MAGNETIC AND THERMAL STUDIES OF DOPED RARE-EARTH CHALCOGENIDE NANOSTRUCTURES IN SOLUTION AND THE SOLID-STATE

A Dissertation
submitted to the Faculty of the
Graduate School of Arts and Sciences
of Georgetown University
in partial fulfillment of the requirements for the
degree of
Doctor of Philosophy
in Chemistry

By

William Lawrence Boncher, B.A.

Washington, DC
11/30/12
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William Lawrence Boncher, B.A.

Thesis Advisor: Sarah L. Stoll, Ph.D.

ABSTRACT

The europium chalcogenides (oxide, sulfide, selenide) are intrinsically ferromagnetic semiconductors. Research with these types of materials is motivated by applications in fields such as spintronics, which can take advantage of the coupling of magnetic and electronic properties. By synthesizing these materials on the nanoscale, we can exercise strong control over their size and morphology for potential application in devices. Changes in size and structure also control their properties.

We have been able to synthesize these materials through both solution-based and solid-state techniques. The solution-based route has allowed the synthesis of ligand capped europium sulfide nanoparticles through the decomposition of a europium dithiocarbamate precursor. Particle size control is accomplished through manipulation of temperature, time and ligand to precursor ratio. Our group has previously shown that this manipulation of particle size can tune the magnetic ordering temperature. By introducing changes in capping ligands used, we can influence particle shape, albeit to a limited degree; this was the motivation for developing a hydrothermal/solid-state synthesis of these materials as well.

By utilizing a hydrothermal method, we can synthesize single-crystalline europium hydroxide (Eu(OH)₃) nanorods and nanowires. This starting material can be used in a variety of chemical transformation methods to create a wide range of materials. Dehydration of the material
yield single-crystalline europium oxide (Eu$_2$O$_3$) which maintains the morphology during the conversion. Eu$_2$O$_3$ can be reacted with hydrogen sulfide to form europium sulfide (EuS), europium metal to form europium monoxide (EuO), ammonium halides to form europium oxyhalides (EuOX), or hydrolyzed back to Eu(OH)$_3$, all while maintaining the wire morphology of the starting material.

In addition, the stoichiometry can be finely controlled in the materials through doping with different elements. By doping the europium chalcogenides with trivalent lanthanides, electrons can be injected into the conduction band. Because of the connection of the magnetic and electronic properties, electron doping can be used to improve the magnetic properties, notably by increasing the magnetic ordering temperature. These materials have a strong magnetic moments, colossal magnetoresistance, and strong magneto-optical Kerr effect, but are limited for application in devices by their low magnetic ordering temperatures, the weakest aspects of these materials.
ACKNOWLEDGMENTS

First and foremost, I have to thank my amazing mentor, Sarah Stoll, for making my time in graduate school productive, educational, and lots of fun. I have truly learned so much from her, and she has always been there and available to help out with anything, scientific or otherwise.

I was told that in order to have a good time in graduate school, you needed to like at least two out of three: your mentor, your research, or your group, and I have been lucky to have all three in my favor. My group members, current and past, have definitely made for great experiences, both in and out of the lab, and am really thankful to have spent time with everyone, especially Chelie, Kayla, Billy, Haydee, Natasha, and Nick.

There are so many people I have to thank for making my graduate school experience as great as it was, not just in my own research group, but across the whole chemistry department. There isn't enough space here to mention everyone that I should, but I do have to a special thanks to Lisette for serving with me on the GSOC. Our department is staffed by many wonderful people, from Travis, Kay, Mo, and Inez in the main office as well as a great selection of faculty. More thanks are in order to everyone who served on my committee throughout the years for their help and guidance: Bahram Moasser, Tim Warren, YuYe Tong, and Steve Metallo.

Lastly, I must thank all of my family who have helped me get this far in my education; I could not have done so without all of their support.
### TABLE OF CONTENTS

**Chapter 1: Molecular precursors for synthesis of lanthanide sulfides** ........................................ 1
1.1 Introduction ............................................................................................................................. 1
1.1.1 Lanthanide sulfides .......................................................................................................... 1
1.1.2 Magnetism ......................................................................................................................... 4
1.1.3 Nanoparticles .................................................................................................................... 9
1.1.4 Electron doping ................................................................................................................. 12
1.2 Results and discussion .......................................................................................................... 14
1.2.1 Dithiocarbamate thermolysis ......................................................................................... 14
1.2.2 Gadolinium-doped europium sulfide ............................................................................... 22
1.2.3 Eu$_{1-x}$Gd$_x$S oxidation ............................................................................................... 25
1.2.4 Eu$_{1-x}$Gd$_x$S nanoparticles ......................................................................................... 30
1.2.5 Morphology control in EuS nanoparticles ................................................................... 36
1.2.6 Thulium sulfide .............................................................................................................. 44
1.3 Experimental ....................................................................................................................... 51

References .................................................................................................................................. 62

**Chapter 2: Chemical transformations and solid-state synthesis of europium sulfide** ................. 66
2.1 Introduction ........................................................................................................................... 66
2.1.1 Magnetic domains .......................................................................................................... 66
2.1.2 Chemical transformations ............................................................................................. 70
2.2 Results and discussion ........................................................................................................ 72
2.2.1 Eu(OH)$_3$ ....................................................................................................................... 72
2.2.2 Eu$_2$O$_3$ ......................................................................................................................... 78
2.2.3 EuS .................................................................................................................................. 82
2.2.4 Sodium-doped EuS ........................................................................................................ 86
2.2.5 Other dopants in EuS .................................................................................................... 105
2.2.6 Gadolinium-doped EuS ............................................................................................... 108
2.3 Experimental ....................................................................................................................... 116

References .................................................................................................................................. 123

**Chapter 3: Solid-state synthesis of europium oxide** ................................................................. 126
3.1 Introduction ........................................................................................................................... 126
3.2 Results and discussion ........................................................................................................ 130
3.2.1 Europium oxide synthesis ........................................................................................... 130
3.2.2 Reaction with electron beam ....................................................................................... 134
3.2.3 Monoclinic Eu$_2$O$_3$ .................................................................................................. 136
3.2.4 Europium oxyhalides ................................................................................................... 140
3.3 Experimental ....................................................................................................................... 148

References .................................................................................................................................. 151

Appendix: Rietveld refinement .................................................................................................. 154
Chapter 1

MOLECULAR PRECURSORS FOR SYNTHESIS OF LANTHANIDE SULFIDES

1.1 Introduction

1.1.1 Lanthanide sulfides

Our goal is to develop a method for synthesizing lanthanide sulfide materials, in the bulk and nanoscale, for use as magnetic materials. We will use a series of molecular precursors as opposed to more traditional solid-state synthetic methods.

Lanthanide sulfides are commonly synthesized from the elements, in solid-state reactions under very high temperatures, on the order of 2000 °C. These harsh conditions are required because of the different rates of diffusion in solid-state syntheses, with high temperatures needed to heat metals above their melting point. The hard nature of the lanthanide series makes synthesis of lanthanides sulfide more difficult because of their oxophilicity.

Lanthanide ions are primarily trivalent, Ln³⁺, with a small radius and high charge which causes them to be very oxophilic. As a result, synthesis with a softer sulfur anion has to take place under air-free conditions, to prevent adventitious oxygen in the atmosphere from promoting oxidation. Synthesis by sulfurization of the oxides with reagents such as hydrogen sulfide and carbon disulfide is effective, but also requires high temperatures, and these reagents are toxic and dangerous, so are not always ideal for industrial applications.

The thermolysis of organometallic precursors, containing the necessary elements, is another route in which these materials can be synthesized. Metal complexes with the desired lanthanide and sulfur atoms present good precursors, an example is lanthanide sulfido clusters...
developed by Brennan\(^5\) which have been used at relatively low temperatures, around 300 \(^\circ\)C, though these have the drawback of very sensitive synthesis, and instability in air. An alternative, which we have utilized in our lab are lanthanide complexes with dithiocarbamate (dtc) ligands as precursors. They are versatile materials, which can be thermally decomposed in a variety of environments; in the solid-state for synthesis of bulk polycrystalline materials, in solution for the synthesis of nanoscale material, and in the gas phase for thin-film synthesis.

The dtc group is the sulfurous analog of the carboxylic acid function group, with the general formula \(S_2\text{CNR}_2\), which \(R\) is an alkyl or aryl group, the diethyl ligand is shown below in Figure 1. They are synthesized by reaction of carbon disulfide, \(\text{CS}_2\) with a secondary amine in the presence of a strong base.\(^3\) Dtc ligands themselves are useful biologically as pesticides,\(^4\) and as an inhibitor in nitric oxide synthase.\(^5\) Because they are good as metal chelators, they are used industrially in sequestering ions for determination of ion concentrations,\(^6\) as well as waste-water treatment.\(^7\)

![Figure 1. Structure of the diethyldithiocarbamate ligand.](image)

The structure of metal dtc complexes varies and is governed by the metal ion size and charge. The dtc ligand is most commonly bound to the metal in a bidentate fashion, but monodentate and bridging binding types are possible as well. For instance, in a series of tin
compounds,\textsuperscript{8} structures with Sn\textsuperscript{2+} have two dtc ligands to balance the charge, and they are bound in a bidentate fashion for steric purposes; to effectively fill the coordination sphere. In some Sn\textsuperscript{4+} complexes, there are four dtc ligands bound; two bidentate and two monodentate. In polynuclear complexes, dtc ligands can be used to bridge multiple ions.

Like in most of coordination chemistry, it is common to have mixed ligand systems. In dtc complexes, often there is a metal ion surrounded by a sufficient number of dtc ligands to balance the ionic charge, and other neutral ligands to fill the coordination sphere, such as pyridine,\textsuperscript{9} bipyridine (bipy),\textsuperscript{10} terpyridine,\textsuperscript{11} and phenanthroline (phen),\textsuperscript{12} tetrahydrofuran.\textsuperscript{13}

Structurally, these metal dtc complexes are good for thermal decomposition because they consist of a metal ion surrounded by a shell of sulfur, surrounded by organic protecting groups, containing all of the necessary elements in one complex. Depending on the full composition of the complex, the environment in which decomposition takes place, and the hardness of the metal ion, different products are possible, including metal sulfide and metal oxysulfide materials. Solid-state decomposition of dtc precursors generally yields bulk, polycrystalline material, however, more controlled synthesis is possible, demonstrating the versatility of these precursors.

When decomposed in the presence of coordinating solvents with amines or phosphines such as oleylamine or trioctylphosphine, nanoparticle of these materials can be made. Examples of these capping ligands are shown below in Figure2. Useful materials such as semiconductor quantum dots of cadmium sulfide\textsuperscript{14,15} and zinc sulfide\textsuperscript{15} have been made in this way. More relevant to my research, our group has made europium sulfide (EuS) nanoparticles with this technique.\textsuperscript{16} The mechanism for nanoparticle growth can be simplified as having the coordinating ligands surrounding the reagents, favoring nucleation over growth, constrained in a nano-
reaction vessel.

Figure 2. Commonly used capping ligands in nanoparticle synthesis; from left to right: oleylamine, trioctylphosphine, triphenylphosphine, and oleic acid.

1.1.2 Magnetism

In order to examine the magnetic properties of these materials, there are a series of measurement techniques which can be used. This section will outline some of the methods in order to assess these magnetic nanostructures.

EuS is a ferromagnetic semiconductor with a band gap of 1.64 eV.\textsuperscript{17} It has a ferromagnetic ordering temperature, $\theta$, of 19 K. This is the temperature in which, below, the material acts as a ferromagnet, and above, thermal kinetic energy overpowers the magnetic ordering, and the material acts as a paramagnet. Shown below in Figure 3 are pictorial representations of paramagnetic, ferromagnetic, and antiferromagnetic ordering.
Figure 3. Pictorial representation of paramagnetism, ferromagnetism, and antiferromagnetism. The arrows indicate the net moment on each magnetic ion in the solid.

