures to be possible, it may not bode well for attempts to free up space through ion-exchange strategies. Pore volume that has been 'rescued' by evacuation of solvents that chemisorb or physisorb into the structure may be significant enough to examine the adsorption properties of small molecules, along with possible chemical sensing applications. The size of the channels that give access to the pores is also of great importance - it is possible for the necessary pore space for a particular adsorbate to be present in a structure, but with channels too small to allow entry. Typically, for the T₂MGe₄S₁₀ structures, channel sizes are ca. 6-7 Å.

Interestingly, though the frameworks for structures involving the Ge₄S₁₀⁺⁺ cluster have been prevalent in the literature, none of the other building blocks have been assembled into a framework structure. The silicon and tin analogues of the thiogermanate tetramers, Si₄S₁₀⁺⁻²⁵ and Sn₄S₁₀⁺⁻⁴⁹ have both been isolated, as well as those for the selenium species. It is thought to be but a matter of time and patience before these, and other thiogermanate building blocks such as Ge₂S₆⁺, Ge₂S₇⁺, and Ge₉S₁₉⁺ are found to form chain, sheet, and framework materials.

1.3.0 Chalcopyrites

In the study of the tetramer cluster, Ge₄S₁₀⁺ and its frameworks one notices that they crystallize in a tetrahedral, cubic close-packed zinc blende type lattice. Distortions from the tetrahedral ideal are found in the S-M(II)-S bonds, and thus tetragonal space groups account for many of the structures, the I 4 space group being predominant. It is interesting to note that the structure of another class of materials, the chalcopyrites, can also be derived from the
zinc blende lattice. The magnetic properties of the chalcopyrite structure, CuFeS$_2$, are well documented in the literature. The basic material is created by removing 1/2 of the Zn(II) in the zinc blende structure and replacing them with Cu(I) while replacing the other half with Fe(III) in an ordered fashion. Chalcopyrite has been shown to be an antiferromagnetic material with a high Néel point (the onset of magnetic ordering upon cooling) at 823 K.$^{51}$

Solid solutions of (ZnS)$_{1-x}$(CuFeS)$_x$ have also been prepared, and it has been shown that the magnetic properties of these materials can be ‘tuned’ by adjusting the Zn(II) content. Single crystals of a material with $x=0.98$ were grown and magnetic susceptibility studies showed a Curie-Weiss behaviour with a antiferromagnetic Weiss constant of -110 K.$^{52}$

Stannite, Cu$_2$FeSnS$_4$ is another structure related to zinc blende, based on replacing half of the chalcopyrite Fe(III) centers with Sn(IV) and reducing the other half to Fe(II). The Fe(II) in this species is especially interesting as it has the same electronic structure, d$^6$, that will be found in the T$_2$FeGe$_4$S$_{18}$ structures later. Also a Ge(IV) structure, briarate, crystallizes with the stannite structure. Cu$_2$FeGeS$_4$ is paramagnetic down to 12 K, where it undergoes antiferromagnetic ordering.$^{53}$ Solid solutions of Cu$_2$Zn$_x$Fe$_{1-x}$GeS$_4$ have also been made, and as with chalcopyrite the magnetic structure of the material can be changed systematically.$^{54}$

The comparison between these close-packed materials and the open-framework thiogermanates is one worth pursuing - while the actual magnetic properties of the materials are expected to be radically different given the larger separation of the magnetic centers in the open-framework materials, it should be possible, as in chalcopyrite, stannite, and briarate, to ‘tune’ the magnetic properties by creating solid solutions with diamagnetic Zn(II) centers. This ‘tunability’ offers much promise in the creation of open-framework materials with specific physical properties, towards the rational synthesis of solid state materials.
1.4.0 References


43. Ahari, H., unpublished results.


49. Young, D., unpublished results.


Chapter 2 - Materials and Structural Characterization

2.1.0 Synthesis

2.1.1 The Precursors

Following the reaction scheme utilized by Yaghi et al., the water-soluble precursors, or tetramers \( \text{T}_4\text{Ge}_4\text{S}_{10} \) where \( \text{T} \) is the cation, were prepared hydrothermally from a mixture of elemental germanium, elemental sulfur, and a hydroxide solution of the templating cation:

\[
4 \text{Ge} + 10 \text{S} + 4.1 \text{T}^+(\text{OH})^- + 150 \text{H}_2\text{O} \rightarrow \text{T}_4\text{Ge}_4\text{S}_{10} \quad \text{(aq)}
\]

Germanium (99.999%, 150 mesh, Atlantic Equipment Engineers) and sulfur (sublimed, 100 mesh, Aldrich) powders were added to an Enflon\textsuperscript{TM} liner after being mixed well in a mortar and pestle. Then the corresponding cationic base, TOH, where TOH = tetramethylammonium hydroxide pentahydrate (TMAOH·5H\textsubscript{2}O) [Aldrich, 97%], cesium hydroxide [50% solution, Fluka, 99.9%], or rubidium hydroxide [50% solution, Aldrich, 99.9%], was added to the liner along with the necessary water. The liner was then placed in a stainless steel hydrothermal autoclave (or ‘bomb’) and placed in a tumbling oven at 150° C for 16 hours. The autoclave was then cooled at room temperature for 1 hour. A deep yellow solution was recovered from the synthesis, often along with unreacted germanium and sulfur which was filtered off. Addition of this solution to a large excess of acetone precipitated a fine white powder, \( \text{T}_4\text{Ge}_4\text{S}_{10} \) which was then filtered and washed with small quantities of acetone. Occasionally, heavy oils were obtained in the synthesis, presumably due to the presence of unreacted starting materials and unwanted byproducts, or possibility impurities in the starting reagents. By dissolving the oil in a minimal amount of water and re-precipitating with absolute ethanol, the desired powder is often obtained. Otherwise the oil was dried over
phosphorus pentoxide in a vacuum dessicator. Purity of the precursor tetramer was verified by powder X-ray diffraction (PXRD) and/or Raman scattering, as will be discussed later.

2.1.2 Framework Preparation

Following the formation of the tetramer, the frameworks were prepared by simple aqueous chemistry utilizing a divalent transition metal salt and an aqueous solution of the corresponding tetramer in a 1:1 reaction mixture. The salts to make the Mn(II), Fe(II), and Zn(II) frameworks were Mn(CH₃COO)₂·4H₂O [Aldrich, 99+%), FeSO₄·7H₂O [Aldrich, 97%], and Zn(CH₃COO)·2H₂O [Fluka, 98%], respectively.

In the case of the Zn(II) framework, the kinetics of the reaction are extremely fast, leading to the formation of very small particle sizes that give peak broadening in the PXRD, as discussed later. By utilizing a suitable complexing agent to slow the delivery of Zn(II) to the solution, larger particle sizes are obtained. Three equivalents of EDTA (ethylenediaminetetraacetic acid disodium salt) has been shown to slow down the delivery of Zn(II) considerably. A yellow-white fine powder was immediately obtained in the Zn(II) reaction without the use of a complexing agent, whereas if EDTA was added to the Zn(II) solution prior to addition of the tetramer a fine pure-white powder was obtained after 10-15 minutes. T₂ZnGe₄S₁₀ was recovered by centrifugation and purity and crystallinity determined by PXRD and Raman.

For the Fe(II) frameworks, an orange precipitate appeared 10-15 minutes after mixing the Fe(II) salt and tetramer solution. This reaction mixture was left for 16 hours, after which a deep orange powder was recovered, T₂FeGe₄S₁₀. In the case of Mn(II) frameworks, it took a
period of about 24 hours to isolate a yellow powder utilizing the TMA tetramer and Mn(II) acetate salt. For the Cs and Rb templates, the Mn(II) framework failed to crystallize at all, even at higher temperatures and/or with the use of different Mn(II) salts. However, these frameworks can be prepared utilizing the Bedard method\(^2\), as will be discussed later. It is unknown at the present time why the Cs and Rb Mn(II) frameworks fail to form under milder aqueous conditions.

Preparation of the mixed metal TMA\(_2\)Fe\(_{x}\)Zn\(_{1-x}\)Ge\(_4\)S\(_{10}\) and TMA\(_2\)Mn\(_x\)Zn\(_{1-x}\)Ge\(_4\)S\(_{10}\) species used for EPR and Mössbauer studies was done in a similar fashion to the above methods. The stoichiometric amounts of the Zn(II), Fe(II) or Mn(II) salts were mixed beforehand and then the TMA\(_4\)Ge\(_4\)S\(_{10}\) solution was added to this mixture with rapid stirring. Immediate precipitation of the framework species was seen, and the product was isolated by centrifugation after 24 hours. PXRD of these solid solutions revealed that amorphous and/or small particle size broadening was occurring, just as for the T\(_2\)ZnGe\(_4\)S\(_{10}\) materials. Attempts to find a complexing agent to slow down the kinetics of Zn(II) release were unsuccessful, as Mn(II) and Fe(II) were even more strongly coupled to all potential candidates. The distribution of the metal centers in these polycrystalline materials will be discussed later.

2.1.3 Preparation of Rb\(_2\)MnGe\(_4\)S\(_{10}\) and Cs\(_2\)MnGe\(_4\)S\(_{10}\)

As mentioned previously, the Mn(II) frameworks templated by Cs and Rb have not been accessible through the milder, aqueous tetramer route. Thus another chemical route had to be found to create these frameworks - and it was thought that framework formation might be possible utilizing the harsher Bedard-type hydrothermal synthesis utilizing amorphous GeS\(_2\) as the starting material.
Two routes to the preparation of GeS₂ were examined - the first being that used in the Bedard et al. patent.² In this synthesis, a large excess of GeCl₄ was added dropwise to a 6N solution of hydrochloric acid with stirring, forming an immediate white precipitate of GeO₂. Then H₂S was bubbled through the reaction mixture until completion. The reaction is assumed to have finished when the trap solution of ZnCl₂ began to precipitate copious amounts of a fine white powder, ZnS. However, PXRD analysis of this reaction indicates that a major impurity of GeO₂ still exists - and attempts to dissolve the GeO₂ in 60-70 °C 6N HCl were unsuccessful. It is proposed that GeS₂ formation occurs on the outer surface of GeO₂ particulates, thus making it extremely difficult to further purify the material. In an attempt to circumvent this problem, an alternate synthesis was attempted³:

\[
\text{GeO}_2 + \text{CH}_3\text{CSNH}_2 \text{(excess)} + \text{HCl} \text{(6N)} \Rightarrow \text{GeS}_2 \text{(s)} + \text{CH}_3\text{CONH}_2
\]

4.0 g of GeO₂ were completely dissolved in 2 litres of 60-70 °C 6N HCl, until a clear solution was obtained. After cooling the acidic solution, 5.5 g of thioacetamide dissolved in 50 mL of distilled water were added to the solution. After several minutes, small white particulates of GeS₂ began to appear. This mixture was left for ca. 6 hours to allow the reaction to complete, and amorphous GeS₂ was filtered off and washed with distilled water and methanol. Yields were typically ca. 75%. The PXRD of this product shows it to be amorphous and containing no trace amounts of GeO₂. Raman spectroscopy, as shown later, verifies the presence of Ge-S vibrational modes.