In Figure 3, the arrows represent the magnetic moment of a molecule, caused by unpaired electrons. In a paramagnetic material, there is no internal ordering, and these magnetic moments can be aligned in any given direction, resulting in no net magnetic moment. In a ferromagnet, all of the magnetic moments are aligned with one another, giving the whole material a magnetic moment in one direction. Antiferromagnetism is a type of magnetic ordering which is highly ordered, but all of the magnetic moments cancel out.

Ferromagnets and antiferromagnets have magnetic ordering temperatures, denoted as the Curie temperature, $T_C$, and the Néel temperature, $T_N$, respectively. When a material is heated above its magnetic ordering temperature, the thermal vibrational energy will overpower the strength of the magnetic ordering and the material will become paramagnetic. If the material is again cooled below that temperature in the presence of an external magnetic field, it will return to its ferromagnetic or antiferromagnetic state. Alternatively, both types of ordering can be expressed through the Weiss constant, $\theta$. A ferromagnet will have a positive $\theta$ value, and an antiferromagnet a negative $\theta$ value.
Although a ferromagnetic ordering temperature can be measured by $T_c$ or $\theta$, these are not measuring the same exact thing. $T_c$ measures long-range ordering, and is determined through the use of Arrott plots, from low-temperature data. By contrast, $\theta$ is a measure of short-range magnetic ordering, and is determined from the high-temperature data of a Curie-Weiss plot. $T_c$ and $\theta$ values are normally similar, with $\theta$ generally being slightly greater.

Magnetic susceptibility, $\chi$, is defined as the degree of magnetization in a material in response to a magnetic field. Measurements with a Superconducting Quantum Interference Device (SQUID) can give the magnetic moment ($m$) at a given temperature and field, and by factoring in the strength of the applied magnetic field ($H$), $\chi$ can be calculated:

$$\chi = \frac{m}{H} \quad (1)$$

Through manipulation of the Curie-Weiss law (2), we can determine $\theta$, the magnetic ordering temperature, by plotting inverse susceptibility versus temperature:

$$\chi = \frac{C}{T - \theta} \quad (2)$$

Given in terms of $y = mx + b$, where $m =$ slope, $b =$ y-intercept:

$$\frac{1}{\chi} = \frac{1}{C} \cdot T - \frac{\theta}{C} \quad (3)$$

By dividing the negative intercept by the slope, $\theta$ can be measured:

$$\theta = -\frac{-(\theta/C)}{(1/C)} \quad (4a) \quad \theta = \frac{-b}{m_{\text{slope}}} \quad (4b)$$

$C$ is the material-dependent Curie constant, which can be canceled from the equation for the purposes of determining the magnetic ordering temperature. This will be discussed in more detail in Chapter 2. From the plot of $1/\chi$ versus $T$, shown in Figure 4, data was used starting from
the point in which the slope stays consistent, at 50 K in the example below.

Figure 4. $\chi$ vs. $T$ and $1/\chi$ vs. $T$ plots used in the determination of the ferromagnetic ordering temperature, $\theta$.

By contrast, Arrott plots can be used to determine $T_C$.\footnote{By contrast, Arrott plots can be used to determine $T_C$. In this approach, the magnetic moment is measured isothermally at series of temperatures around the $T_C$ with varied fields. For a given isotherm, the results are plotted as a function of the magnetic moment squared against the field over moment, as shown below in Equation 5, and graphed in Figure 5.

$$m^2 = \frac{A}{B} \left( \frac{H}{M} \right) + \frac{1}{B} (\theta - T) \quad (5)$$}
When $\frac{H}{m} = 0$, the equation is simplified to:

$$m^2 = \frac{1}{B}(T_c - T) \quad (6)$$

Finally, when $m^2 = 0$, $T = T_c$. To find this, the y-intercepts of each isotherm are determined and plotted against the temperature of the isotherm, shown below in Figure 6:
Figure 6. Results of an Arrott plot; the $T_C$ is determined by the x-intercept of the trend line, shown here at 17 K.

The $T_C$ is determined by where the trend line of the plotted y-intercepts vs. isotherm temperature intercepts the x-axis. For the plot above, the $T_C$ is shown to be 17 K.

1.1.3 Nanoparticles

Controlled thermolysis of molecular precursors is an effective technique for synthesizing nanoparticles with fine-tunable properties, so we used this approach to synthesis EuS nanoparticles.

There has been a strong interest in the synthesis and properties of nanoscale EuS, an intrinsic magnetic semiconductor.\textsuperscript{19–23} This stems from the search for novel luminescent,\textsuperscript{22,23} magnetic\textsuperscript{16,18,24} and photomagnetic properties observed in this class of materials. Europium sulfide has a strong magneto-optical Kerr effect,\textsuperscript{25} colossal magnetoresistive effects,\textsuperscript{25} and demonstrated spin-filtering effects with potential applications as spin-valves\textsuperscript{26} or in spintronics.\textsuperscript{27,28}

Our research group has previously synthesized EuS nanoparticles of controllable sizes.\textsuperscript{16} It was shown by varying particle size, the band gap of the material changes
systematically; smaller particles narrow the bands within the material, causing the electronic structure to shift from a bulk band structure, to a molecular orbital structure. The effect of narrowing the bands is an increase in the band gap. This change in electronic structure takes place when the size of the material falls beneath the Bohr radius, the size in which quantum effects begin to affect a material based on particle size. For EuS, the Bohr radius is calculated to be 5.8 nm.\(^{18}\)

Through means of varying reaction time, temperature, and the amount of coordinating solvent present, we were able to control particle size of EuS nanoparticles and change the electronic and magnetic properties. Factors which results in smaller particle size include increased capping ligand:precursor ratio, shorter reaction time, and higher reaction time. For a given amount of EuS, if the relative amount of capping ligands increases, smaller individual particles are stabilized because of the high surface area. An increased reaction temperature promotes faster nucleation of material, whereas an increased reaction time gives more opportunity for growth in particles, via Ostwald ripening. As explained, smaller particles will result in an increased band gap, and correspondingly lower magnetic ordering temperatures.

The band gap for a material below the Bohr radius, \(E_{\text{g nano}}\), can be calculated by the Brus equation:\(^{29,30}\)

\[
E_{\text{g nano}} = E_g + \frac{\hbar^2 \pi^2}{2 \mu r^2} - \frac{1.8 e^2}{4 \pi \varepsilon_0 \varepsilon r} \quad (5)
\]

In Equation 5, \(\hbar\) is the reduced Planck's constant, \(\mu\) is the reduced exciton mass, \(e\) is the elementary charge, \(\varepsilon_0\) is the vacuum permittivity, \(r\) is the particle radius, and \(\varepsilon\) is the optical dielectric constant of the material.

The magnetic ordering in a class of materials including EuS, comes from communication
of electrons in the conduction band, which results in a direct coupling of the electronic and magnetic structures. By changing the size of this energy gap, the concentration of electrons in the conduction band changes as a result of the Boltzmann distribution. Since the conduction electrons dictate magnetic communication, a change in the number of conduction electrons should affect the magnetic properties as well.

Our group has demonstrated this relationship by decreasing the size of EuS nanoparticles, which causes a systematic shift in the band gap of the materials, accompanied by a decrease in the magnetic ordering temperature. Nanoparticles with particle sizes of 7.2, 5.7, and 4.9 nm had $T_c$ values of 14.3, 13.8, and 13.2 K respectively, shown below with Arrott plots in Figure 7.\(^\text{16}\)

![Arrott plots demonstrating the relationship between the magnetic ordering temperature, $T_c$, and particle size. Used without permission from Regulacio.\(^\text{16}\)](image)

Furthermore, this has been confirmed in theoretical studies, in terms of the magnetic exchange interaction.\(^\text{31}\) By increasing the band gap ($E_g$), the exchange interaction parameter ($J$)
decreases, which results in less magnetic exchange and communication, so a weaker magnetic ordering:

\[ J = \frac{lb^2}{E_g^2} \]  

(2)

Technological applications demand ordering temperatures which do not require expensive coolants, so there is a press to control \( T_C \). The ordering temperature of 16.9 K for EuS is difficult to achieve, only possible with liquid helium; much too expensive for widespread commercial use. Because of this, it would be beneficial to understand the mechanisms by which we can manipulate and fine-tune this ordering temperature.

1.1.4 Electron doping

A general understanding of the different mechanisms by which we can alter the magnetic properties is helpful, but it is generally more important to be able to increase rather than decrease, the magnetic ordering temperature, for use in applications. Because of the role of conduction electrons demonstrated in the \( E_g \) studies, the question is how to increase the number of conduction electrons. Another approach to increasing the concentration of conduction electrons is through electron doping. By placing more electrons into the conduction band, stronger magnetic coupling should be present.

Electron doping in the europium chalcogenides has been demonstrated through chemical substitution of a non-redox active, trivalent lanthanide such as gadolinium. In order to maintain charge balance, the substitution of trivalent gadolinium is accompanied by donation of an electron into the conduction band:

\[ \text{Eu}^{2+}_{1-x}[\text{Gd}^{3+}(e^-)]_x \text{X} \ (X = \text{O, S, Se, Te}) \]

Most of the lanthanides have shown evidence of electron doping, however, gadolinium is
the most commonly used, because of its electron configuration. Trivalent gadolinium, Gd$^{3+}$ is especially stable, because it is left with a half-filled f-orbital, [Xe]$4f^7$, having lost its two 6s and one 5d electrons, which is energetically favorable, negating any realistic possibility of it existing in the Gd$^{2+}$ state. This half-filled stability is also the reason for europium's affinity for the Eu$^{2+}$ state. Lanthanum has also be effectively used as a dopant, by contrast the La$^{3+}$ is stable with a [Xe] electron configuration, with an empty $4f$ electron shell. Gadolinium was chosen as a dopant, because it has the same $4f^7$ valence configuration as Eu$^{2+}$, which should be less disruptive to the magnetic lattice.

Europium oxide has a base $T_C$ of 69 K, but it has been shown by Ott$^{32}$ that by electron doping with gadolinium, $T_C$ can be increased to ~170 K, as shown below in Figure 8. The highest $T_C$ was achieved at an optimum doping level of $x = 0.04$. The ordering temperature increases up until this peak in the graph, and then the ordering temperature decreases again.
This behavior has been explained by theoretical calculations. A greater amount of Ln\(^{3+}\) doping introduces free carriers, which induce the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which suppresses the magnetic ordering.\(^{33}\) Furthermore, higher levels of gadolinium incorporation will increase the likelihood of phase separation, which wouldn't result in the electron doping. Increasing the number of conduction electrons, which enhances magnetic coupling and increases \(T_c\) must be balanced with limiting the negative effect of the RKKY interactions and phase separation.

### 1.2 Results and discussion.

#### 1.2.1 Dithiocarbamate thermolysis

I have synthesized a series of dtc complexes as thermolysis precursors for the whole lanthanide series, except the radioactive promethium, with the general formula,
Ln(S₂CNR₂)₃phen. We investigated the whole lanthanide series to better understand their reactivity, and the products formed by their decomposition. The entire series of complexes isostructural due to the relatively similar size, charge, and reactivity and properties of the lanthanides.

In these complexes, the lanthanide ion is always in the Ln³⁺ state, and the ion size is relatively similar, only varying slightly from 2.07 to 1.87 Å due to the lanthanide contraction. The Lewis structure of these materials is shown below in Figure 9, represented by a europium complex with R = ethyl. Our group has shown in the past that the R group used on the dtc ligand has little effect on its thermal properties, so all complexes were synthesized with the diethyldithiocarbamate ligand, as it is commercially available.

![Lewis structure](image)

*Figure 9. Structure of Eu(dtc)₃phen, where R = ethyl in the dtc ligand.*

The tris-phen complex was the most consistently stable across the series, so it was the logical choice to study across the lanthanide series without out further complication through
other variables. Although the anionic tetrakis complex ([Ln(S₂CNEt₂)₄][Et₂HN]⁺) was stable for europium, the synthesis was unsuccessful for other lanthanides. Such complexes are known, however they have been reported to be less stable, so the series of compounds was not further pursued. Synthesis of the tris complexes was not attempted, because it is known that they are unstable and easily prone to hydrolysis. The choice of phen over other neutral ligands such as 2,2'-bipyridine (bipy), which has also been used with lanthanide tris dtc complexes, is insignificant, as the bipy and the phen have extremely similar properties. The tris-phen complexes have been studied by our group for their luminescent properties in the past. The mixed-ligand nature of these complexes leads to chirality, which has been taken advantage of in asymmetric catalysis in the europium system.