Amorphous GeS₂ reacts with O₂ to form GeO₂ after several days, so the samples were placed under N₂ and used as soon as possible for subsequent syntheses. The reaction to produce the Mn(II) frameworks of Cs and Rb templates is as follows:
$$2\text{TOH} + 4\text{GeS}_2 + \text{Mn(CH}_3\text{COO)}_2 + 100\text{H}_2\text{O} \Rightarrow T_2\text{MnGe}_3\text{S}_{10}\cdot x\text{H}_2\text{O}$$

The reaction proceeded hydrothermally at 150 °C for 16 hours, after which a dull yellow precipitate of the framework was isolated, often in yields of 25% or less. The water content was quantified by TGA, as will be discussed later, and consists both of chemisorbed and physisorbed water. PXRD shows the absence of any crystalline impurities, especially α-GeS$_2$ or GeO$_2$. The Cs and Rb tetramers have been isolated from the filtrate, as well as an unique Cs-acetate open-framework cluster compound, Cs$_2$Mn$_3$(CH$_3$COO)$_8$. It is thought that the competing reaction to create the cluster framework could be responsible for the low yield. However, the use of other Mn(II) salts has not resulted in the isolation of a pure framework compound.

2.2.0 Characterization

2.2.1 FT-Raman Spectroscopy

Raman scattering has proven to be an excellent method to probe the vibrational properties of the germanium sulfide precursor materials, T$_4$Ge$_4$S$_{10}$, as well as the corresponding frameworks. The Ge$_4$S$_{10}^-$ species exist as independent oscillators, with only a weak correlation coupling of the vibrational modes between adjacent clusters. Thus, they can be examined by group theoretical point group analysis to determine the allowed and forbidden modes in both infrared and Raman spectroscopy. Vibrational modes that result in a change in the polarizability are Raman active, while those that result in a change in the dipole moment are active in the infrared.
Raman spectra were collected using a Bomens MB-157 Fourier Transform spectrometer with an InGaAs near-IR laser. The Spectra Physics diode pumped Nd:YLF laser emitted at 1064 nm with a 350 KHz repetition rate. The laser power was set at 100 mW and lowered only when sample burning or luminescence occurred, upon which it was lowered until a stable spectrum was obtained. A notch filter covering the ranges 150-3750 cm\(^{-1}\) was used to block Rayleigh scattering. The instrument was configured in 180° back-scattering mode, using sealed glass capillary tubes to hold the samples. Spectra were routinely collected with a resolution of 4 cm\(^{-1}\), and 50-100 scans were taken as needed to achieve an adequate signal to noise ratio.

**Figure 2.1** shows the typical Raman spectra for the tetramers, with T =TMA, Cs, and Rb. Not shown for the TMA framework are the C-H stretching and bending modes in the regions around 3000 cm\(^{-1}\) and 1400 cm\(^{-1}\) respectively, and a weak water signal can be seen for the Cs and Rb materials at approximately 3200 cm\(^{-1}\). Visual inspection of the three spectra show striking similarities. The Ge\(_4\)S\(_{10}\)^{4-} cluster has point group T\(_d\), and a symmetry analysis gives 15 vibrational modes \(3A_1 + 3E + 3T_1 + 6T_2\), of which the \(3A_1 + 3E + 6T_2\) are Raman active and only \(6T_2\) are infrared active. By comparison of the far-infrared and Raman spectra, one should be able to label all the A\(_1\), E, and T\(_2\) modes. We expect to see the totally symmetric A\(_1\) vibrations as strongly polarized lines, while the E modes will be depolarized.

Several generalities can be applied in the analysis of the adamantanoid cluster. The terminal Ge-S stretching modes should be at higher frequency due to a shortening of the Ge-S bond as opposed to the bridging bonds, and thus an increase in the pi-character of the bond. Thus the strong A\(_1\) mode for the terminal Ge-S bonds is at ca. 464 cm\(^{-1}\), while the intense mode at ca. 340 cm\(^{-1}\) is the stretching of the bridging Ge-S bonds, while the
Figure 2.1
Raman Spectra of $T_4Ge_4S_{10}$
for $T = (a) \text{TMA} (b) \text{Cs} (c) \text{Rb}$
(* for S impurity modes)
remaining Ge-S A₁ deformation mode appears at 190 cm⁻¹. Several groups have examined the vibrational spectroscopy of the Ge₄S₁₀⁻⁴ cluster utilizing Raman⁷ and far-IR⁸. Table 2.1 shows the observed modes and labels from an inspection of the literature. Several deviations in the spectra are seen due to relative intensities of the individual modes as well as sulfur impurities. A small peak at approximately 260 cm⁻¹ in the Rb and Cs tetramers is seen, which could be due to the presence of water in these samples, leading to Cs-O and Rb-O vibrations in this region. Raman spectroscopy below 150 cm⁻¹ would reveal the missing T₂ and E modes, but this was not attempted.

**Table 2.1 Observed Modes and Labels for Raman Spectrum of T₄Ge₄S₁₀⁻⁴**

<table>
<thead>
<tr>
<th>Observed Mode (cm⁻¹)</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>472 (v.strong)</td>
<td>Sulfur</td>
</tr>
<tr>
<td>464 (v. strong)</td>
<td>v₁(A₁)</td>
</tr>
<tr>
<td>455 (strong)</td>
<td>v₁₀(T₂)</td>
</tr>
<tr>
<td>405 (med)</td>
<td>v₁₁(T₂)</td>
</tr>
<tr>
<td>398 (weak)</td>
<td>v₄(E)</td>
</tr>
<tr>
<td>380 (med)</td>
<td>v₁₂(T₂)</td>
</tr>
<tr>
<td>366 (weak)</td>
<td>?</td>
</tr>
<tr>
<td>340 (strong)</td>
<td>v₂(A₁)</td>
</tr>
<tr>
<td>260 (weak)</td>
<td>?</td>
</tr>
<tr>
<td>218 (med)</td>
<td>Sulfur</td>
</tr>
<tr>
<td>205 (med)</td>
<td>v₁₃(T₂)</td>
</tr>
<tr>
<td>190 (strong)</td>
<td>v₃(A₁)</td>
</tr>
</tbody>
</table>
The gap between 320 and 220 cm$^{-1}$ should be noted as an excellent window into viewing M-S modes in the frameworks, which appear in this frequency range.

Also of interest are the spectra of GeO$_2$ and GeS$_2$ shown in Figure 2.2. The major band at 350 cm$^{-1}$ in amorphous GeS$_2$ is the $A_1$ stretching mode for the tetrahedral GeS$_4$ species. Upon changing the O to S, the analogous Ge-O mode is expected to appear at a higher frequency using the harmonic oscillator approximation. Indeed, crystalline GeO$_2$ ($\alpha$-quartz) shows an intense $A_1$ mode at ca. 440 cm$^{-1}$ which is due to symmetric Ge-O-Ge stretching.$^9$ A look at the Raman spectra of the amorphous GeS$_2$ shows there can be only a trace amount of GeO$_2$ present.

Figure 2.3 shows the FT-Raman spectra for the Mn(II) frameworks templated by Cs, Rb, and TMA. Again, the inherent similarity of the spectra is obvious. The major change in the cluster modes is a lowering of the energy in the bridging S bonds, from approximately 464 cm$^{-1}$ to 445 cm$^{-1}$, as is expected with a lengthening of the Ge-S bond from 2.12 Å to 2.19 Å upon the reaction with a transition metal. A lowering of the energy is also expected as the effective mass of the terminal Ge-S bonds increases with the addition of the transition metal species Mn(II) to the sulfur. The presence of M-S modes within the window between 320 cm$^{-1}$ and 220 cm$^{-1}$ is seen, as shown in the insert of Figure 2.3. These correspond to the A+B+E modes of a M(II) bound to four sulfurs with $S_4$ symmetry. The actual position of the modes is dependent on the nature of the transition metal cation, Zn(II)-S bond lengths being shorter than those for Mn(II) and Fe(II) lead to shifts to higher frequency for the analogous modes.$^5$

Though a solution for the complete vibrational characterization of adamantanoid clusters, Ge$_4$S$_{10}^+$, or the corresponding frameworks was not attempted, the power of FT-
Figure 2.2
Raman Spectra of
(a) GeO$_2$ (b) amorphous GeS$_2$
Figure 2.3
Raman Spectra of $\text{T}_2\text{MnGe}_4\text{S}_{10}$
for $T = (a) \text{TMA} (b) \text{Cs} (c) \text{Rb}$
insert shows M-S modes for Cs
Raman is shown in its identification of compounds containing the cluster. Many hygroscopic tetrameric species are amorphous in the PXRD, yet their adamantanoid structure can be easily verified through Raman spectroscopy.

2.2.2 **Thermal Gravimetric Analysis (TGA)**

With open-framework structures, the thermal stability of the material is a very important factor for any possible applications. Thermal Gravimetric Analysis, or TGA, allows one to look at the weight loss of the material as a function of temperature. The system used was a Perkin-Elmer TGA-7 machine. Approximately 10 mg of sample was loaded into a platinum boat which was then placed in the furnace under a constant flow of N₂. Profiles were taken at a heating rate of 5 °C per minute.

Figure 2.4 shows the TGA profiles obtained for TMA₂MnGe₄S₁₀. No physisorbed water is given off below 100°C, and the framework is stable until the reaction of the organic tetramethylammonium cation with the framework at approximately 390°C. It was not possible to retain the integrity of the framework upon template removal. The reaction pathway likely occurs as follows:

\[
\text{TMA}_2\text{MnGe}_4\text{S}_{10} \rightarrow 2 \text{N(CH}_3\text{)}_3 + \text{S(CH}_3\text{)}_2 + \text{"MnGe}_2\text{S}_9\text{"}
\]

Indeed, mass spectra of the volatile components for this material at 450 °C verifies the presence of trimethylamine and dimethyldisulfide as the principal products. The 24% weight loss of the material agrees well with the calculated 29.4% loss expected from reaction of the TMA cation with the sulfur atoms in the framework. "MnGe₂S₉" was found to be PXRD amorphous. It may be possible to retain the integrity of the framework with template
Figure 2.4
TGA of TMA$_2$MnGe$_4$S$_{10}$
removal by slowly removing the template at a temperature slightly below the 390 °C TGA transition and creating small amounts of sulfur vacancies in the adamantanoid structure.

For the Rb and Cs materials, the TGA profiles show two weight losses occurring before 170 °C, both of which are due to the loss of water by the framework, as shown in Figure 2.5. The first peak at 90° C, accounting for a weight loss of about 3.5% for Cs and 4.5% for Rb, is likely due to the presence of physisorbed water in the sample, while the second peak, easily seen with the 2nd derivative profile, only accounts for 0.5% weight loss for Cs and 1.5% loss for Rb. These weight losses are due to physisorbed and chemisorbed water, respectively. Calculated water content from TGA analysis shows 2.2 and 3.0 waters per Ge₄S₁₀⁴⁺ cluster. As the TGA is run under a flow of N₂, there is a possibility that water loss occurs before sample acquisition begins. Ideally one would work with a flow of air saturated with H₂O to minimize water loss. It is interesting to note that the Rb material contains more water - this is expected with the ionic radii of Rb⁺ being smaller than that of Cs⁺, 1.61 Å and 1.74 Å respectively for 8 coordinate species. Thus there might be slightly more void space for water to fill in the Rb templated material.

Both of these materials show amazing thermal stability for open-framework inorganic compounds, and no weight loss is seen until about 600°C, at which temperature the sublimation of GeS₄ occurs. The TGA indicates that under optimal conditions the framework should retain its structural integrity, creating void space in the ‘pores’ of the framework which could be filled by other species.
Figure 2.5
TGA of (a) Cs$_2$MnGe$_4$S$_{10}$ (b) Rb$_2$MnGe$_4$S$_{10}$
2.2.3 Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction is one of the most valuable techniques available to examine the crystallinity and structure of open-framework materials. A common problem in this branch of materials science is the inability to grow crystals of sufficient size (usually 100 μm in each direction) to do single crystal X-ray diffraction (SCXRD). With the advent of large area CCD detectors structures for 10 μm crystals can be obtained. However, even with powdered materials it is still possible to determine the space group and lattice constants of a particular material. In fact, as shall be shown later, if an adequate starting model can be proposed one can generate the full crystal structure as well.

The powder X-ray diffractometer used was a Siemens D5000 using a Cu tube source and a Kevex Peltier-cooled “Drifted Li-Si” solid state detector. The detector was set to discriminate against Kα, leaving the Kα1,2 Cu X-ray lines. Tube voltage and current were set at 50 kV and 35 mA, respectively. Samples were prepared on homemade Bragg-Brentano low background flat plates made of polyethylene.

A standard PXRD pattern of TMA₄Ge₄S₁₀ is shown in Figure 2.6. This compound crystallizes in the cubic space group P 43n, with a = 19.554(2) Å. It is interesting to note that no water co-crystallizes with this species, as the other tetramers, Rb₄Ge₄S₁₀ and Cs₄Ge₄S₁₀ are both PXRD amorphous, likely due to the hygroscopic nature of these materials. Two polymorphs of the Cs tetramer are known, Cs₄Ge₄S₁₀·3H₂O crystallizes in the monoclinic space group Cc with a=12.558(6) Å, b=12.322(6) Å, c=16.698(8) Å and β=92.20(3)°, while Cs₄Ge₄S₁₀·4H₂O crystallizes in the same monoclinic space group with a=12.549(5) Å, b=12.305(5) Å, c=16.721(6) Å and β=92.30(4)°. The purity of the Rb and
Figure 2.6
Powder X-Ray Diffraction Pattern of $\text{TMA}_4\text{Ge}_4\text{S}_{10}$
Cs tetramers used was therefore determined by Raman spectroscopy and the materials were then used in subsequent reactions to create the corresponding frameworks.

As mentioned earlier, Zn(II) salts react with tetramers quickly to give small particle sizes and/or poorly crystalline materials, and thus broadening in the PXRD. Figure 2.7 shows the PXRD pattern of TMA$_2$ZnGe$_4$S$_{10}$ prepared with and without the use of EDTA as a complexing agent. Scanning Electron Microscopy (SEM) results showed no appreciable increase in the average particle size of ca. 1 µm. Slow delivery of the transition metal species to the reaction leads to a much lower number of crystal seeds and thus larger particle sizes and improved crystallinity. In fact, the Cs-Fe species which was used as a starting model for Rietveld refinement was grown utilizing CsF as a complexing agent for Fe(II), thus allowing the growth of crystals several hundred microns in size.\textsuperscript{16}

All the frameworks for the templates TMA, Cs, and Rb crystallize in the space group I \( \bar{4} \). Figure 2.8 shows the representative powder X-ray diffraction profiles for the T$_2$MnGe$_4$S$_{10}$ materials and the Miller indices for the first several peaks. Indexing of the profiles for the Mn(II) frameworks gives the unit cell parameters found in Table 2.2.

<table>
<thead>
<tr>
<th>Template</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>9.513(1)</td>
<td>14.281(2)</td>
<td>1292.4(3)</td>
</tr>
<tr>
<td>Cs</td>
<td>8.5735(1)</td>
<td>14.7940(2)</td>
<td>1087.4(1)</td>
</tr>
<tr>
<td>Rb</td>
<td>8.5289(5)</td>
<td>14.7743(12)</td>
<td>1074.7(1)</td>
</tr>
</tbody>
</table>

Some variation has been found in the unit cell parameters for the Cs and Rb materials, most likely as a result of variable water content. Indeed, variable temperature PXRD shows the flexibility of the framework as a function of water content. The changes in
Figure 2.7
Powder X-Ray Diffraction Patterns of TMA$_2$ZnGe$_4$S$_6$

(a) Without EDTA  (b) With EDTA

<table>
<thead>
<tr>
<th>2θ</th>
<th>3.077</th>
<th>3.022</th>
<th>2.831</th>
<th>2.755</th>
<th>2.621</th>
<th>2.579</th>
<th>2.429</th>
<th>2.346</th>
<th>2.284</th>
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<tr>
<td></td>
<td>4.053</td>
<td>4.732</td>
<td>6.699</td>
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<td></td>
<td></td>
<td>7.087</td>
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<td></td>
<td></td>
<td>4.864</td>
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</tr>
</tbody>
</table>
Figure 2.8
Powder X-Ray Diffraction Pattern of $T_2\text{MnGe}_2S_{10}$
$T = (a) \text{TMA} \ (b) \text{Cs} \ (c) \text{Rb}$
unit cell dimensions under N\textsubscript{2} directly correlate to the water loss in the TGA, as seen in Figure 2.9 for Cs\textsubscript{2}MnGe\textsubscript{5}S\textsubscript{10} and Figure 2.10 for Rb\textsubscript{2}MnGe\textsubscript{4}S\textsubscript{10}. For both materials, reversibility of water adsorption/desorption is seen, showing a great deal of promise for this type of material for chemical sensing applications. Table 2.3 shows the indexing of the unit cells at different temperatures for the two materials. The variable temperature PXRD were collected from alcohol slurries of the materials dried on a platinum strip, which was then heated. Sample displacement shifts were taken into account by comparing room temperature data with the corresponding zero-displacement Bragg-Brentano data, though there are unavoidable errors due to localized heating effects and bending of the Pt strip at higher temperatures.

<table>
<thead>
<tr>
<th>Template</th>
<th>Temperature (°C)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>25</td>
<td>8.534(1)</td>
<td>14.774(1)</td>
<td>1076.0(2)</td>
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<tr>
<td></td>
<td>100</td>
<td>8.257(3)</td>
<td>14.843(7)</td>
<td>1011.9(7)</td>
</tr>
<tr>
<td>Rb</td>
<td>25</td>
<td>8.528(4)</td>
<td>14.750(1)</td>
<td>1072.7(7)</td>
</tr>
<tr>
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<td>50</td>
<td>8.436(6)</td>
<td>14.667(14)</td>
<td>1043.8(14)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>8.240(8)</td>
<td>15.011(7)</td>
<td>1019.2(15)</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>8.091(4)</td>
<td>15.066(15)</td>
<td>986.2(12)</td>
</tr>
</tbody>
</table>

It is interesting to see an increase in the c-parameter upon the shrinking of the unit cell, this is in fact a common phenomena for adamantatoid compounds upon heating\textsuperscript{17,18}. In order for the structure to contract, the clusters have to ‘unwind’, leading to lengthening in one direction. While the structural changes taking place cannot be solely accounted for by water loss and cation rearrangement and could be temperature induced as well, the agreement
Figure 2.9
Variable Temperature PXRD of Cs-MnGS-3
(a) 25°C (b) 100°C (c) 25°C
Figure 2.10
Variable Temperature PXRD of Rb$_2$MnGe$_4$S$_{10}$
(a) 25°C (b) 50°C (c) 100°C (d) 145°C (e) 25°C
between the TGA and *in-situ* VT PXRD leads one to believe that the changes are mostly a function of water loss.

It is interesting to note the appearance of the 200 and 103 peaks in the Rb$_2$MnGe$_3$S$_{10}$ diffraction patterns at temperatures above 140 °C. As shall be seen in the next section, the absence of these peaks is an indication that the Rb electron density does not lie on these planes for the material at room temperature, yet a rearrangement of the structure at higher temperature causes an appreciable electron density to be present on these planes.