The thermal decompositions of the dtc complexes generally yielded the sulfide, oxysulfide, or oxide, depending on the decomposition temperature, conditions, and the relative oxophilicity of the lanthanide. TGA studies of selected lanthanides from the series is shown below in Figure 10. The decomposition temperature for complexes was generally ~250 °C, and decreases as you go across the series. The decomposition temperature is orders of magnitude less than required for solid-state syntheses from the elements, which is one major advantage of the precursor thermolysis route. Although TGA studies take place under flowing nitrogen, simulating an air-free environment, the lanthanides are extremely oxophilic, so any trace amount of oxygen leads to oxidation. As a result, thermolysis product for all of the complexes was Ln₂O₂SO₄, the oxysulfate. The oxophilic nature of the lanthanides is due to the hard nature of the Ln³⁺ cations favoring reaction with the harder O²⁻ anions versus the softer S²⁻ anions. This ensures that the oxidation products will always preferentially form unless extreme measures are taken to ensure
an oxygen-free environment.

Figure 10: TGA thermograms of lanthanide dtc complexes. Reproduced without permission from Regulacío.65

As seen in Figure 11, the thermolysis of the Pr(dtc)₃phen complex begins around 248 °C, determined by the change in heat flow, where the weight decreases to about 34%, which corresponds to the formation of praseodymium oxysulfate, Pr₂O₂SO₄, as identified by the PXRD pattern. Pr₂O₂SO₄ is calculated to give 26.6%, so it is likely that there is some residual carbon; this is discussed in more detail later. Temperatures around 700 °C are sometimes used in order to obtain a more crystalline product; this can also be achieved by annealing the material post-synthesis.
Figure 11. TGA-DTA thermogram showing the decomposition of Pr(dtc)·phen.

The series of complexes was decomposed under closed conditions, sealed under nitrogen, and under dynamic vacuum. The resulting products are shown below in Table 1.

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<th>Pr</th>
<th>Nd</th>
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Table 1: Materials synthesized by decomposition of the lanthanide dtc complexes under vacuum (V) and closed (C) conditions. \( S = Ln_2S_3 \), \( S^* = LnS \), \( OS = Ln_2O_2S \), \( OSu = Ln_2O_3SO_4 \), \( O = Ln_2O_3 \), \( O^* = LnO_2 \).

There are two main trends observed in Table 1; increased oxidation across the series, and more so under vacuum versus closed conditions. Going across the lanthanide series, the ionic radii decreases from 2.07 to 1.87 Å.\(^{35}\) In all of the dtc complexes, the lanthanide ion is trivalent, so the consequence is that lutetium is a harder cation than lanthanum. By the same concept, oxygen is a much harder anion than sulfur, making the lanthanides more oxophilic across the series. With a few notable exceptions to be discussed later in chapter, this is observed in our results, with more oxygen in the resulting products; the products contain more oxygen as you go from the sulfide to the oxysulfide to the oxide.
In the closed-tube reactions which yield the sulfide products, different polytypes of Ln$_2$S$_3$ are observed. These different phases are outlined below in Figure 12. Romero has shown the stability of different phases through a range of temperatures,\(^{40}\) and in all cases where Ln$_2$S$_3$ is the observed products, the most stable, highest temperature phase is observed through decomposition of the dtc complexes. The exceptions to this are Eu, Tb, Tm, Yb, and Lu; in the case of Eu, EuS is always the most stable phase, and with the latter three, the elements are so oxophilic that trace oxygen always resulted in formation of the oxysulfide.

![Figure 12. Stability of different polytypes of Ln$_2$S$_3$, and the results of our closed-tube experiments shown above. Adapted from Romero.\(^{40}\)](image)

In almost all cases, the materials synthesized under vacuum conditions resulted in more oxygen containing compounds than those synthesized under closed conditions. There are two contributing factors for this; back-flow of oxygen and removal of sulfurous byproducts. It is impossible to achieve a perfect vacuum; the millitorr pump used during synthesis can only pull a vacuum to $\sim 10^{-3}$ torr, so there will be some trace back-flow of oxygen. Secondly, when the dtc ligands are decomposed, organic sulfurous byproducts are formed, which are both reducing and
sulfurizing, and when the lanthanides are heated in their presence, formation of sulfides are encouraged; we believe the latter is more important.

In addition to the phase identity of the products, a trend was seen in terms of their crystallinity. In most cases, when comparing the powder x-ray diffraction patterns of materials formed by decomposition under vacuum versus closed condition, the materials synthesized under vacuum appear much more crystalline, with sharper, more intense peaks observed, shown below in Figure 13.

![Figure 13. PXRD patterns of the products formed through decomposition of La(dtc)phen and Ce(dtc)phen, under both closed and vacuum conditions, demonstrating the difference in resulting crystallinities.](image)

In addition to being less crystalline, the products formed under closed conditions tended to contain significant amounts of carbon. This was not observed during nanoparticle synthesis, and presumably would not be seen in thin-film synthesis, however this shows that the dtc precursors are not ideal for more basic solid-state thermolysis. Rather, these decompositions
serve to show us trends in reactivity, and give us lessons to be translated into other synthetic methods we have explored.

The three most notable exceptions to these trends are seen in lanthanum, cerium, and europium. When the lanthanum complex was decomposed under vacuum, based on the trends in products observed, it would be expected that the sulfide and possibly the oxysulfide would form, but instead, lanthanum oxysulfate formed, the only observed instance of the oxysulfate in this series of decompositions. It has been reported that the stability of the $\text{Ln}_2\text{O}_2\text{SO}_4$ phase decreases across the series, due to the increasing stability of the $\text{Ln}_2\text{O}_3$ phase, so it is not surprising that the only observed instance of the oxysulfate phase was in the case of lanthanum.

When the cerium complex was decomposed under vacuum, the same products would be expected as for lanthanum, the sulfide and possibly the oxysulfide. Instead, an oxide was formed, but not in the form of $\text{Ln}_2\text{O}_3$, as was observed in all of the other oxides, but rather $\text{CeO}_2$. For the case of cerium, this can be easily explained the electron configuration. Most of the lanthanides are most stable as $\text{Ln}^{3+}$, however, when reacted under conditions which could possibly lead to oxidation, $\text{Ce}^{4+}$ is very stable because this results in the noble gas configuration, \([\text{Xe}]\). Once oxidized to $\text{Ce}^{4+}$, only the oxide would be expected because the hardness of the ion.

Similarly, for europium, only the sulfide was synthesized, but instead of the form of $\text{Ln}_2\text{S}_3$, EuS was observed. Divalent europium results in a half-filled $f$ orbital, which gives extra stability based on the electron configuration. The divalent europium is softer and less prone to reacting with oxygen. Like $\text{Ce}_2\text{O}_3$, $\text{Eu}_2\text{S}_3$ is unstable based on the lanthanide oxidation state stability. Because EuS was synthesized under both closed and vacuum conditions, it was concluded that the europium dtc complex is a very good precursor to europium sulfide. Our lab
has successfully used these precursors for the synthesis of europium sulfide nanoparticles.\textsuperscript{16}

\subsection*{1.2.2 Gadolinium-doped europium sulfide}

So far we have studied the synthesis of binary metal sulfide compounds. We are also interested in developing tertiary compounds; synthetic routes to gadolinium-doped EuS, Eu\textsubscript{1-x}Gd\textsubscript{x}S, to enhance the magnetic ordering temperature as compared to undoped EuS. The previous section has shown us that by decomposing Eu(dtc)\textsubscript{3}phen, EuS results, and the decomposition of Gd(dtc)\textsubscript{3}phen gives Gd\textsubscript{2}S\textsubscript{3}. However, by decomposing the two precursors together in the solid-state, at least with relatively small amounts of Gd(dtc)\textsubscript{3}phen, Eu\textsubscript{1-x}Gd\textsubscript{x}S results. This will also be applied to the synthesis of tertiary metal-sulfide nanoparticles.

Synthesis of Eu\textsubscript{1-x}Gd\textsubscript{x}S was performed by first dissolving the precursors together in solution, then removing the solvent, then further ground to ensure homogeneity. The precursors were then thermally decomposed, either in the solid-state or in solution. Doping can be done systematically, resulting in a series of Eu\textsubscript{1-x}Gd\textsubscript{x}S material, with controlled doping levels.

The products were characterized by powder x-ray diffraction to ensure this; an example diffraction pattern is shown below in Figure 14. Vegard's law states that the lattice parameters should shift with increasing dopant concentration, based on their different ionic radii.\textsuperscript{42} However, this lattice shift was not observed in our work, due to the low doping levels, and the relatively close lattice constants of EuS and GdS.
The results of doping studies are shown below in Figure 15 and Table 2. A similar trend is seen as in the Eu$_{1-x}$Gd$_x$O system. A modest increase in $\theta$ from 19 to 30 K is measured at $x=0.0027$. This corresponds to a very small amount of gadolinium, less than 1%. Additionally, the spike in ordering temperature appears with an extremely narrow range, the next data point at $x=0.0031$ only shows a $\theta$ of 21.23 K. This data does not include samples which resulted in $\theta$ values below 19 K, the base, undoped $\theta$.

Data published by Jin shortly after is shown below in Figure 16. To compare, the maximum $T_C$ measured was very close to 30 K as we measured, however, data presented by Jin show the increase in ordering to be maintained over a much larger range, through $x=0.05$, and dropping to intermediate levels beyond that, before saturating back to $\sim$19 K. Another difference is that our data shown here shows measurements of $\theta$, whereas Jin's data is measured with $T_C$; this difference in measurement technique is discussed shortly. Although our data does show proof of concept of electron doping, it is clear that there are additional variables influencing $\theta$. 
Figure 15. Doping level, $x$, vs. $\theta$ in $\text{Eu}_{1-x}\text{Gd}_x\text{S}$ material synthesized by decomposition of $\text{Eu(dtc)}_3\text{phen}$ and $\text{Gd(dtc)}_3\text{phen}$.

<table>
<thead>
<tr>
<th>x</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
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</tr>
<tr>
<td>0.0027</td>
<td>30.08</td>
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<tr>
<td>0.0031</td>
<td>21.23</td>
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<td>0.0264</td>
<td>18.06</td>
</tr>
<tr>
<td>0.0676</td>
<td>17.97</td>
</tr>
</tbody>
</table>

Table 2. Magnetic results, $\theta$, of doping level, $x$, in $\text{Eu}_{1-x}\text{Gd}_x\text{S}$ polycrystalline samples.
1.2.3 EuS oxidation

Our initial hypothesis was that oxidation was the key variable in the decrease in magnetic ordering temperature. Oxidation decreases the magnetic communication in EuS, which results in a lower magnetic ordering temperature. When Eu(dtc)₃phen is decomposed, EuS results, however if there is any oxygen present, europium oxysulfide (Eu₂O₂S) will show up as an impurity. Shown below in Figure 17 is a PXRD pattern of a sample which showed significant amounts of Eu₂O₂S; the resulting θ value was only 9.4 K.

<table>
<thead>
<tr>
<th>Magnetism type</th>
<th>Relative strength (emu/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>Para/antiferromagnetism</td>
<td>10⁻⁵ - 10⁻³</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>10³</td>
</tr>
</tbody>
</table>

*Table 3. Relative strengths of the different types of magnetism. Compiled from Spaldin.*

As explained earlier, ferromagnetic ordering temperatures can be measured either from the θ or T_c. Although θ is a more versatile comparison, being able to measure the extent of
ferromagnetic and antiferromagnetic coupling in a direct comparison, it is much more susceptible to interference from an impurity. As shown above in Table 3, magnetic contributions to \( \chi \) resulting from ferromagnetic and paramagnetic contributions are of different orders of magnitude, so non-ferromagnetic impurities should not have a major effect on measurements of \( \chi \). Because \( \theta \) is measured from the high-temperature portion of a Curie-Weiss plot, the material is above the ordering temperature and is acting as a paramagnet. Any other paramagnetic or diamagnetic material present, such as oxidized impurities like Eu\(_2\)O\(_3\)S would be able to contribute to the measured magnetic moment, and decreased the measured \( \theta \) value. Because of this, \( T_c \) may serve as a more accurate measurement technique to see the effect of Gd-doping, with results less obscured by the presence of additional magnetic materials.