### 2.3.0 Rietveld Refinement

#### 2.3.1 Introduction to the Rietveld Method

Rietveld refinement was developed by Hugo Rietveld in 1967 as a route to elucidating crystal structures of compounds from neutron powder diffraction data. Prior to that time, the only possible method to obtain structures from powder diffraction data was using pattern decomposition, which involves integrating the intensity of each individual Bragg reflection to determine the structure factors. From the structure factors, the structure can then be solved by standard single crystal methods. The main limitation to the pattern decomposition method is that it only works well for cubic, high symmetry structures. As structures drop in symmetry and become more complicated, peak overlap prevents one from resolving the individual Bragg reflections. The Rietveld method overcomes this problem by incorporating the whole diffraction pattern, including the background.

Rietveld refinement involves a least-squares refinement carried out until a best fit is obtained between the observed diffraction pattern and the calculated pattern based on a
starting model of the crystal structure. The residual being minimized is found in Equation 2.1:

\[ S_y = \sum_i w_i (y_{\text{obs}} - y_{\text{calc}})^2 \]  

(2.1)

where \( w_i \) is the weighting factor, \( y_{\text{obs}} \) is the observed intensity at angle 2\( \theta \), and \( y_{\text{calc}} \) is the calculated intensity at the same angle. The calculated intensity comes from a combination of many functions (Equation 2.2):

\[ y_{\text{calc}} = s \sum_k L_k |F_k|^2 \phi(2\theta - 2\theta_k) P_k A + y_{\text{bi}} \]  

(2.2)

Where:
- \( s \) scale factor
- \( K \) Miller indices, hkl, for Bragg reflection
- \( L \) Lorentz, polarization and multiplicity factors
- \( \phi \) profile function (Gaussian, Lorentzian, or a convolution of the two)
- \( P_k \) preferred orientation function
- \( A \) absorption factor
- \( F_k \) structure factor
- \( y_{\text{bi}} \) background intensity

The most important development in the Rietveld method, which allowed the technique to be used to refine PXRD data as well as neutron data, was the development of the profile functions for X-ray peaks. Constant wavelength neutron peaks are Gaussian in nature, but the shape of X-ray peaks are much more complex, and are best fit by a convolution of Lorentzian (Equation 2.3) and Gaussian (Equation 2.4) functions, better known as a pseudo-Voigt function. For X-ray data generated at low step sizes (0.01° 2\( \theta \)) and moderate
step times (5-6 s) primarily Lorentzian functions will be seen; however instrumental effects will give these peaks a slightly Guassian nature as well.

\[
\gamma = \frac{(X + X_e \cos \Phi)}{\cos \Theta} + \frac{(Y + Y_e \cos \Phi)}{\tan \Theta}
\]

\[
\sigma^2 = U \tan^2 \Theta + V \tan \Theta + W + \frac{P}{\cos \Theta}
\]

The values \(X, X_e, Y, Y_e, U, V, W,\) and \(P\) are all found through refinement of the whole profile. However, they should not simply be regarded as constants that allow the refinement to be carried out, as they contain some valuable physical information as well. For example, from the Lorentzian constants \(X\) and \(X_e\), it is possible to estimate particle sizes, as seen in Equation 2.5.

\[
p_{\perp} = \frac{18000K\lambda}{\pi X} \quad p_{||} = \frac{18000K\lambda}{\pi(X + X_e)}
\]

where \(p_{\perp}\) is the particle size in the perpendicular direction, \(p_{||}\) is the size in the parallel direction, \(\lambda\) is the wavelength of X-ray radiation, and \(K\) is the Scherrer coefficient, a constant. Strain effects and the registry of layered materials can also be determined using the other coefficients.

The most important part of Rietveld refinement is the choice of an adequate starting model of the crystal structure. Though \(ab\text{-initio}\) structures have been determined utilizing direct methods, entropy minimization and other techniques,\textsuperscript{23,24} it is usually of great help to have a structural model of an isomorphous material at hand. The better the initial starting model, the larger chance of getting a successful refinement. Rietveld refinement, however, is not infallible - it is possible to get trapped into false minima, especially if a poor starting
model is chosen. By careful examination of the physical values extracted from the refinement, like bond angles and bond lengths, one can often spot such minima as being chemically unlikely.

The success of a refinement is based on a number of statistics developed to aid the experimenter in finding the correct minima, much as the statistics in single crystal analysis. They include:

\[ R_p = \frac{\sum |Y_{obs} - Y_{calc}|}{\sum Y_{obs}} \]  

(2.6)

\[ R_{wp} = \left[ \frac{\sum w_i (Y_{obs} - Y_{calc})^2}{\sum w_i Y_{obs}^2} \right]^{\frac{1}{2}} \]  

(2.7)

\[ R_{exp} = \left[ \frac{(N - P)}{\sum w_i Y_{obs}^2} \right]^{\frac{1}{2}} \]  

(2.8)

\[ \chi^2_r = \left( \frac{\sum w_i (I_e - I_c)^2}{N - P} \right) \]  

(2.9)

\[ GOF = \left( \frac{R_{wp}}{R_{exp}} \right)^2 \]  

(2.10)

where \( N \) is the number of observations (data points) and \( P \) is the number of variables refined. \( R_{exp} \) is based only on the counting statistics and is the minimum \( R_{wp} \) that is possible with a perfect refinement. With perfectly weighted data and a perfect refinement, \( R_{wp} \) would equal \( R_{exp} \), and the GOF would be one. As with all other statistical methods, it is possible for the numbers to 'lie', that is, by collecting a better background it is possible to lower the \( R_p \) values
without affecting the refinement at all. It is best to look at all of the data, including the graphical representation of the residuals to determine how good a refinement is and whether or not it can be improved.

2.3.2 $\text{T}_2\text{MnGe}_4\text{S}_{10}$ Refinements

It is interesting to note that the thiogermanate framework materials have been extensively studied utilizing Rietveld refinement in the literature, both with conventional\textsuperscript{25} and synchrotron\textsuperscript{26} X-ray data. These materials present a large library of isomorphous materials, in which different transition metals are used without changing the basic structure of the framework much at all. Indeed, it is has been shown that the materials are also isostructural with regard to different templates of similar size. Thus a good starting model can often be developed for the refinement of unknown structures. Utilizing Fourier electron density difference and Patterson maps can also be helpful in finding templating or guest materials within the ‘cages’ of the framework, much as is done in zeolite work.\textsuperscript{27}

Rietveld refinements were undertaken using a software package called GSAS - General Structure Analysis System.\textsuperscript{28} GSAS allows for either X-ray, neutron or, intriguingly, the combination of both X-ray and neutron powder data. Good quality PXRD data was recorded on the Siemens D5000 diffractometer with moderate counting times of 5-6 s and step sizes of 0.01° 2θ, ranging from 10 to 80° on the 2θ scale. H atoms were not refined, as previous experience has indicated no improvement in the refinement after including them.

For the refinement of $\text{Cs}_2\text{MnGe}_4\text{S}_{10}$, the starting model used was the single crystal XRD data from an isomorphous $\text{Cs}_2\text{FeGe}_4\text{S}_{10}$ (Appendix A3), by replacing Fe with Mn in the structure. Background was corrected by a 6th order cosine Fourier series. Inclusion of
absorption, extinction, and preferred orientation factors in the refinement did not lead to improvements, so they were left out. Isotropic temperature factors were obtained for all atoms except for O, which did not refine well, possibly due to static or dynamic disorder. There was no benefit to refine the anisotropic temperature factors, as Rietveld refinement usually does a poor job of refining temperature factors.

Table 2.4 shows the refinement statistics for Cs$_2$MnGe$_4$S$_{10}$·xH$_2$O, while the atomic coordinates are given in Table 2.5. Selected bond lengths and bond angles are given in Table 2.6. It crystallizes in the tetragonal space group I $\bar{4}$ with $a = 8.5735(1)$ Å and $c = 14.7940(2)$ Å. The observed and calculated powder profiles are seen in Figure 2.11, along with the residual. Also, a Cerius model of the structure is shown in Figure 2.12, with an enlarged view of the building blocks in Figure 2.13. The Ge-S and Mn-S bond lengths and angles agree well with literature values.$^{10}$

| Table 2.4 Refinement Statistics for Cs$_2$MnGe$_4$S$_{10}$·xH$_2$O |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $R_p$ %         | $R_{wp}$ %      | $R_{exp}$ %     | $\chi^2$        | number of parameters | data points | Bragg reflections |
| 8.59            | 11.47           | 7.41            | 2.398            | 40               | 7600          | 446             |
Table 2.5 Fractional Atomic Coordinates and Isotropic Temperature Factors

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<tr>
<th>Atom</th>
<th>x (Å)</th>
<th>y(Å)</th>
<th>z(Å)</th>
<th>U$_{iso}$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
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<td>1.00</td>
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<td>.0651(32)</td>
<td>.3515(21)</td>
<td>.02500</td>
<td>.746(28)</td>
</tr>
</tbody>
</table>

Table 2.6 Selected Bond Distances and Angles

| Ge(1) - S(1) | 2.192(10) | S(1)-Ge(1)-S(2) | 105.5(4) | Ge(1)-S(2)-Ge(1) | 106.4(6) |
| Ge(1) - S(2) | 2.251(9) | S(1)-Ge(1)-S(3) | 113.1(4) | Ge(1)-S(3)-Ge(1) | 106.2(4) |
| Ge(1) - S(3) | 2.305(13) | S(2)-Ge(1)-S(3) | 111.1(3) | Ge(1)-S(1)-Mn(1) | 110.1(5) |
| Ge(1) - S(3) | 2.189(8) | S(1)-Mn(1)-S(1) | 123.7(4) |          |          |
| Mn(1) - 4S(2) | 2.318(12) | S(1)-Mn(1)-S(1) | 102.9(2) |          |          |
Figure 2.11
Observed, Calculated, and Residual Profiles for
\( \text{Cs}_2\text{MnGe}_4\text{S}_{10-x}\text{H}_2\text{O} \)
Figure 2.12
Cerius™ Representation of [010] Plane of Cs₂MnGe₄S₁₆·xH₂O

Cs green, O red, S yellow, Mn purple, Ge blue
Figure 2.13
Enlarged View of the Building Blocks of Cs$_2$MnGe$_4$S$_{10}$·xH$_2$O
One has to be skeptical of the O(2) fractional occupancy, and even its nature, as in both the Fe(II) framework and the Mn(II) framework it could be either a Cs cation at very low occupancy or an oxygen atom with a very high isotropic temperature factor. Cs(1) sits on a special position of multiplicity 2, while Cs(2) has a multiplicity of 8, giving a Cs content for the cell of only 3.57(6) and not the expected 4. There is obviously some static or dynamic disorder present in this system, and it is possible that the Cs cations are undergoing thermal motion within the cages. $^{133}$Cs NMR with relaxation data may give an indication of the local environments and dynamics of different Cs$^+$ ions. Also, by doing a refinement of both neutron and X-ray diffraction data simultaneously it should be possible to better examine the atoms present inside the cages through electron difference maps. Neutron data is especially helpful since the H$_2$O molecules can be found using the contrast between D$_2$O profiles and H$_2$O profiles to find the hydrogen atoms.

The Rietveld refinement of Rb$_2$MnGe$_4$S$_{10}$·xH$_2$O was also attempted using the same starting model, Cs$_2$FeGe$_4$S$_{10}$·xH$_2$O (Appendix A3). The Rb cations could not be placed in the same positions as the Cs cations, as the 200 and 031 peaks are absent in the Rb framework structure. Cs(1) lies on these planes in the Cs$_2$MnGe$_4$S$_{10}$ structure. The refinement was attempted with only the framework atoms, using electron density difference maps to find the missing Rb and O atoms. Although some progress has been made, an adequate structure has not yet been solved as only 3 of the 4 Rb atoms can be found. It is hoped that neutron diffraction data taken in the near future will improve the quality of the data. Also, in the recent past Sheldrick et al. have synthesized the germanium selenide analogues of the Rb and Cs materials, showing fractional occupancies of Cs/Rb ions and O atoms from water in well
defined positions. Efforts are being made to use this data as a starting model for the thiogermanate system. The growth of single crystals of the analogous Rb₂FeGe₄S₁₈ structure has been attempted, but at the time of writing this thesis no single crystals have been synthesized.

It should be of great interest to follow the structural changes in these materials as the water molecules are being lost - *i.e.*, by doing *in situ* variable temperature neutron and X-ray powder diffraction studies. Structural characterization of these materials is the first step in being able to predict and understand their physical properties. Rietveld refinement is a technique that yields structures for materials for which single crystals simply cannot be grown.

### 2.4.0 References


4. Young, D., unpublished results.


Chapter 3 - Magnetic Properties

3.0.0 Preamble

In the first chapter, chalcopyrite and related materials were discussed as being benchmarks for which open-framework germanium sulfide materials could be examined magnetically. The work has focused on two goals, and each will be examined. The first being, simply, what are the properties of these materials? While one can borrow from the zeolite literature to some extent, especially from the Mn(II) aluminophosphates and silicoaluminophosphates MnAPOs\textsuperscript{1,2} and MnAPSOs\textsuperscript{3}, both of these materials contained Mn(II) sites that were poorly structurally characterized. Problems with inter- and intra-framework Mn(II) centers were commonplace. In contrast, the T\textsubscript{2}MGe\textsubscript{4}S\textsubscript{10} family of materials offers M(II) centers in well-defined positions, which allows for a greater understanding of the observed physical properties. The local magnetic field around a M(II) center is extremely sensitive to perturbations in the environment surrounding it - bonding and symmetry arrangements must be examined.

Secondly, the possibility of chemical sensing through Mössbauer spectroscopy, Electron Paramagnetic Resonance spectroscopy, and bulk magnetization measurements by examining the influence of ‘guest’ species on the magnetic centers in these open-framework materials. Although these materials have small pore volumes and are thus not ideal for the examination of host-guest properties of larger organic species, the adsorption properties of small molecules such as water and ammonia can be examined. It is simply a matter of time
before thiogermanate materials are developed which have larger pore volumes -- allowing the possibility for the examination of host-guest interactions of a myriad of guest species.

3.1.0 Electron Paramagnetic Resonance (EPR)

3.1.1 Introduction

Electron Paramagnetic Resonance (EPR), or alternatively Electron Spin Resonance (ESR) gives valuable insights into the coordination state and the local electronic and magnetic environments about Mn(II) centers. EPR spectroscopy measures the transitions between spin states for unpaired electrons, and is very sensitive to perturbations in the environment around the magnetic center. EPR of transition metal ions can be extremely useful due to the presence of unpaired d-electrons in such materials.4,5,6

EPR spectra are typically recorded by varying the magnetic field while applying a constant microwave frequency. The microwave radiation is set to resonate in the cavity, and the field is swept until such time as the difference in spin energy levels is exactly equal to the energy of the microwave radiation. At that point, the resonance is lost in the cavity and the detector then records the absorption of radiation as a first derivative spectrum. Typically, in the X-band frequency range (9.6 GHz) the magnetic field is swept from 0 to 10,000 Gauss.

High spin Mn(II) is an extremely sensitive EPR center as it has five unpaired d electrons, to give a total spin quantum number, \( S = \frac{5}{2} \), and a angular momentum quantum number \( L = 0 \). Six energy levels are present, with \( m_s = \pm \frac{5}{2}, \pm \frac{3}{2} \) and \( \pm \frac{1}{2} \). First order selection rules of \( \Delta m_s = \pm 1 \) leads to the presence of five magnetic dipole allowed transitions, often called the fine structure. Each of these five transitions is further split into six by the \(^{55}\text{Mn(II)}\) nucleus itself, which has a spin \( I = 5/2 \). This further splitting is referred to as the
hyperfine structure. Thus for a simple, first order spectrum, five sets of six lines are expected to be present. The relative positions of the fine structure transitions depends on many factors, amongst them the relative strengths of the external and internal fields, the anisotropy around the magnetic center, and the concentration of the paramagnetic centers.

If the Mn(II) centers are in a completely isotropic environment, the fine structure will become superimposed and six well resolved lines occur centered about the free-electron value g=2.0023. However, axial and orthorhombic distortions will lead to different values for the m, energy levels. Such distortions cause the m, transitions to change their field positions as the azimuthal angles θ, φ, of the principal symmetry axis vary with respect to the field. In a powdered sample this leads to a complex spectrum as all the values of θ and φ are present in the random distribution of the particles. These axial and orthorhombic distortions in the crystal field are represented by the zero-field splitting parameters D and E. For our tetragonal systems there are no orthorhombic distortions and thus E can be treated as zero.

EPR experimental spectra can be represented by a spin Hamiltonian (Equation 3.1):

\[ H = \beta g \cdot H \cdot S + S \cdot A \cdot I + S \cdot D \cdot S + g_s \beta_n H \cdot I \]  

where: \( \beta \) is the Bohr Magneton, a constant for a given electron or nucleus

\( g \) is the g-factor

\( \beta g \cdot H \cdot S \) is the electronic Zeeman

\( S \cdot A \cdot I \) is the Hyperfine splitting, or electron-nuclear splitting

\( S \cdot D \cdot S \) is the axial zero-field splitting (zfs)

\( g_s \beta_n H \cdot I \) is the nuclear Zeeman
For Mn(II), the absence of orbital angular momentum (L=0) leads to isotropic g-values lying about the free-electron value (g=2.0023) as no spin-orbit coupling is present. The appearance of an EPR spectrum is determined by the relative strengths of each of these interactions. It is not always the case that the electronic Zeeman splitting is the dominant term; in fact, for transition metal systems that is rarely the case. The relative strengths of H, D, and A determine the appearance of the spectrum. The axial zero-field splitting parameter, D, can be thought of as being made up from electron-electron interactions around the nuclei as well as interactions between the electrons of other magnetic centers. Typically for tetragonal Fe(III) and Mn(II) systems the strength of the zero-field splitting is much greater than the electronic Zeeman and hyperfine terms, and can be considered as the strongest interaction. The nuclear Zeeman is typically negligible, but sometimes needs to be included in complex simulations.

Figure 3.1 shows a representation of the splitting in a Mn(II) system. Before the field is applied, the degeneracy of the ±5/2, ±3/2, and ±1/2 Kramers doublets has already been split by the internal crystal field. Application of a field, H, splits these doublets to produce the five-line fine structure, which is further split by electron-nuclear hyperfine interactions. The actual positions of the fine structure transitions are determined by the relative magnitudes of the zero-field splitting and magnetic field. The figure does not show second order effects and forbidden transitions (Δm_s = ±2) which can occur when D is much larger than the magnetic field. Such effects can be simulated by theory, but often it is easier to remove them by looking at higher frequency bands. K and Q bands are used to minimize second order effects and spread out the EPR resonances to facilitate the spectral interpretation.
Figure 3.1
Fine and Hyperfine Energy Levels for S=5/2 Center

Zero field energy levels
High field energy levels
Permissible transitions \( \Delta M_S = 0 \)

Permissible transitions \( \Delta M_S = \pm 1 \)
Nuclear splitting
3.1.2 \( T_{2}\text{MnGe}_{4}S_{10} \) Results

EPR Spectra were taken on a Brüker ESP300 instrument operating at the X-band frequency of \( \text{ca. 9.62 GHz} \). The magnetic field could be swept from 0 to 10,000 G. An organic radical, 2,2-di(4-tert-octylphenyl)-1-picrylhydrazyl (DPPH) was used as a free electron standard, having a \( g \)-value of 2.0023. Samples were placed in quartz capillaries and capped to prevent contamination. Collection times were typically of the order of 500 seconds. The power of the microwave radiation was adjusted so that no saturation was occurring at the sample. This was done by examining the double-integrated area under the EPR peak as a function of the square root of microwave power.\(^4\)

For pure Mn(II) systems, \( T_{2}\text{MnGe}_{4}S_{10} \) where \( T = \text{TMA}, \text{Cs}, \text{and Rb} \), representative EPR spectra are seen in Figure 3.2. No fine or hyperfine structure is apparent for any of these spectra. This is due to the high concentration of magnetic centers in these materials - they are ‘magnetically concentrated’. The axial zero-field splitting parameter \( D \) can contain electronic interactions between magnetic centers as well as those caused by the zero-field splitting, as seen in Equation 3.2:\(^5,9\)

\[
D_{\text{total}} = D_{\text{zfs}} + D_{\text{dipole}} + D_{\text{exchange}}
\]

(3.2)

Dipole-dipole and exchange interactions can both occur. However, as seen in Figure 3.3 each Mn(II) atom in these open-framework systems is surrounded by 12 others; 6 at a distance of \( \text{ca. 9.4 Å} \) and another 6 separated by \( \text{ca. 9.8 Å} \) for \( \text{TMA}_{2}\text{MnGe}_{4}S_{10} \) (Appendix A1). Very fast fluctuations in the local magnetic fields due to significant dipole-dipole and exchange terms lead to a collapse of the spectrum to one broad isotropic peak. These
Figure 3.2
Electron Paramagnetic Spectra of $\text{T}_2\text{MnGe}_4\text{S}_{10}$
For $T = (a) \text{TMA} (b) \text{Cs} (c) \text{Rb}$
Figure 3.3
Coordination Sphere Around the Magnetic Metal Center in $T_2\text{MnGe}_4\text{S}_{10}$
fluctuations occur with relaxation times a magnitude of over a hundred times those seen for electronic Zeeman and hyperfine interactions.