![Figure 17. PXRD pattern of an Eu\(_{1-x}\)Gd\(_x\)S sample which showed a significant amount of oxidation; blue stars indicate EuS, and red circles Eu\(_2\)O\(_3\)S. \( \theta = 9.4 \) K.](image)

In light of the negative magnetic effects of oxidized material in EuS, the oxidation of EuS was studied in more detail. Shown below in Figure 18 are PXRD patterns as EuS is heated from
room temperature to 1200 °C under dynamic vacuum, first oxidizing to Eu₂O₂S, then Eu₂O₂SO₄, and finally Eu₂O₃.

![Image of PXRD patterns](image)

**Figure 18. PXRD patterns of EuS heated to 1200 °C under dynamic vacuum.**

Figure 18 shows that EuS is stable until about 500 °C. Under ambient conditions, only EuS is observed by PXRD even after samples being exposed to air for years. In further exploring the stability, it was found that by heating EuS in air at lower temperatures, 300 °C, another phase was observed, shown forming in Figure 19. This phase has not been reported, except for by Naboka in 1989,⁴⁴ reported to be EuS₁₋ₓOₓHₓ; crystal structure information was not given, but PXRD patterns can be qualitatively matched based on Figure 20.
In order to eliminate effects from oxidation, it was our hope to anneal the decomposition products in the presence of hydrogen sulfide (H₂S). At high temperatures, H₂S reacts both with Eu₂O₃ and Eu₂O₂S to give EuS. This should hopefully sulfurize impurities and result in higher θ values by eliminating the effect of oxidized material. Most materials appeared to be pure EuS by PXRD, but some materials have shown small amounts of Eu₂O₂S in their diffraction patterns.

The case shown in Figure 17 is an extreme case, however it's important to note that x-ray
diffraction only reveals the presence of crystalline material, so the presence of any amorphous material will not appear. In this case, magnetic measurements are more sensitive.

Because of potential oxidation unobserved by PXRD, all samples were annealed in H₂S. The x-ray and magnetic measurements were performed again with the hope that θ values at or slightly below 19 K might be underestimated, and annealing should improve the θ vs. x curve. Shown below in Figure 21 is a representative result of this; a material with a slightly underperforming θ (18.1 K) but no Eu₂O₂S present appeared unchanged by PXRD. However, the more sensitive SQUID magnetic measurement showed little improvement in θ (annealed θ = 18.1 K). Some materials which showed Eu₂O₂S by PXRD, such as that in Figure 17, gave very modest increases in θ, but H₂S annealing did not appear to improve the θ vs. x graph.
Figure 21. PXRD patterns of a material before and after annealing in H$_2$S; the initial sample showed no Eu$_2$O$_2$S, but only resulted in a $\theta$ of 18.1 K, which was unchanged upon annealing.

Under closed-tube conditions, used in order to prevent oxidation during synthesis, significant carbon can remain in these materials, which is unsurprising given the amount of carbon in the starting precursor; 24 carbon atoms per europium atom. The carbon content can be measured by C/H/N elemental analysis, with samples ranging from 13 to 19% carbon content. Unfortunately, this extra variable did not yield fruitful results; no clear trend could be observed connecting low $\theta$ values with carbon content. Nonetheless, although dtc precursors may not be the most effective way to synthesize bulk Eu$_{1-x}$Gd$_x$S samples, dtc complexes are still a strong precursor of EuS-based nanoparticles.

1.2.4 Eu$_{1-x}$Gd$_x$S nanoparticles
Although we have shown that EuS nanoparticles can be synthesized by decomposition of Eu(dtc)$_3$phen in coordinating solvent, with little effect of the R group on the dtc group, complications arise when attempting to synthesize Gd-doped EuS nanoparticles. When a mixture of Eu and Gd dtc precursors used, nanoparticles were successfully synthesized as shown below in Figure 22:

![TEM image of attempted synthesis of Eu$_{1-x}$Gd$_x$S nanoparticles, synthesized in oleylamine and triphenylphosphine.]

Unfortunately, when these particles were analyzed by ICP-MS to determine the Gd-doping level, Gd was not found at levels above the background. Nanoparticles were synthesized by putting Eu and Gd dtc complexes in solvent, and heating the system to 265 °C, and holding the temperature for 1 hour. We suspected that because of very slight differences in the decomposition temperatures of the dtc complexes, the Eu complex decomposed first, forming undoped EuS nanoparticles.

In order to resolve this, the precursors were to be injected once the coordinating solvent
was increased to 265 °C, so the solvent would be above the decomposition temperature for both precursors. As an extra step of precaution, we decided to use alternative precursors which would be more soluble in oleylamine, the solvent being used for injection. For the Eu-complex, the tetrakis complex, \([\text{Eu}(\text{dtc})_4][\text{NH}_2\text{Et}_2]^+\) was used, being more soluble in oleylamine than the tris-phen complex. Unfortunately, the tetrakis Gd-complex was significantly less stable, so the tris-phen complex was still used, but in order to maximize solubility in the long-chain oleylamine, the R group on the dtc ligands were changed from ethyl groups to diisobutyl groups.

The diethyldithiocarbamate was most commonly used because it is commercially available from Sigma-Aldrich, however the synthesis of different types of dtc ligands is relatively easy. The synthesis takes place by reacting a secondary amine with carbon disulfide in the presence of a base. The synthesis of the diisobutylidithiocarbamate is shown below in Figure 23:

![Figure 23. Scheme for synthesis of diisobutylidithiocarbamate.](image)

Although the synthesis of the gadolinium tris-diisobutylidithiocarbamate phen (Gd(\(\text{Bu}_2\text{dtc})_3\text{phen}\)) complex followed the same basic synthesis as the other dtc complexes (scheme shown below in Figure 24), and its crystal structure was isostructural with other reported complexes, such as the Pr(\(\text{Bu}_2\text{dtc})_3\text{phen}\) complex,\(^{38}\) its structure was not reported in the Cambridge Structural Database.
The complex was recrystallized in acetonitrile, and single crystals crashed out of solution. With the assistance of Michele Pablico, the crystal was mounted on the single-crystal x-ray diffractometer, and the data was collected. The structure was solved and refined using the X-Seed interface,\textsuperscript{45} utilizing SHELXS and SHELXL,\textsuperscript{46} visualized below in Figure 25, with an image generated by POV-ray.\textsuperscript{47} The crystal structure was co-crystallized with one acetonitrile molecule. Like the analogous complexes, the crystal was monoclinic, with the $P\ 21/c$ space group; more detailed structural information is below in Table 4; the crystal structure is awaiting publication.

\textbf{Figure 24. Scheme for synthesis of Gd(Bu$_2$dtc)$_3$phen.}
Figure 25. POV-ray representation of the crystal structure of Gd(Bu₃dtc):phen.
Injection of Eu(dtc)$_4$ and Gd($^t$Bu$_2$dtc)$_3$phen resolved the problem of gadolinium incorporation; ICP-MS was performed on three samples with different doping levels, and gadolinium was found in all of them. It was expected that the ordering temperature would increase as a function of doping-level, unfortunately, significantly decreased ordering temperatures were observed for all samples, as shown below in Table 5. As gadolinium is more oxophilic than europium, it is possible that the resulting nanoparticles are more prone to
oxidation as well; we expect this would be seen more in nanoparticles than the bulk polycrystalline samples because of the significant surface area on the nanoscale. As discussed previously, $T_C$ may serve as a better measurement because of oxidized impurities.

<table>
<thead>
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<th>$x$</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>0.006(2)</td>
<td>7.8</td>
</tr>
<tr>
<td>0.017(8)</td>
<td>5.9</td>
</tr>
</tbody>
</table>

*Table 5. Ferromagnetic ordering temperatures, $\theta$, of different Gd-doping levels in $\text{Eu}_{1-x}\text{Gd}_x\text{S}$ nanoparticles.*

Some deeper scrutinization of Jin's work is warranted; although some improved magnetic results are certainly presented, some of the experimental methodology is questionable. Whereas we chose to use the tetrakis-europium complex and the tris-diisobutyl-gadolinium complex, Jin selected a pyrrolidine dtc ligand to make tris-complexes which he reports in his paper. He argues this ligand gives the most consistently monodisperse nanoparticles, synthesized with oleylamine and trioctylphosphine. The reaction temperature of 290 °C is higher than that of the 265 °C we chose, which could possibly negate the need for increased solubility. Less orthodox are examples in his work where multiple injections of Gd(dtc)$_3$phen are used, in order to obtain a higher doping level. It is unclear why this would be an effective method for Gd-doping; I suspect this would result in less homogenous Gd-doping, which would not result in effective electron doping.

1.2.5 Morphology control in EuS nanoparticles

As discussed, Regulacio in our lab has previously demonstrated the ability to synthesize EuS nanoparticles with tunable size, and the resulting effects on magnetic ordering. Particle size was controlled through variation of synthetic time and temperature, and capping ligand ratio. These are effective for controlling size, however the identity of the capping ligand has been
shown in many systems to govern the nanoparticle morphology in terms of shape. For instance, very impressive work has been done by Kim with lead sulfide, where changes in the relative amounts of octylamine, relative to oleic acid, 1-octadecene, and trioctylphosphine, could vary the morphology between single-crystalline octagonal nanoparticles and high aspect ratio nanowires, shown below in Figure 26.

![Figure 26. TEM images of lead sulfide nanoparticles forming nanowires through oriented attachment. Reproduced without permission from Kim.]

With this motivation in mind, the effect of capping ligand on EuS nanoparticle shape was studied by keeping synthetic conditions consistent with the exception of capping ligand identity. Results from this are seen in Table 6, and TEM images in Figure 27. Efforts to adapt the synthesis of PbS nanowires to EuS were unsuccessful on the whole, however some very modest shape control was exercised. As seen by TEM in Figure 27, synthesis with hexadecylamine and oleylamine yielded very clean distinctly cube-like particles, in contrast with trioctylamine as a capping ligand, which gives significant agglomeration, without any distinctly clean morphology.
Figure 27. TEM images of EuS nanoparticles synthesized in a variety of solvents, a) oleylamine/hexadecylamine, b) oleylamine/1-octadecene, c) trioctylamine, d) oleylamine/triptylphosphine, and e) oleylamine/triphenylphosphine.