The relaxation times can be quantified by examining the full-width at half height for each of these spectra. Two possible mechanisms exist for the relaxation of the spins back to equilibrium - spin-lattice relaxation ($T_1$), and spin-spin relaxation ($T_2$). Typically, for magnetically concentrated systems, $T_2$ is much faster than $T_1$ and can be easily calculated from Equation 3.3:

$$\frac{1}{T_2} = \kappa \gamma_e \Gamma$$

(3.3)

where: $\kappa = 1$ for Lorentzian lineshapes, $(\sigma \ln 2)^{1/2}$ for Gaussian

$\gamma_e =$ electronic magnetogyric ratio

$\Gamma =$ full width at half height (peak-peak width for 1st derivative)

The linewidths were found to be approximately Lorentzian. $T_2$ values are compiled for all three materials in Table 3.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak-Peak Width</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA$_2$MnGe$<em>4$S$</em>{10}$</td>
<td>450 G</td>
<td>$1.0 \times 10^{-10}$ s</td>
</tr>
<tr>
<td>Cs$_2$MnGe$<em>4$S$</em>{10}$</td>
<td>329 G</td>
<td>$1.7 \times 10^{-10}$ s</td>
</tr>
<tr>
<td>Rb$_2$MnGe$<em>4$S$</em>{10}$</td>
<td>280 G</td>
<td>$2.0 \times 10^{-10}$ s</td>
</tr>
</tbody>
</table>

Typical relaxation times for electronic Zeeman and hyperfine interactions are in the order of $10^8$ to $10^9$ s. An extremely interesting feature of these spectra is the decrease in
peak-peak width from TMA\textsuperscript{+} to Cs\textsuperscript{+} to Rb\textsuperscript{+} materials. The nearest Mn(II)-Mn(II) separation in TMA\textsubscript{2}MnGe\textsubscript{2}S\textsubscript{10} is 9.37 Å (Appendix A1) while in the Cs\textsubscript{2}MnGe\textsubscript{2}S\textsubscript{10} material it is much smaller, at 8.41 Å. Dipole-dipole interactions are expected to increase as a function of \(1/r^3\) and therefore interactions should be stronger for the Cs\textsuperscript{+} material. However, increased dipole-dipole coupling results in shorter relaxation times and broader lines in EPR, while exchange coupling results in narrowing.\textsuperscript{9} In order to see line-narrowing, exchange interactions need to occur, either through direct overlap, electrostatic Heisenberg coupling or anisotropic exchange involving spin-orbit or lattice effects.\textsuperscript{10} In our system, direct Heisenberg coupling is obviously impractical given the large separation between magnetic centers, and thus the possibility arises that the decrease in relaxation time is due to exchange taking place through the lattice: superexchange or the more likely alternative, spin polarization effects.\textsuperscript{11}

Other effects can also lead to the broadening of the single isotropic line - there is no basis to assume that \(T_2\) is necessary the largest relaxation occurring - \(T_1\) effects can also be involved. Indeed, in extracting relaxation time measurements out of the spectra, one is making the assumption that the relative relaxation times for the electronic Zeeman, hyperfine, and nuclear Zeeman interactions are negligible compared to that of the dipole-dipole interaction. It is necessary to verify the presence of exchange interactions by examining the magnetic susceptibility as a function of temperature. Bulk magnetic susceptibility measurements will indicate the presence of antiferromagnetic or ferromagnetic interactions. Double integration of the area under an EPR curve is a measure of the magnetic susceptibility of a material, but with very low precision.

Fe(II) and Co(II) are also magnetic centers, but neither can be easily probed by EPR. For Fe(II) the electronic configuration is d\textsuperscript{6}, which leads to a situation where there is no
Kramers doublet to split and hence no signal will be observed. However, EPR peaks corresponding to Fe(III) impurities are observed in our spectra. They are present either as low levels of Fe₂O₃ impurities or through a substitution of Fe(III) for Fe(II) centers in the framework. Co(II), with a d⁷ configuration, does have a Kramers doublet and thus should be a sensitive EPR probe. However, the presence of low level excited states prevent signal detection except at very low temperatures as the signal is broadened out completely by rapid relaxation rates back to the ground state. At temperatures below 20 K, Co(II) EPR peaks can be seen, but even these spectra are extremely broadened and often contain little additional information.⁴⁵

3.1.3 Ternary Frameworks TMA₂MnₓZn₁₋ₓGe₄S₁₀ where 0 ≤ x ≤ 1

For a complete examination of the magnetic properties of these materials, one needs to develop materials for which the Mn(II)-Mn(II) dipole and exchange interactions are minimized to the extent that fine and hyperfine coupling is seen. This is done by separating the Mn(II) centers by using Zn(II) as a diamagnetic dilutant. Stoichiometric amounts of Zn(II) and Mn(II) were reacted with the tetramer species with vigorous stirring as discussed earlier. Neutron activation analysis undertaken with Dr. Ron Hancock at the Slowpoke reactor at the University of Toronto indicated that the Mn/Zn ratios were within 5% of the stoichiometric amounts used.¹² There are large inherent errors (±5%) in neutron activation for these two species due to overlap in the isotope half-lives, and more rigorous elemental analysis is needed.
Several possibilities exist for the distribution of Mn(II) and Zn(II) centers in a solid solution, ranging from a completely random arrangement to phase separation of the Mn(II) and Zn(II) frameworks. It is also possible that the concentration of Mn(II) is graded throughout the sample, since the kinetics of the Zn(II) reaction to form the framework are considerably faster than those for Mn(II). Polycrystalline materials are generated from seeds of TMA$_2$ZnGe$_4$S$_{10}$, with Mn(II) incorporated into the structure as the seeds grow. Other possibilities include phase separation, physical domains of one framework within the other, and the formation of a superlattice. EPR spectra for these mixed frameworks show a loss of the broad central peak with decreasing Mn(II) concentration. Figure 3.4(a) shows the peak-peak (FWHM) separation as a function of Mn(II) concentration in the mixed frameworks for this central peak. Lowering the Mn(II) concentration causes a decrease in the FWHM, which is to be expected since, as Mn(II) becomes diluted in the structure, the average Mn(II)-Mn(II) separation increases. The average Mn-Mn distance is obtained by examination of the volume and number of Mn atoms in the unit cell, as seen in Equation 3.4:\textsuperscript{13}

\[ d = \left( \frac{V}{nx} \right)^{1/3} \]  

(3.4)

where:

\( d \) = Average Mn(II)-Mn(II) distance

\( V \) = Volume of unit cell

\( n \) = Number of M(II) centers in unit cell

\( x \) = Percentage Mn(II) in mixed framework
Figure 3.4
Dipole-Dipole Interactions in $\text{TMA}_2\text{MnGe}_4\text{S}_{10}$
Plot of (a) FWHM vs. % Mn and (b) FWHM vs $1/d^3$
Since the dipole-dipole interactions decreases as a function of \(1/d^3\), one should expect the plot of \(1/d^3\) vs. FWHM to be linear. However, as seen in Figure 3.4(b), this is not the case. At high Mn(II) concentrations, the assumption of a completely random distribution of metal centers may be incorrect - Zn(II) and Mn(II) phase segregation and/or gradient formation occurs.

Attempts are ongoing to determine the metal ion distribution in these solid-state materials - high spatial resolution energy-dispersive spectroscopy (EDS) could provide elemental maps that clearly show the presence or absence of gradients. Ongoing neutron diffraction experiments at Chalk River on mixed framework materials may be able to indicate the distribution of metal centers, by taking advantage of the large contrast between Mn(II), Fe(II), and Zn(II) scattering lengths. The scattering power of these ions with X-rays is virtually indistinguishable, as it is a function of the atomic number, \(Z\).\(^{14}\)

Representative EPR spectra for TMA\(_2\)Mn\(_x\)Zn\(_{1-x}\)Ge\(_4\)S\(_{16}\) are shown in Figure 3.5 for \(x = 0.01, 0.02, \text{ and } 0.10\). The effects of increasing the concentration of Mn(II) centers are seen in the growth of the broad peak centered at \(g = 2.00\). Local Mn(II) dipole-dipole and/or exchange interactions cause a collapse of the fine and hyperfine interactions as in the magnetically concentrated systems. However, at low Mn(II) levels we see the presence of both fine and hyperfine interactions, giving rise to five six-peak regions, as in Figure 3.1. The spectra are complex due to the presence of anisotropy and second order transitions, making it difficult to see this clearly. The hyperfine splitting of \(ca. 70\) Gauss agrees favourably with literature values for tetrahedral Mn(II)S\(_4\) centers.\(^{15}\)

Simulation of the X-band spectra was attempted using two software packages - EPRNMR\(^{16}\), written by Weil and Mombourquette at the University of Saskatchewan, a full
Figure 3.5
Electron Paramagnetic Resonance Spectra
for $\text{TMA}_x\text{Mn}_1\text{Zn}_{1-x}\text{Ge}_4\text{S}_{10}$ where $x = (a) 0.10 \ (b) 0.02 \ (c) 0.01$
spectral simulation which makes no prior assumptions about the relative energy levels of the Hamiltonian terms, and WinSimfonia from Bruker, which relies on perturbation theory, i.e. the Zeeman splitting is larger than the zero-field splitting (fine structure) which is in turn greater than the hyperfine interactions. This assumption is valid for simple S=1/2 systems such as Cu$^{2+}$ and Ti$^{3+}$, but can begin to fail in systems which have a large zero-field splitting - i.e., those with S values greater than 1/2. In both cases, X-band spectra were too complex to simulate, as least-squares fitting routines were not available in either software routine for powdered samples. The need to average the simulated spectra over all possible orientations (azimuthal angles $\theta$ and $\phi$) dramatically increases the needed computer power. A full structure calculation of a powdered sample with no prior assumptions about the relative intensities of each of the perturbations is not a simple task.