Oleylamine was used in most syntheses, seen in Table 6, because it has been shown to reduce the decomposition temperature of the dtc complexes. This is demonstrated in rows 3 and 4, where oleylamine and trioctylphosphine resulted in EuS nanoparticles, and just trioctylphosphine does not give EuS. Fortunately, synthesis of EuS is visually apparent during synthesis; in reactions which successfully yield EuS, upon injection of the orange dtc complex into the clear capping ligand, the solution turns dark brown very briefly, and quickly evolves to purple. If EuS is not formed, the solution will remain mostly clear with a yellow tint. If the yellow product is isolated through the standard centrifugation and washing techniques, the product is generally too amorphous to identify by PXRD, but can sometimes be indexed to Eu$_2$O$_3$. 
<table>
<thead>
<tr>
<th>Solvent(s)</th>
<th>[Ligand] (mmol)</th>
<th>Time</th>
<th>PXRD</th>
<th>Shape</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OA/TPP</td>
<td>15/15</td>
<td>1 hr</td>
<td>EuS</td>
<td>Blobs</td>
</tr>
<tr>
<td>2</td>
<td>OA</td>
<td>30</td>
<td>1 hr</td>
<td>EuS</td>
<td>Cubes</td>
</tr>
<tr>
<td>3</td>
<td>OA/TOP</td>
<td>15/15</td>
<td>1 hr</td>
<td>EuS</td>
<td>Blobs</td>
</tr>
<tr>
<td>4</td>
<td>TOP</td>
<td>30</td>
<td>1 hr</td>
<td>EuS</td>
<td>Cubes</td>
</tr>
<tr>
<td>5</td>
<td>OA/HDA</td>
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<td>1 hr</td>
<td>EuS</td>
<td>Messy cubes</td>
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<tr>
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<td>15/15</td>
<td>1 hr</td>
<td>EuS</td>
<td>Cubes</td>
</tr>
<tr>
<td>7</td>
<td>OA/HDA</td>
<td>15/15</td>
<td>15 min</td>
<td>EuS</td>
<td>Cubes</td>
</tr>
<tr>
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<td>OA/HDA</td>
<td>15/15</td>
<td>5 min</td>
<td>EuS</td>
<td>Cubes</td>
</tr>
<tr>
<td>9</td>
<td>8A/ODE/OLA</td>
<td>15/15/15</td>
<td>0 min</td>
<td>EuS</td>
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<tr>
<td>10</td>
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<td>15/15/15</td>
<td>0 min</td>
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<td>25 min</td>
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<tr>
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<td>T8A</td>
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<td>30 min</td>
<td>EuS</td>
<td>Agglomeration</td>
</tr>
<tr>
<td>14</td>
<td>ODE/T8A/TPP</td>
<td>7.5/7.5/15</td>
<td>20 min</td>
<td>EuS</td>
<td>Agglomeration/cubes</td>
</tr>
</tbody>
</table>

Table 6. Summary of ligand variation in EuS nanoparticle synthesis. Black cells indicate syntheses which didn't form EuS. Light gray rows indicate syntheses which used Eu1-xGdx(dtc)3phen, x=0.01/0.05. (OA: oleylamine, TPP: triphenylphosphine, TOP: trioctylphosphine, HDA: hexadecylamine, 8A: octylamine, ODE: 1-octadecene, OLA: oleic acid, T8A: trioctylamine.) * = just cubes measured, small sample set (33 particles.)

This same result, the failed synthesis of EuS, is obtained when using oleic acid; whether oleic acid is the only capping ligand, or mixed with others which are known to give EuS, such as oleylamine, EuS cannot be obtained, seen in rows 9-11. Although oleic acid is a commonly used capping ligand in nanoparticle synthesis,48,50 EuS is more oxophilic than most II-VI semiconductor nanoparticle syntheses such as CdS and ZnSe, and it's possible that the oxygen in oleic acid is too harsh for EuS. It's more likely that EuS could be made with these oleic acid given different conditions, likely higher temperatures, because Scholes reports the synthesis in octadecene/oleylamine/oleic acid at 300 °C,19 but we have not yet explored this avenue. It is surprising that oleylamine reduces the necessary temperature to allow synthesis at 265 °C with
trioctylphosphine, but not with oleic acid.

In terms of particle size, a few trends can be observed. Compared to when solely amine capping ligands are used, when phosphines and amines are used together, smaller particles are observed. This trend can be observed when comparing rows 2, 6, and 12, with rows 1 and 3. In comparing the particle sizes obtained with different amines, in order of increasing particle size were: oleylamine, oleylamine/hexadecylamine, and oleylamine/octadecene, seen in rows 2, 6, and 12. Trioctylamine was not an effective solvent for nanocrystal synthesis, as shown in rows 13 and 14, and Figure 27c.

Because one of the initial aims in these EuS nanoparticle syntheses was to see the effect of electron doping through gadolinium incorporation, the early syntheses (rows 1-5) in Table 6 utilized a mixture of precursors, $\text{Eu}_x\text{Gd}_{1-x} (\text{dtc})_3 \text{phen}$ (either $x=0.01$ or $x=0.05$). We expected that gadolinium-doping should not have an effect on morphology, however if rows 5 and 6 are compared where the only controlled difference between syntheses is the use of gadolinium in row 5, which resulted in messier morphology, seen below in Figure 28.

![Figure 28. TEM images of EuS nanoparticles synthesized with oleylamine and hexadecylamine. Image on the left made with $\text{Eu}_x\text{Gd}_{1-x} (\text{dtc})_3 \text{phen}$, versus $\text{Eu}(\text{dtc})_3 \text{phen}$ on the right.](image-url)
Magnetic results from syntheses of gadolinium-doped materials were not any more successful than those in Table 5; two samples were measured which had θ values of -2 and -20 K, and T_c value of 15 and 17 K, respectively, which is strong evidence for difference in measurements of θ and T_c.

A further demonstration of the high variability in nanoparticle synthesis can be shown by comparing TEM images in Figure 22 and 27e. Both syntheses were using oleylamine and triphenylphosphine; aside from the slightly different amount of gadolinium incorporation target (x=0.01 vs. 0.025) the only controlled differences were that the particles in Figure 22 were made using the diethyldithiocarbamate complex in a one-pot reaction, whereas the particles in Figure 27e used the diisobutyldithiocarbamate complex, and used hot injection. Although we would expect better solubility with the diisobutyl ligand, and a cleaner reaction with a rapid decomposition of the precursor, this was not seen in the TEM images.

Reproducibility in nanoparticle synthesis is an issue caused by minor, difficult to control changes in synthetic conditions, such as precise heating and cooling rates, and variations in compositions of capping ligands. This lack of reproducibility can be seen by comparing nanoparticles I have synthesized in oleylamine and trioctylphosphine with those done previously in our lab. When these conditions can be controlled, for example, through the use of high-throughput robotic control, as has been implemented with workstation for automated nanocrystal discovery and analysis (WANDA), variation in obtained products vary significantly less.

In addition to varied synthetic conditions, the solvents themselves add a lot variation in obtained products. Commonly used ligand like oleylamine and trioctylphosphine are generally obtained as 'technical grade', which ranges from 70-90%. Reproducibility between batches can
significantly change obtained products. This has been studied in great detail by Buhro for the case of trioctylphosphine oxide (TOPO); the growth of CdSe nanowires is actually attributed to dioctylphosphine oxide, an impurity generally found in technical grade TOP/TOPO.

In addition to synthesizing nanoparticles of a homogenous material, as we have done here with EuS, it is possible to create nanoparticle of different types of material. If two materials, with compatible crystal structures are decomposed together, they can alloy together, as we have done with Eu$_{1-x}$Gd$_x$S, and has been done in many other systems such as Zn$_{1-x}$Cd$_x$Se and CdSe$_{1-x}$Te$_x$.

When this is done by first creating a nanoparticle of one material, followed by subsequent injection of another precursor, a core-shell nanoparticle is formed, where the initial nanoparticle will be the core, and the second injection will create a shell of the second material on the already nucleated nanoparticle. This approach was taken to try and synthesize EuS@ZnS (core-shell nanoparticles are generally denoted by core@shell) nanoparticles by formation of EuS nanoparticle followed by injection of Zn(dtc)$_2$ precursor. PXRD gave ambiguous results, however, HRTEM and EDX suggest that synthesis of EuS@ZnS nanoparticles was successful, as shown by the image in Figure 29.
Significant variation in nanoparticle shape control of EuS with control of structures such as nanowires were unsuccessful through solvent variation using dtc precursors. Although there are some general trends which can be seen in solution nanoparticle synthesis, many aspects are very system dependent. For instance, lead sulfide was able to form nanowires through oriented attachment, just as lead selenide. Murray has explained in great detail that lead selenide undergoes oriented attachment as a result of the arrangement of lead and selenium ions in the lead selenide crystal structure. Statistically, a large amount of lead selenide nanocrystals (89%) will possess a dipole moment, which is the driving force behind the anisotropic growth of oriented attachment.

An alternate method for modifying the synthesis of EuS nanoparticles could be through the use of a europium dtc complex containing divalent europium. All of the lanthanide dtc complexes we have synthesized contain a trivalent lanthanide ion, even though the oxidation state of europium in EuS is divalent. The dtc ligands themselves are redox active, with different
oxidized organic byproducts which can come off during synthesis, which has been explored in more detail by Regulacio.\textsuperscript{20} If one of the hurdles in successful EuS synthesis is the reduction from Eu\textsuperscript{3+} to Eu\textsuperscript{2+}, starting with Eu\textsuperscript{2+} could be beneficial. Dickerson has explored use of divalent europium in some syntheses; by decomposing Eu\textsuperscript{2+}(dtc)\textsubscript{3}phen at 700 °C under N\textsubscript{2}, he observes material which he assigns to be sub-2 nm nanocrystals.

1.2.6 Thulium sulfide

Europium is one of the redox active lanthanides which is not restricted to the Ln\textsuperscript{3+} oxidation state; in addition, samarium, ytterbium, and thulium can be in the divalent state. This can be observed below in Figure 30, showing the lattice constants for lanthanide monochalcogenides. For each of these lanthanides which can be divalent, they have a larger lattice constant because of the larger ionic radius. As seen below, thulium has an interesting trend, apparently shifting valencies going down the chalcogenide series from the sulfide to the telluride.

![Figure 30. Cell parameters for the cubic lanthanide monochalcogenides. Trivalent lanthanides shown in green, divalent in blue, and thulium, with variable valency in red. Modified from Johnson.\textsuperscript{63}](image-url)
Based on this, it was our hope to be able to synthesize thulium sulfide, TmS, and be able to control the valency by the same means which the electronic and magnetic properties were manipulated in EuS, by controlling nanoparticle size. As shown previously in Table 1, when the thulium dtc complex was decomposed, only the oxysulfide product was obtained. The same product was obtained when nanoparticle synthesis was attempted. Unfortunately, Tm$^{2+}$ is not nearly as stable as Eu$^{2+}$, so in order to obtain TmS from the dtc complex, harsher synthetic conditions would be required. In comparing the results from the closed and the vacuum conditions in Table 1, being in the presence of a more sulfurous environment would promote formation of the sulfide. By adding in more sulfur containing compounds, it was our hope that TmS could be made.

In a solid-state decomposition of the thulium dtc complex ground with sulfurous compounds, a material similar to thulium sulfide was observed in the powder x-ray diffraction pattern. When an excess thiourea or elemental sulfur were ground with the thulium complex, a cubic material was seen in the powder x-ray diffraction pattern, very similar to that of thulium sulfide, TmS; this material is shown below in Figure 31.
Figure 31: Material synthesized by decomposition of thulium dtc, with the reference peaks of thulium sulfide.

Although this material in Figure 31 resembles TmS, the blue reference lines, labeled with their hkl faces indicate where the diffraction peaks should be seen. This corresponds to a larger unit cell than the reference material; the TmS material in the reference pattern is trivalent, $\text{Tm}^{3+} (e^-) \text{S}^{2-}$.

In x-ray diffraction, Bragg's law gives the relationship between $\lambda$, the wavelength of x-ray irradiation, $d$, the spacing between planes in the crystal lattice, and $\theta$, the observed angle which x-rays are scattered. $n$ is an integer relating to the harmonics of the given wavelength, and for the purposes of our experiments can always be considered 1. This relationship is given by:

$$n\lambda = 2d \sin \theta$$

For a given crystallographic structure, Miller indices, $h$, $k$, and $l$, can be assigned to different crystal faces, of which reflections can be observed off of. In a cubic structure, such as TmS, the relationship between $d$, the spacing between planes in a crystal lattice, $a$, the lattice constant, or cell dimension for the structure, and the hkl value is given by:
\[ d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

By using this relationship, and the reported TmS structure and powder pattern reported in the literature, we can manually determine what the lattice constant for the TmS material synthesized with thiourea is, based on the average of each reflection. However, this process can be performed more effectively with a method called Rietveld refinement. Developed by Hugo Rietveld,\textsuperscript{56} this technique allows different aspects of a powder diffraction pattern (from either or x-rays or neutrons) to be modeled, creating a calculated pattern, generated from a series of properties of a crystalline material.

With this technique, an experimental powder pattern is input, and by refining a model based on different variables, such as lattice size, atomic positions, thermal parameters, and a range of Gaussian and Lorentzian factors governing peak shape. By allowing the calculated and experimental powder patterns to converge, structural information can be determined about the material. Rietveld refinement was performed using the program GSAS,\textsuperscript{57} with the user interface EXPGUI.\textsuperscript{58}

The diffraction pattern in Figure 31 was examined by GSAS refinement, and it was shown, that as suggested by visual examination, the lattice constant of the material is indeed shifted, from 5.391 to 5.460(3) Å. This is consistent with the reduction of Tm\textsuperscript{3+} to Tm\textsuperscript{2+}, given the increase in radius from 1.02 to 1.17 Å. In the decomposition of the europium complex, a reduction takes place from Eu\textsuperscript{3+} to Eu\textsuperscript{2+}, during the synthesis of EuS, demonstrating the possibility of reduction during the decomposition of the dtc ligand.

In order to further verify that the shift was due to a change in the lattice constant as opposed to a shift in the zero-offset, for instance due a displacement in the sample height, (which
is unlikely given the geometry of the diffractometer used, however) a standard, LaB$_6$ was spiked into the x-ray powder sample. The shift was still observed to the same degree, verifying the lattice shift.

The stability of the TmS decreased with increased reaction temperature; when synthesized at 900 °C, peaks from the thulium sesquisulfide, Tm$_2$S$_3$ were observed. At increased reaction times, the relative peak ratios changed, showing an increase of the sesquisulfide over time, as observed below in Figure 32.

![Figure 32. Powder x-ray diffraction pattern of decomposition of the thulium dithiocarbamate complex with thiourea at increased reaction temperatures and times. Blue stars indicate TmS, and red carats indicated Tm$_2$S$_3$.](image)

Samarium is another of the lanthanides which can be in the divalent state, as it is in the samarium sulfide system, SmS. It has been shown that by applying pressure to the system, a
change from black to golden yellow is observed, along with a corresponding decrease in the lattice constant from 5.86 to 5.68 Å. This lattice shift is caused by the pressure-induced compression in the cell from an oxidation of Sm$^{2+}$ to Sm$^{3+}$. The ~9% decrease in cell volume in SmS compared to the ~5% increase in cell volume in the synthesized TmS material suggests that the material has an intermediate valency somewhere between Tm$^{3+}$ and Tm$^{2+}$.

X-ray photoelectron studies (XPS) were performed on the material to determine the oxidation state. By irradiating a material with x-ray radiation under ultrahigh vacuum, it is possible to determine the number of electrons emitted at a given energy, which corresponds to the binding energy of those electrons. Different oxidation states possess different binding energy values for their core electrons, which allow materials of different oxidation states to be measured. The XPS spectrum around the Tm 4d energy level is shown below, in Figure 33, however, only Tm$^{3+}$ is observed at 176.4 eV. If Tm$^{2+}$ were observed, it would appear at a lower energy of 172.5 eV, where no peak appears.

![Figure 33. XPS spectrum around the 4d energy band for Tm.](image)
XPS is an extremely surface sensitive technique\textsuperscript{60} however, so any surface oxidation could obscure the detection of Tm\textsuperscript{2+}, as has been observed in case of TmSe.\textsuperscript{61} This can be resolved by sputtering the surface to remove the surface oxide layer, however, this is not a perfect solution, as the sputtering technique performed with Ar\textsuperscript{+} ions has been known to cause reduction in materials, including rare-earth oxides.\textsuperscript{62} X-ray absorption spectroscopy (XAS) is a similar technique which can be used to determine oxidation state, and is not subject to the same surface sensitivity, which would be much more suited to our purpose, however synchrotron radiation is required. Another alternative would be XPS measurements using synchrotron radiation, which can measure as a function of depth without sputtering with Ar\textsuperscript{+} ions.

Also determined from the XPS data, and confirmed by C/H/N elemental analysis was a very large presence of carbon (~70%). This was not surprising, given the amount of carbon present in the dtc complex, as well as the added thiourea. This is not ideal, as one of the more common ways to remove carbon is via oxidation to CO\textsubscript{2}, which would also very likely oxidize our material. Nanoparticle synthesis should bypass the excess of carbon, however, all attempts to synthesize TmS nanoparticles have been unsuccessful so far. The addition of additional sulfur sources such as thiourea or elemental sulfur, which were successful in the solid-state, did not translate into the nanoparticle synthesis.

As was attempted with EuS, we tried to synthesize a core-shell nanoparticle system in order to prevent oxidation of TmS. It is possible that we could be synthesizing TmS nanoparticles in solution, but they quickly oxidized to Tm\textsubscript{2}O\textsubscript{3}/Tm\textsubscript{2}O\textsubscript{3} during workup. Using the same Zn(dtc)\textsubscript{2} precursor, we attempted to synthesize TmS@ZnS nanoparticles, but still no TmS was observed by PXRD.
It was hoped that by synthesizing TmS nanoparticles, valency could be controlled via particle size, however intermediate valency was suggested in our solid-state synthesis. This leads us to believe that the polycrystalline material formed is of a size-regime smaller than the bulk, but this has not been verified.

The same synthetic method for making TmS was used with Yb(dtc)$_3$phen and thiourea, to try and synthesize YbS, as ytterbium is another of the redox active lanthanides. As shown in Table 1, decomposition of Yb(dtc)$_3$phen by itself only yielded the ytterbium oxysulfide, Yb$_2$O$_2$S. When thiourea was added, similar results were seen from that of Figure 31; Rietveld refinement showed a lattice constant of $a = 5.465(3)$ when refined based on YbS. This is very close to the obtained result for TmS, $a = 5.460(3)$.

1.3 Experimental.

General information. Diisobutylamine, tetramethylammonium hydroxide, carbon disulfide, diethylammonium diethyldithiocarbamate, 1,10-phenanthroline, lanthanum(III) nitrate hexahydrate, cerium(III) nitrate hexahydrate, praseodymium(III) nitrate hexahydrate, neodymium(III) nitrate hexahydrate, samarium(III) nitrate hexahydrate, gadolinium(III) nitrate hexahydrate, terbium(III) nitrate hexahydrate, dysprosium(III) nitrate hexahydrate, holmium(III) nitrate hexahydrate, erbium(III) nitrate hexahydrate, ytterbium(III) nitrate hexahydrate, oleylamine, triphenylphosphine, trioctylphosphine, trioctylamine, and thiourea were obtained from Sigma-Aldrich. Europium(III) nitrate hexahydrate, thulium(III) nitrate hexahydrate, and lutetium(III) nitrate hexahydrate were obtained from Strem. Diethylammonium tetraakis-diethylammoniumdithiocarbamate was obtained from Srotoswini Kar. All chemicals were used as received. Fourier Transformed Infrared (FTIR) spectra were measured in the range 600-4000
cm$^{-1}$ as a thin film, prepared in dichloromethane on NaCl plates on a Varian 800 Scimitar Series FT-IR. Thermal analysis was performed on an SDT Q600 TA instrument. Simultaneous TGA-DTA data were studied from samples in an alumina pan from 25-1000 °C under a N$_2$ flow of 20 mL/min, with a heating rate of 10 °C/min. Elemental (C, H, N) analysis was performed using a Perkin Elmer 2400 Series II CHN/O analyzer. XPS analysis was performed on a Kratos AXIS 165 spectrometer. TEM images were taken on a JEOL JEM 1200 EXII TEM operated at 80 keV using a high resolution Tietz F224 camera at Villanova University. EDX was performed with an Oxford Instruments X-Max Silicon Drift Detector.

**ICP-MS.** Europium-gadolinium ratios were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Samples were ablated using a 213 nm wavelength ultraviolet laser (New Wave UP213) and ratios measured using a ThermoFinnigan Element 2 magnetic sector, single collector ICP-MS. Samples were ablated with a 15 µm spot and a photon flux between 2 and 3 J/cm$^2$ and a laser repetition rate of 7 Hz. A mixture of both spots and lines were used for measurement, with no discernible difference in the results. Ablation was into a stream of helium, with downstream mixing into the Ar flow for introduction into the plasma. NIST610 (a synthetic glass doped with lithophile trace elements) was ablated under matching conditions (though with a larger spot size) for standardization. Both Eu isotopes (151 and 153) were measured as were all 7 Gd isotopes (152, 154, 155, 156, 156, 158 and 160). All were measured in analog mode due to the high Eu and Gd concentrations, but $^{152}$Gd and $^{154}$Gd were not usefully determined due to their low natural abundance. The other five Gd isotopes were used for elemental ratio determination. Other rare earths were measured, but remained largely below detection. Elemental ratios
were determined using LAMTRACE software, with an assumed Eu abundance – hence ratio determination rather than absolute abundances. Both Eu and the abundant Gd isotopes gave internally consistent results and isotopic ratios with the expected natural abundances. Samples were mounted on double sided tape, with the fine powders pressed into the tape with a clean spatula to ensure adherence to the surface. Based on the Eu:Gd ratio, the composition for the polycrystalline samples was determined from ICP-MS.

**X-ray diffraction.** Diffraction patterns were obtained using a Rigaku RAPID Curved IP X-ray powder diffractometer with CuKα radiation at 40 kV and 30 mA with an image plate detector, or a Rigaku Ultima IV X-ray powder diffractometer with CuKα radiation at 40 kV and 44 mA with a D/teX silicon strip detector. For high-temperature PXRD studies, material was loaded on a platinum sample plate, which was heated according to the specifications of the experiment. For example, Figure 18 was generated with the following conditions: the heating rate was set to 10 °C/min, with 2 minute equilibration steps, followed by an x-ray measurement, all performed under dynamic vacuum.

Intensity data for single-crystal x-ray diffraction was collected on a Bruker SMART 1000 CCD diffractometer using MoKα radiation (λ = 0.71073 Å). The data were integrated using the SAINT suite of software, and absorption corrections were calculated using SADABS. Crystal structures were solved and refined using the SHELX-86 and -97 packages, with the assistance of X-Seed. The structures were solved using direct methods and refined by full- matrix least-squares methods with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were located in calculated positions and refined isotropically.

Rietveld refinement was performed using GSAS, through the EXPGUI interface. As
appropriate, the parameters which were refined were cell lattice constants, thermal parameters (for each phase, all atoms were constrained to give the same parameter), background, zero-point error, phase fractions, and GW, LY, and asym profile parameters.

Magnetism. Magnetic measurements were made on a Quantum Design MPMS SQUID with Evercool, from 5 K to 100 K in a 7,000 Oe field. Crystalline, powdered samples containing ~10 mg of compound were loaded into a gelatin capsule. The sample was positioned within a plastic straw for analysis. The diamagnetic correction for the sample was calculated using \( \chi_d = (-184.03/2)10^{-6} \) emu/mole, and was subtracted. The ferromagnetic Weiss temperature, \( \theta \), was determined using \( 1/\chi \) versus \( T \) plots. The plots were fit using a linear regression.

Tetramethylammonium diisobutyldithiocarbamate. Diisobutylamine (8.68 mL, 50 mmol) was dissolved in tetramethylammonium hydroxide (50 mL, 50 mmol), and carbon disulfide (3.02 mL, 50 mmol) was added while stirring. The solution was stirred for 1 hour, and turned gold yellow immediately upon addition. The solution was dried under vacuum, then washed with diethyl ether (60 mL).

La(dtc)\(_3\)phen. A solution of diethylammonium diethyldithiocarbamate (1.33 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of La(NO\(_3\))\(_3\)·6 H\(_2\)O (0.87 g, 2 mmol) in 2-propanol (10 mL). Light yellow solid precipitated after approximately 5 minutes. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm\(^{-1}\)):\( \nu_{C-N} = 1482(\text{s}), \nu_{C-S} = 995(\text{m}), \nu_{\text{phen}} = 3045, 1624, 1589, 1573, 843, 729. \) Anal. Calcd. For C\(_{27}\)H\(_{38}\)N\(_5\)S\(_6\)La: C, 42.45; H, 5.01; N, 9.17; Found: C, 42.44; H, 5.13; N, 9.24. Percent yield: 50.5%.

Ce(dtc)\(_3\)phen. A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and
1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of
Ce(NO$_3$)$_3$·6 H$_2$O (0.86 g, 2 mmol) in 2-propanol (10 mL). Solution turned dark brown, but no
precipitate formed. Solution stirred for 30 minutes total. When more 2-propanol was added,
brown precipitate came out. Solid was isolated by vacuum filtration and washed with 2-propanol.
Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Ce: C, 42.38; H, 5.01; N, 9.15; Found: C, 35.50; H, 4.28; N, 7.76.
Percent yield: 53.9%.