At the time of writing this thesis, samples were sent to the Continuous Wave Electron Paramagnetic Resonance Spectroscopy Service at University of Manchester, where Q and higher band frequencies up to 500 MHz can be used to probe the magnetic structure of these materials. High frequency spectra will spread the peaks out over a larger range, as well as minimize second order effects, allowing the simulation of EPR spectra to determine the Hamiltonian parameters.

3.1.4 Chemical Sensing with EPR

One of the goals of this work was to examine the possibility of utilizing magnetic measurements to examine the host-guest properties of this class of microporous materials. Several papers on MnAPSO materials were published by the Russian group of Nikolaeva et al. that examined the dehydration of those doped zeolites and the inclusion of other small
guest molecules in the free void space, such as ammonia. They found that the effect on the EPR spectra of these materials was seen in the change in the spin-lattice relaxation time $T_1$. Thus Mn-OH$_2$ and Mn-NH$_3$ interactions cause full width at half maximum (FWHM) changes in the EPR spectra.

The Cs$_2$MnGe$_4$S$_{10}$ material was examined in detail, by removal of the chemi- and physisorbed water at 300° C for 4 hours under vacuum. Dehydration was undertaken in a specially designed Wilmad EPR tube that allowed for preparation of air and moisture sensitive materials - a valve could be closed at the top of the tube to retain the vacuum conditions. Figure 3.6 shows the EPR spectra of Cs$_2$MnGe$_4$S$_{10}$ with and without water -- a noticeable narrowing of the peak is seen from 329 Gauss to 240 Gauss. The possibilities for this narrowing are twofold: either an increase in the $T_1$ spin-lattice relaxation time occurs with the loss of Mn-O interactions (O from water), or exchange coupling between Mn(II) centers has increased, leading to exchange narrowing. It is difficult to pinpoint the source of the narrowing to either of these interactions - though from dipole-dipole considerations we would expect to see a broadening of the peak as the Mn(II) atoms become closer together in the lattice with the loss of water (see variable temperature pXRD results). Attempts at looking at the effect of dehydration on zero-field splitting strength in magnetically dilute Mn(II) materials has not, to this point, yielded any useful information. The fact that little change is seen in these materials leads us to the possibility that spin-lattice effects might be small - as the loss of H$_2$O-Mn interactions in a diluted material should perturb the local zero-field strength.

Incorporation of NH$_3$ into the pore volume freed up during dehydration was attempted - it was thought that NH$_3$ might be able to replace water as the kinetic diameters of
Figure 3.6
Electron Paramagnetic Resonance Spectra
of Cs$_2$MnGe$_4$S$_{10}$ (a) With H$_2$O (b) Without H$_2$O
each of the species is roughly the same, 2.8 Å. However, no change in the EPR spectra was seen with exposure to NH₃ - it is possible that it is excluded from entering the cavities. Further studies utilizing Mid-IR spectroscopy to examine whether NH₃ adsorption is occurring are underway.

The use of larger templates, and thus creating larger pore volumes will allow for a much more thorough examination of host-guest properties of thiogermanate framework systems. The large change in the spectra upon dehydration definitely shows promise for the use of Electron Paramagnetic Resonance as a very useful tool in the examination of the host-guest interactions.

3.2.0 Bulk Magnetization Measurements

3.2.1 Of SQUIDs and Susceptibilities

Traditionally the magnetic susceptibility (χ) of a material has been measured using a Gouy balance, in which a cylindrical sample is suspended from the beam of an analytical balance. The change in weight in the presence of a magnetic field indicates the susceptibility of the sample. However, this method has serious disadvantages in that it requires relatively large samples and requires a uniform sample density, which is difficult to achieve upon packing powders into a quartz tube. The Faraday method corrects many of these difficulties by providing a constant field gradient across the sample, allowing small sample sizes and the absence of packing errors, but still holds an error of ±1%.

The use of a magnetometer equipped with a Superconducting QUantum Interference Device (SQUID) to measure the magnetic susceptibility of materials dramatically increases
the sensitivity of the technique. A SQUID device consists of a closed superconducting loop that contains several switchable Josephson junctions. A solid is packed into a cylindrical column and passed through the superconducting detection coils, as seen in Figure 3.7. The magnetic moment of the sample induces an electrical current in the detection coils, which is sensed by the sensitive detector circuit below the apparatus. The SQUID functions as a highly linear current to voltage generator, and for a calibrated system the voltage variations from the SQUID detector are proportional to the magnetic moment of the sample. The use of liquid helium surrounding the superconducting wires allows for susceptibility-temperature measurements down to approximately 2 K.

When the sample is placed in a magnetic field, \( H \), the density of the lines of force in the sample, known as the magnetic induction, \( B \), is given by \( H \) plus a contribution by the sample itself, \( 4\pi I \) (Equation 3.5):

\[
B = H + 4\pi I
\]

where \( I \) is the magnetic moment of the sample per unit volume. The susceptibility of a sample, \( \kappa \), can be defined by Equation 3.6:

\[
\kappa = \frac{I}{H}
\]

Finally, the molar susceptibility, \( \chi_m \), can be determined if the density (\( \rho \)) and molecular weight (\( M_w \)) of the sample is known (Equation 3.7):

\[
\chi_m = \frac{\kappa M_w}{\rho}
\]

For diamagnetic substances, \( B < H \) and \( \kappa \) and \( \chi_m \) are both small and slightly negative. However, for paramagnetic, ferromagnetic and antiferromagnetic substances \( B > H \)
Figure 3.7
Layout of Magnetometer Equipped With Superconducting Quantum Interference Device (SQUID)\textsuperscript{22}
and $\kappa$ and $\chi_m$ both have large positive values. Thus diamagnetic substances are slightly repelled by a magnetic field whereas paramagnetic substances are attracted.

The magnetic properties of a material can be evaluated by examining the temperature dependence of its molar susceptibility. Paramagnetic materials follow the Curie law, found in Equation 3.8:

$$\chi = \frac{C}{T}$$

where $C$ is the Curie constant. However, many materials show deviations from perfect paramagnetism, and are best described by the Curie-Weiss law (Equation 3.9):

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

where $\theta$ is the Weiss constant. Plots of the inverse susceptibility $1/\chi$ vs. temperature give a slope of $C$ and an intercept of $\theta$. Ferro- and antiferromagnetic substances do not exhibit either Curie or Curie-Weiss behaviour. Instead, ferromagnetic substances show an extremely large susceptibility at low temperatures that decreases rapidly as the temperature increases, until the Curie temperature is reached upon which the material acts as a normal paramagnet. For antiferromagnetic materials, on the other hand, the susceptibility increases with temperature until the Néel point, $T_N$ is reached, upon which paramagnetic behaviour is exhibited.

The Curie constant, $C$, is a function of the magnetic moment of a material, or the number of unpaired electrons, as seen in Equation 3.10:

$$C = \frac{N\beta^2 \mu^2}{3k}$$
where \( N \) is Avogadro’s number, \( \beta \) is the Bohr magneton and \( k \) is Boltzmann’s constant. The experimentally determined magnetic moment can be compared to the theoretical value, which is a function of the spin quantum number of the magnetic center, \( S \), the orbital angular momentum quantum number, \( L \), as shown in Equation 3.11:

\[
\mu = \sqrt{4S(S+1) + L(L+1)}
\] (3.11)

Quenching of orbital angular momentum or the presence of exchange interactions which can substantially lower the magnetic moment through a delocalization of electrons between magnetic centers both serve to reduce the magnetic moment.

One of the assumptions that is often made when interpreting magnetic susceptibility data is that positive Weiss constants denote ferromagnetic behaviour and negative Weiss constants are the result of antiferromagnetic interactions. In fact, most deviations from the Curie law are due to the zero-field splitting term in the Hamiltonian resulting from paramagnetic anisotropies in the material. When axial and/or orthorhombic anisotropy is present in the sample the susceptibilities in the parallel and perpendicular directions differ significantly. The susceptibility for powdered materials is an average of all possible orientations, and is given in Equation 3.12.

\[
\langle \chi \rangle = \frac{\chi_u + 2\chi_z}{3}
\] (3.12)

Thus for large, internal zero-field splitting substantial deviations in the Weiss constant are seen from perfect paramagnetic behaviour, and non-zero values are obtained. While it is true that non-zero Weiss constants can be an indication of non-paramagnetic behaviour, one must be careful in making such assumptions without supporting evidence.
3.2.2 Results

Susceptibility measurements were undertaken on a Quantum Design's Magnetic Property Measurement System (MPMS) at McMaster University by Dr. John Greedan. Plots of temperature vs. molar susceptibility were collected from 2 K to 300 K at a constant magnetic field of 100 Gauss. Approximately 100 mg of each sample was used. Diamagnetic corrections with the corresponding Zn(II) frameworks were attempted, but an adequate signal was not obtained. The diamagnetic corrections should be negligible compared to the large susceptibilities of the Mn(II) and Fe(II) species.

Susceptibility data was collected on a number of materials, T$_2$MnGe$_4$S$_{10}$ for T = TMA, Cs, and Rb, as well as T$_2$FeGe$_4$S$_{10}$ for T = TMA and Cs. A representative plot of susceptibility vs. temperature is seen in Figure 3.8 for TMA$_2$MnGe$_4$S$_{10}$. All materials showed nearly perfect paramagnetic behaviour down to 2 K, albeit with small negative Weiss constants. Table 3.2 lists the Weiss constants and magnetic moments measured for each of the materials. The theoretical values for the magnetic moment of Mn(II) and Fe(II) are 5.92 and 4.90 Bohr magnetons, respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>Magnetic Moment ($\mu_B$)</th>
<th>Weiss Constant ($\theta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA$_2$MnGe$<em>4$S$</em>{10}$</td>
<td>5.64(3)</td>
<td>-2.2(4)</td>
</tr>
<tr>
<td>Cs$_2$MnGe$<em>4$S$</em>{10}$</td>
<td>5.30(3)</td>
<td>-2.9(7)</td>
</tr>
<tr>
<td>Rb$_2$MnGe$<em>4$S$</em>{10}$</td>
<td>5.59(2)</td>
<td>-2.9(5)</td>
</tr>
<tr>
<td>TMA$_2$FeGe$<em>4$S$</em>{10}$</td>
<td>4.86(1)</td>
<td>-2.3(2)</td>
</tr>
<tr>
<td>Cs$_2$FeGe$<em>4$S$</em>{10}$</td>
<td>4.76(4)</td>
<td>-3.8(10)</td>
</tr>
</tbody>
</table>
Figure 3.8
Magnetic Susceptibility Plot of $\text{TMA}_2\text{MnGe}_2\text{S}_{10}$
It is not a simple task to reconcile the EPR and susceptibility data for the Mn(II) materials. There is a slight trend towards more negative Weiss constants upon replacing TMA with Cs in the materials. This could be due to an enhancement of exchange interactions between Mn atoms on a local level - the shifting of the effective magnetic moment to lower values supports this possibility. The shifts are too small to make any generalities - the absence of a Curie transition to an antiferromagnetic state also yields the possibility that anisotropic effects and experimental errors could be the source of the small negative Weiss constants. However, an inspection of the symmetry about the Mn(II) and Fe(II) centers shows that Cs frameworks are much closer to tetrahedral symmetry - thus the paramagnetic anisotropy should be smaller than that for the corresponding TMA frameworks.

3.3.0 Mössbauer Spectroscopy

3.3.1 Introduction

Mössbauer spectroscopy readily yields valuable information about the electron density distribution about the active nuclei due to the crystal field exerted upon it.\textsuperscript{24,25} The oxidation state and coordination number of the nucleus can be obtained by observing the isomer shift (\(\delta\)) and quadrupolar splitting (\(\Delta E_Q\)), respectively. Absorption of \(\gamma\)-ray radiation occurs from the I=1/2 ground state of the \(^{57}\)Fe nuclei to the I=3/2 excited state. As the energy of the \(\gamma\)-ray radiation is a constant, the Doppler effect is utilized to give a range of frequencies. This is done by continuously cycling the sample with respect to the \(\gamma\)-source in constant acceleration mode. The need to use the Doppler shift to facilitate absorption results in a large percentage of the signal lost due to nuclear recoil of the sample upon bombardment
with \(\gamma\)-radiation. This limits the use of Mössbauer spectroscopy to solid state systems in which the active Mössbauer nuclei is well constrained in its lattice - \textit{i.e.} nuclei that have low vibrational and/or rotational motions.

Anisotropic electric field gradients about the active Mössbauer nucleus will lead to quadrupolar splitting of any observed peaks for nuclei with less than cubic symmetry. Figure 3.9 shows the splitting of energy levels for a Fe(II) nucleus due to anisotropic electric field gradients \((V_{zz})\) and the presence of an internal magnetic field \((H_{int})\). The quadrupole splitting, \(\Delta E_q\), is a function of the symmetry of the ligand field around the active Mössbauer nucleus. Low temperature measurements can be used to examine magnetic ordering in substrates, as ferromagnetic or antiferromagnetic substances have internal magnetic fields which induce further splitting of the doublets \((m_i = \pm 1/2, \pm 3/2\)). External magnetic fields can also be used to split these doublets and give additional magnetic information.

3.3.2 Results

\(^{57}\text{Fe}\) Mössbauer spectra were collected at room temperature using a Ranger Scientific MS-1200 instrument in constant acceleration mode. The \(^{57}\text{Fe}\) \(\gamma\)-ray source was 10 mCi of \(^{57}\text{Co}\) which had dissipated two half-lives. Data was collected in 1024 channels with a maximum velocity of \(\pm 15.8\) mm/s. Iron powder was used as a Mössbauer standard and the center of the 6 line spectrum was set at 0 mm/s as a reference for all other samples. Spectra were folded and background Fe impurities in the beryllium window were subtracted using a MathCad\textsuperscript{TM} program kindly provided by Dr. Ömer Dag, with some modifications. The data was then transferred to Jandel PeakFit\textsuperscript{TM}, and the spectra were fitted by minimizing the
Figure 3.9
Mössbauer Splitting of a Fe(II) Center and Representative Spectra

The diagrams illustrate the Mössbauer splitting of a Fe(II) center, showing the transitions and energy levels for different spin states. The label 

$\delta_{Fe}$

represents the iron splitting, and $\Delta E_0$ represents the energy difference between the levels. The diagrams also depict the magnetic field effects ($H_{int}$) and the transitions for different spin states ($m_I = \pm \frac{1}{2}$).
residual of a Voigt area function. **Figure 3.10** shows the Mössbauer spectra for TMA$_2$FeGe$_4$S$_{10}$. Two peaks are seen with an isomer shift of 0.65 mm/s and a quadrupole splitting of 3.45 mm/s, diagnostic of Fe(II) centers. There are also trace amounts of Fe(III) with small quadrupole splittings lying near 0 mm/s. It was not known if the Fe(III) centers were a result of incomplete background correction for the beryllium window iron impurities that are known to exist or possible Fe(III) defect centers in the framework. **Table 3.3** lists the Fe(II) isomer shifts and quadrupole splittings obtained for each of the iron frameworks, T$_2$FeGe$_4$S$_{10}$ where $T = \text{TMA, Cs, and Rb}$.

**Table 3.3 Isomer Shifts and Quadrupolar Splitting of Fe(II) in T$_2$FeGe$_4$S$_{10}$**

<table>
<thead>
<tr>
<th>Material</th>
<th>Isomer Shift (mm/s)</th>
<th>Quadrupole Splitting (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>0.65(2)</td>
<td>3.45(2)</td>
</tr>
<tr>
<td>Cs</td>
<td>0.62(2)</td>
<td>3.22(2)</td>
</tr>
<tr>
<td>Rb</td>
<td>0.62(2)</td>
<td>3.28(2)</td>
</tr>
</tbody>
</table>

The isomer shifts lie on the low side of typical Fe(II) high spin systems, which typically have values of 0.6 - 1.6 mm/s. Quadrupole splittings fall close to those seen for other tetrahedrally coordinated Fe(II)-S compounds such as briartite, CuFe$_{0.5}$Ge$_{0.5}$S$_2$ which has a isomer shift of 0.85 mm/sec relative to sodium nitroprusside and a quadrupole splitting of 2.56 mm/s.$^{26}$

**Figure 3.11** shows the angles $\phi_1$ and $\phi_2$ around a distorted tetrahedral Fe(II)S$_4$ site. With a greater distortion from the ideal tetrahedral angle, 109° 28', the quadrupole splitting will increase. **Table 3.4** shows the relation between the splitting observed and the angles around the Fe(II) centers for T$_2$FeGe$_4$S$_{10}$ for $T = \text{TMA and Cs (Appendix A2, A3)}$. 
Figure 3.10
Mössbauer Spectrum of TMA$_2$FeGe$_4$S$_{10}$

Quadrupolar Splitting Fe(II)

Isomer Shift Fe(II) $(\delta)$
Figure 3.11
Tetragonal Distortion About $T_2FeGe_4S_{10}$ Frameworks
**Table 3.4 - Quadrupolar Splitting and Tetragonal Angles for T₄FeGe₂S₁₀**

<table>
<thead>
<tr>
<th>Material</th>
<th>Quadrupolar Splitting (mm/s)</th>
<th>φ₁</th>
<th>φ₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA</td>
<td>3.45(2)</td>
<td>122.4</td>
<td>103.4</td>
</tr>
<tr>
<td>Cs</td>
<td>3.22(2)</td>
<td>116.0</td>
<td>106.3</td>
</tr>
<tr>
<td>Rb</td>
<td>3.28(2)</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

Extrapolation of the quadrupole splitting data to the Rb framework suggests that the latter will have angles slightly more distorted than those of Cs - but should be closer to Cs than TMA. This agrees well with PXRD results, which show that the Rb structure has nearly the same unit cell dimensions as those for Cs. The bulk magnetization and Mössbauer results do show discontinuities between the Cs and Rb structures, most likely as a result of the different locations of the cations within the cavities.

Future work involves examining the Mössbauer spectra after dehydration of the materials, as well as exploring the possibility of detecting guest molecules such as NH₃ within the pore structure through alterations in the Mössbauer parameters. Also, the effect of dilution of Fe(II) centers with Zn(II) will be examined in detail.

### 3.4.0 References


Table A1

Fractional Atomic Coordinates and Isotropie Temperature Factors for TMA$_2$MnGe$_4$S$_{10}$ (I $\bar{4}$, a=9.5130(10) Å, c=14.281(2) Å)


<table>
<thead>
<tr>
<th>Atom</th>
<th>x (Å)</th>
<th>y(Å)</th>
<th>z(Å)</th>
<th>$U_{iso}$</th>
<th>Occupancy</th>
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Selected bond distances and angles

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<th>Angle (°)</th>
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<td>- S(2)</td>
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<td>- S(3)</td>
<td>2.242(3)</td>
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<td>Mn(1) - 4S(1)</td>
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<td>102.5(1)</td>
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<td>Ge(1)-S(1)-Mn(1)</td>
<td>116.5(2)</td>
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Table A2

Fractional Atomic Coordinates and Isotropic Temperature Factors for TMA$_2$FeGe$_4$S$_{10}$ (I $\bar{a}$, a=9.374(3) Å, c=14.174(4) Å)


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<th>z(Å)</th>
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Selected bond distances and angles

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<td>111.5(2)</td>
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<td>111.4(3)</td>
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Table A3

Fractional Atomic Coordinates and Isotropic Temperature Factors for
Cs$_2$FeGe$_4$S$_{10}$·xH$_2$O (I 4, a=8.413(7) Å, c=14.75(2) Å)


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Selected bond distances and angles

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<tr>
<th>Bond</th>
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<tbody>
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