**Pr(dtc)$_3$phen.** A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and
1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of
Pr(NO$_3$)$_3$·6 H$_2$O (0.87 g, 2 mmol) in 2-propanol (10 mL). Bright green solid precipitated after
approximately one minute. Solution stirred for 30 minutes total. Solid was isolated by vacuum
filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $\nu_{C-N} = 1481$(s), $\nu_{C-S} =$
997(m), $\nu_{phen} = 3045, 1624, 1589, 1572, 843, 729$. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Pr: C, 42.34; H,
5.00; N, 9.14; Found: C, 42.17; H, 4.88; N, 9.21. Percent yield: 76.8%.

**Nd(dtc)$_3$phen.** A solution of diethylammonium diethyldithiocarbamate (1.33 g, 6 mmol) and
1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of
Nd(NO$_3$)$_3$·6 H$_2$O (0.88 g, 2 mmol) in 2-propanol (10 mL). Teal solid precipitated after
approximately 30 seconds. Solution stirred for 30 minutes total. Solid was isolated by vacuum
filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $\nu_{C-N} = 1481$(s), $\nu_{C-S} =$
998(m), $\nu_{phen} = 3047, 1624, 1589, 1575, 843, 729$. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Nd: C, 42.16; H,
4.98; N, 9.10; Found: C, 42.19; H, 5.00; N, 9.17. Percent yield: 81.5%.

**Sm(dtc)$_3$phen.** A solution of diethylammonium diethyldithiocarbamate (0.98 g, 4.4 mmol) and
1,10-phenanthroline (0.26 g, 1.5 mmol) in acetonitrile (15 mL) was added to a solution of
Sm(NO$_3$)$_3$·6 H$_2$O (0.65 g, 1.5 mmol) in 2-propanol (10 mL). Light yellow solid precipitated after approximately 30 seconds. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $v_{C-N} = 1481$(s), $v_{C-S} = 1000$(m), $v_{phen} = 3045, 1625, 1589, 1573, 843, 729$. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Sm: C, 41.82; H, 4.94; N, 9.03; Found: C, 41.71; H, 5.09; N, 9.17. Percent yield: 75.1%.

**Eu(dtc)$_3$phen.** A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Eu(NO$_3$)$_3$·6 H$_2$O (0.89 g, 2 mmol) in 2-propanol (10 mL). Bright orange solid precipitated immediately. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $v_{C-N} = 1482$(s), $v_{C-S} = 1000$(m), $v_{phen} = 3046, 1625, 1589, 1573, 843, 729$. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Eu: C, 41.74; H, 4.93; N, 9.01; Found: C, 41.22; H, 4.96; N, 9.16. Percent yield: 81.1%.

**Eu('Bu$_2$dtc)$_3$phen.** Europium nitrate hexahydrate (0.446 g, 1 mmol) was dissolved in acetonitrile (5 mL). Tetramethylammonium diisobutyldithiocarbamate (0.835 g, 3 mmol) and 1,10-phenanthroline (0.180 g, 1 mmol) were dissolved in a solution of 1:1 acetonitrile:ethanol (30 mL), and poured into the europium solution. The solution immediately turned bright red, and after ~30 seconds, bright red material precipitated from solution. After 20 minutes of stirring, the product was vacuum filtered. Percent yield: 84.6%

**Gd(dtc)$_3$phen.** A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Gd(NO$_3$)$_3$·6 H$_2$O (0.90 g, 2 mmol) in 2-propanol (10 mL). Light yellow solid precipitated immediately. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and
washed with 2-propanol. FTIR (thin film on NaCl, cm\(^{-1}\)): \(\nu_{\text{C-N}} = 1481(\text{s})\), \(\nu_{\text{C-S}} = 1001(\text{m})\), \(\nu_{\text{phen}} = 3048, 1624, 1589, 1575, 843, 728\). Anal. Calcd. For C\(_{27}\)H\(_{38}\)N\(_5\)S\(_6\)Gd: C, 41.46; H, 4.90; N, 8.95; Found: C, 40.47; H, 4.77; N, 9.04. Percent yield: 87.1%.

**Gd(Bu\(_2\)dtc)\(_3\)phen.** Gadolinium nitrate hexahydrate (0.451 g, 1 mmol) was dissolved in acetonitrile (5 mL). Tetramethylammonium diisobutylthiocarbamate (0.835 g, 3 mmol) and 1,10-phenanthroline (0.180 g, 1 mmol) were dissolved in a solution of 1:1 acetonitrile:ethanol (30 mL), and poured into the europium solution. The solution immediately turned bright yellow, and after refrigeration, large yellow crystals precipitated from solution. Percent yield: 69.4%

**Tb(dtbc)\(_3\)phen.** A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Tb(NO\(_3\))\(_3\)·6 H\(_2\)O (0.91 g, 2 mmol) in 2-propanol (10 mL). Light yellow solid precipitated immediately. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm\(^{-1}\)): \(\nu_{\text{C-N}} = 1482(\text{s})\), \(\nu_{\text{C-S}} = 1002(\text{m})\), \(\nu_{\text{phen}} = 3046, 1625, 1589, 1574, 844, 728\). Anal. Calcd. For C\(_{27}\)H\(_{38}\)N\(_5\)S\(_6\)Tb: C, 41.37; H, 4.89; N, 8.93; Found: C, 39.39; H, 4.76; N, 9.03. Percent yield: 87.3%.

**Dy(dtbc)\(_3\)phen.** A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Dy(NO\(_3\))\(_3\)·6 H\(_2\)O (0.91 g, 2 mmol) in 2-propanol (10 mL). Light yellow solid precipitated immediately. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm\(^{-1}\)): \(\nu_{\text{C-N}} = 1482(\text{s})\), \(\nu_{\text{C-S}} = 1003(\text{m})\), \(\nu_{\text{phen}} = 3046, 1625, 1589, 1574, 844, 728\). Anal. Calcd. For C\(_{27}\)H\(_{38}\)N\(_5\)S\(_6\)Dy: C, 41.18; H, 4.86; N, 8.89; Found: C, 39.79; H, 4.69; N, 9.04. Percent yield: 85.3%.
**Ho(dtc)phen.** A solution of diethylammonium diethyldithiocarbamate (1.33 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Ho(NO$_3$)$_3$·6 H$_2$O (0.92 g, 2 mmol) in 2-propanol (10 mL). Pink solid precipitated immediately. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $\nu_{\text{C-N}} = 1482$(s), $\nu_{\text{C-S}} = 1004$(m), $\nu_{\text{phen}} = 1625$, 1590, 1575, 844, 728. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Ho: C, 41.05; H, 4.85; N, 8.87; Found: C, 39.46; H, 4.57; N, 8.88. Percent yield: 88.86%.

**Er(dtc)phen.** A solution of diethylammonium diethyldithiocarbamate (1.33 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Er(NO$_3$)$_3$·6 H$_2$O (0.92 g, 2 mmol) in 2-propanol (10 mL). Light pink solid precipitated immediately. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $\nu_{\text{C-N}} = 1482$(s), $\nu_{\text{C-S}} = 1004$(m), $\nu_{\text{phen}} = 3047$, 1625, 1590, 1575, 844, 728. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Er: C, 40.93; H, 4.83; N, 8.84; Found: C, 38.45; H, 4.54; N, 8.64. Percent yield: 85.2%.

**Tm(dtc)phen.** A solution of diethylammonium diethyldithiocarbamate (1.33 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Tm(NO$_3$)$_3$·6 H$_2$O (0.93 g, 2 mmol) in 2-propanol (10 mL). Light yellow solid precipitated after approximately 5 minutes. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $\nu_{\text{C-N}} = 1482$(s), $\nu_{\text{C-S}} = 1004$(m), $\nu_{\text{phen}} = 3047$, 1625, 1590, 1576, 844, 728. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Tm: C, 40.85; H, 4.82; N, 8.82; Found: C, 38.06; H, 4.49; N, 8.57. Percent yield: 81.2%.

**Yb(dtc)phen.** A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and
1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Yb(NO$_3$)$_3$·6 H$_2$O (0.93 g, 2 mmol) in 2-propanol (10 mL). Bright yellow solid precipitated after approximately one minute. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $\nu_{C-N} =$ 1482(s), $\nu_{C-S} =$ 1005(m), $\nu_{phen} =$ 1625, 1589, 1576, 844, 728. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Yb: C, 40.63; H, 4.80; N, 8.78; Found: C, 35.49; H, 3.97; N, 8.35. Percent yield: 76.9%.

**Lu(dtc)$_3$phen.** A solution of diethylammonium diethyldithiocarbamate (1.34 g, 6 mmol) and 1,10-phenanthroline (0.36 g, 2 mmol) in acetonitrile (15 mL) was added to a solution of Lu(NO$_3$)$_3$·6 H$_2$O (0.94 g, 2 mmol) in 2-propanol (10 mL). Light yellow solid precipitated after approximately 30 seconds. Solution stirred for 30 minutes total. Solid was isolated by vacuum filtration and washed with 2-propanol. FTIR (thin film on NaCl, cm$^{-1}$): $\nu_{C-N} =$ 1483(s), $\nu_{C-S} =$ 1006(m), $\nu_{phen} =$ 1624, 1589, 1575, 843, 724. Anal. Calcd. For C$_{27}$H$_{38}$N$_5$S$_6$Lu: C, 40.54; H, 4.79; N, 8.75; Found: C, 35.45; H, 3.78; N, 8.87. Percent yield: 74.8%.

dtc Precursor thermolysis. From this point on, unless otherwise specified, all dtc ligands are the diethyldithiocarbamate ligand. Lanthanide dtc precursors were thermally decomposed under vacuum (Method 1) or in a closed tube in a nitrogen atmosphere (Method 2).

**Method 1, vacuum.** Generally, ~0.1 g precursor was placed in a quartz tube, and heated to a temperature of 900 °C under a dynamic vacuum in a Lindberg/Blue M horizontal tube furnace. The temperature was held constant for 5 hours and let naturally cool to around room temperature, at which point the vacuum was turned off.

**Method 2, closed.** Generally, in the glovebox, ~40 mg precursor was packed into a porcelain combustion boat. The boat was placed in a quartz tube, and a stopcock was closed, so the
environment was under nitrogen. The tube was removed from the glovebox and heated to 900 °C in a Lindberg/Blue M horizontal tube furnace. The temperature was held constant for 5 hours, then let naturally cool.

**Polycrystalline Eu$_{1-x}$Gd$_x$S.** Precursors with ratios of the dtc precursors (Eu(dtc)$_3$phen:Gd(dtc)$_3$phen) to result in x=0.002, 0.004, 0.006, 0.01, 0.03, and 0.05 were dissolved in CH$_2$Cl$_2$, for intimate mixing, and the solvent evaporated. The powders were loaded in a quartz tube inside a glove box and the system was sealed and heated to 700 °C for 5 hours. Black crystalline materials were isolated. Obtained powder x-ray diffraction patterns could be indexed to EuS, PDF 00-026-1419 (ICDD, 1974).

**Polycrystalline Eu$_{1-x}$Gd$_x$S resulfurization.** Sample material was heated on a graphite boat in a quartz tube in a Lindberg/Blue M horizontal tube furnace. A mixture of 5% H$_2$S, 95% N$_2$ gas was then flowed through the quartz tube over the material, and the furnace was set to 900 °C, and H$_2$S was flowed for 2 hours. After heating, the tube was removed from the furnace, and once cooled to room temperature, the stopcocks and valves were closed, and the flow of H$_2$S gas was ceased. Obtained powder x-ray diffraction patterns could be indexed to EuS, PDF 00-026-1419 (ICDD, 1974).

**Eu$_{1-x}$Gd$_x$S nanoparticles.** [Eu(dtc)$_4$][NEt$_2$H$_2$]$(0.20$ g, $0.25$ mmol) or Eu(‘Bu$_2$dtc)$_3$phen (0.20 g, 0.21 mmol) and Gd(‘Bu$_2$dtc)$_3$phen (appropriate amount to give targeted doping level) were dissolved in oleylamine (1.94 g, 7.25 mmol) in the glove box and loaded into a syringe. A solution of oleylamine (1.94 g, 7.25 mmol) and triphenylphosphine (3.81 g, 14.5 mmol) was loaded inside of the glove box in a 3-neck round bottom flask with a thermocouple adapter, condensor with gas inlet adapter, and stopper. This was taken out of the glove box, put on the
Schlenk line, and evacuated and flushed with nitrogen 3 times. This was then heated to 70 °C under nitrogen, then held at this temperature for 15 minutes under vacuum. The solution was then heated to 265 °C under nitrogen, at which point the stopper was exchanged with a septum, and the syringe of precursors was injected. The solution turned a purple-black color, and was held at this temperature for 1 hour. The temperature was then reduced to 70 °C, and anhydrous ethanol (100 mL) was added to the solution. In a glove box the solution was transferred to a centrifuge tube, and centrifuged at 3500 rpm for 30 minutes. The yellow supernatant was discarded, and the black powder dissolved in anhydrous heptane (~2 mL). Fresh ethanol (100 mL) was added to the dark purple solution, and the precipitate was isolated by centrifugation, and dried in vacuo. Obtained powder x-ray diffraction patterns could be indexed to EuS, PDF 00-026-1419 (ICDD, 1974).

**EuS nanoparticles.** Eu(Bu2dtc)3phen (0.20 g, 0.21 mmol) was dissolved in a liquid capping ligand (oleylamine, trioctylphosphine, trioctylamine, 7.5 mmol) in the glove box and loaded into a syringe. A solution of other capping ligands generally totaling 22.5 mmol were loaded inside of the glove box in a 3-neck round bottom flask with a thermocouple adapter, condensor with gas inlet adapter, and stopper. This was taken out of the glove box, put on the Schlenk line, and evacuated and flushed with nitrogen 3 times. This was then heated to 70 °C under nitrogen, then held at this temperature for 15 minutes under vacuum. The solution was then heated to 265 °C under nitrogen, at which point the stopper was exchanged with a septum, and the syringe of precursors was injected. The solution turned a purple-black color, for samples which formed EuS, and was held at this temperature for some period of time. The temperature was then reduced to 70 °C, and anhydrous ethanol (100 mL) was added to the solution. The solution was
transferred to a centrifuge tube, and centrifuged at 3500 rpm for 10 minutes. The yellow supernatant was discarded, and the black powder dissolved in anhydrous heptane (~2 mL). Fresh ethanol (100 mL) was added to the dark purple solution, and the precipitate was isolated by centrifugation, and dried in vacuo. Obtained powder x-ray diffraction patterns could be indexed to EuS, PDF 00-026-1419 (ICDD, 1974).

**Polycrystalline TmS.** Tm(dtc)₃phen was mixed with a 1000% molar excess of thiourea, and ground with a mortar and pestle. Generally, in the glovebox, ~40 mg of this precursor was packed into a porcelain combustion boat. The boat was placed in a quartz tube, and a stopcock was closed, so the environment was under nitrogen. The tube was removed from the glovebox and heated to 700 °C in a Lindberg/Blue M horizontal tube furnace. The temperature was held constant for 5 hours, then let naturally cool. Reaction time and temperature were varied. This material was indexed close to TmS, PDF 00-026-1498 (ICDD, 1974), and analyzed with Rietveld refinement.

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62
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2.1 Introduction

2.1.1 Magnetic domains

Because we are synthesizing nanoscale europium sulfide, it is important to consider the differences between bulk and nanoscale magnetic materials. Magnetic nanostructures can have significant advantages over their bulk counterparts; many of which are attributed to the concept of domain size. In a ferromagnetic material, magnetic moments are all aligned in one direction, giving a material a strong magnetic moment in one direction. However, this produces a demagnetizing field as seen in Figure 1. To reduce the internal energy caused by the demagnetizing field, called magnetostatic energy, the material can break into smaller magnetic zones, called domains. This is depicted below in Figure 1.
Domain theory was proposed by Pierre-Ernest Weiss in 1906, and can be visualized with a Kerr microscope, or scanning SQUID microscope. Shown below in Figure 2 is an image generated from a scanning SQUID microscope of a sample of Co-doped TiO$_2$, shown to exhibit room temperature ferromagnetism.\textsuperscript{1} In this image, the different colors represent different magnitudes of the magnetic moment, showing the sample broken into zones which are aligned in different directions. Different materials have different intrinsic domain sizes. For a given material, there will be a minimum size which that magnetic domain can be, beyond a certain point, a material will not be able to break into smaller domains.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Representation of a ferromagnetic material breaking into magnetic domains in order to reduce magnetostatic energy.}
\end{figure}
Figure 2. Image generated from a scanning SQUID microscope, showing the presence of magnetic domains in a sample of Co-doped TiO$_2$. Used without permission from Koinuma. Image size: 200 x 200 μm.

Superparamagnetism occurs when the dimensions of a material are less than the domain size. A superparamagnetic material is a material which acts as a paramagnet, and will magnetically align in the presence of an external magnetic field. It is termed 'super'-paramagnetic because it has a much stronger magnetic moment than a typical paramagnet. Superparamagnetic particles can be made by creating a material with a particle size equal to or less than that minimum domain size for a material, so it cannot further break into smaller domains and will always possess the maximum magnetic moment for the material. Superparamagnetic nanoparticles have strong applications in many fields of bio-medicine, specifically as contrast...
agents for magnetic resonance imaging.\textsuperscript{3}

Shown below in Figure 69 is an illustration depicting a ferromagnet, a supermagnetic nanoparticle, and a ferromagnetic nanowire. If a ferromagnetic material could be synthesized with the morphology of a nanowire, with the diameter being of the minimum magnetic domain size, it could possess a strong magnetic moment relative to a bulk ferromagnetic material. Because the nanowire would only exhibit domain confinement in one dimension, it is possible for the material to break into individual domains along the length of the wire, but that is unlikely for a few reasons.

![Figure 3. Illustration of a bulk ferromagnetic material, a superparamagnetic nanoparticle, and a ferromagnetic nanowire.](image)

As seen in Figure 67, the largest source of magnetostatic energy rises along the length of the material, and is eased by the formation of a domain wall along the length of the material. Such a domain wall would not be possible in the case of this nanowire. Furthermore, preferred
alignment of the magnetic moments will tend to take place along the axis of the wire for the same reason that the wire was synthesized along that axis, due to what are referred to as hard and soft axes.

2.1.2 Chemical transformations

Demonstrated in the previous chapter, the most common method for synthesizing EuS nanoparticles is by thermal decomposition of Eu dtc complexes in coordinating solvents. However, there are downsides to this approach; ligand capped nanoparticles can leave a barrier for charge or ion transport when incorporated into devices, limiting their applications. Furthermore, no effective method of shape control capable of forming nanowires through a solution-based route was found through the variation of capping ligands. By utilizing preformed nanowires, we have investigated the Eu₂O₃ as a templating precursor to form uncapped, nanostructured EuS at reduced temperatures through sulfurization reactions, a combination of anion replacement and europium reduction.

Chemical transformation of nanostructures is an effective synthetic tool, with the potential to broaden the range of materials synthesized with morphological control. Many synthetic transformations have been demonstrated, from galvanic replacement, oxidation, diffusion, but perhaps the most successful technique is cation exchange. One of the earliest examples is the remarkable exchange of cadmium in CdSe with silver to form Ag₂Se, which is reversible, even at room temperature. Similarly, nanoparticles of CdS have undergone cation-exchange with copper and lead, as well as platinum and palladium. This technique has also been demonstrated in nanowires, for example ZnS nanowires have been transformed to sulfides.
of copper, silver, antimony and bismuth\textsuperscript{11} maintaining the morphology of the parent structure. Another strong example is shown below in Figure 4, where Xia synthesized single-crystal tellurium nanowires,\textsuperscript{12} which can be topotactically reacted with silver to form Ag$_2$Te; these can be further transformed through cation-exchange to form CdTe, ZnTe, and PbTe.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{TEM images showing chemical transformation of tellurium nanowires. Single-crystal Te nanowires are topotactically converted to Ag$_2$Te, and can undergo cation-exchange to CdTe, ZnTe, or PbTe. Reproduced without permission from Xia.\textsuperscript{12}}
\end{figure}

Conversion chemistry for ‘anion exchange’ has also been demonstrated for reaction of oxides with nitrogen and sulfur sources to form metal nitrides\textsuperscript{13–17} and sulfides.\textsuperscript{18,19} Frequently anion exchange is associated with the formation of hollow nanomaterials, depending on the diffusivity of the cation versus anion.\textsuperscript{6} It is also possible to form core-oxide/shell-sulfide structures from nanowires of metal oxides.\textsuperscript{20} The conversion of oxide nanowires to sulfides was initially explored as an approach to prepare sulfur analogs of carbon nanotubes, where layers of a
given material such as MoS$_2$, WS$_2$, NbS$_2$ compose the concentric graphene sheets. Another advantage of anion conversion is that nanowire arrays of metal oxides, which are easily prepared such as for ZnO, can be converted to sulfide nanowires of materials such as ZnS, which are quite difficult to prepare.

Single-crystal nanowires of the series of lanthanide hydroxides, Ln(OH)$_3$, have been synthesized by Li,$^{21}$ shown below in Figure 5. Li has further shown that further reaction$^{22}$ of these nanowires by dehydration yields the sesquioxide, Ln$_2$O$_3$, and similar hydrothermal routes can yield the oxysulfide, Ln$_2$O$_2$S, or the oxyfluoride, LnOF. Because the formed Ln(OH)$_3$ nanowires are single-crystalline as synthesized, they serve as a good precursor with which to perform chemical transformation, to reductively form EuO and EuS.

![Figure 5. TEM images of different Ln(OH)3 nanowires. Reproduced without permission from Li.$^{21}$](image)

2.2 Results and discussion

2.2.1 Eu(OH)$_3$

As Li has discussed,$^{21}$ the hexagonal Ln(OH)$_3$ materials, like ZnO,$^{23}$ exhibit anisotropic
growth under hydrothermal conditions. The synthesis of Ln(OH)₃ wires proceeds first through a simple metathesis reaction, shown below for europium:

$$\text{Eu(NO}_3\text{)}_3 + 3 \text{NaOH} \rightarrow \text{Eu(OH)}_3 + 3 \text{NaNO}_3$$

A white flocculent material precipitates, and the obtained hydroxide material is then heated under hydrothermal conditions, where anisotropic growth takes place. If the material is isolated and washed before hydrothermal growth is initiated, it is identified by PXRD as Eu(OH)₃. Shown below in Figure 6 is an SEM image of europium hydroxide nanocrystals isolated before hydrothermal growth.

![Figure 6. SEM image of Eu(OH)₃ before hydrothermal growth.](image)

Depending on the concentration of hydroxide, [OH⁻], present during hydrothermal growth, different morphologies are obtained: with dilute [OH⁻], nanoplates form, with moderate [OH⁻], nanowires form, and stronger [OH⁻], nanorods form. These morphologies are shown below in Figure 7.
Shown in Figure 7 are images from optimized syntheses of Eu(OH)₃ nanostructures. This synthesis was adapted from Li, which was performed with dissolution of Ln₂O₃ in nitric acid to form the nitrate, Ln(NO₃)₃, followed by subsequent reaction with base, and anisotropic growth took place in an autoclave. Our rationale for starting with Eu(NO₃)₃ instead of the Eu₂O₃ will be discussed in detail later. Initial attempts at reproducing this synthesis resulted in the formation of rods; in these syntheses, Eu(OH)₃ was isolated and washed with water, followed by growth in a hydrothermal bomb with water. Before the [OH⁻] level was varied, the first conditions which was manipulated were reaction time and temperature; results from these reactions are shown below in Table 1. Li’s synthesis was performed at 180 °C for 12 hours, so variations based on these initial set of conditions were used.
Table 1. Optimization of reaction time and temperature in order to obtain the highest aspect nanowires. Yellow highlighted rows show the optimal time and temperature.

Looking at the first four rows of Table 1 where the temperature was varied, and the time was held constant at 12 hours, it was shown that the best aspect ratio was obtained at 180 °C, the same temperature which Li used. Following this, reaction time was varied, and we found that the highest aspect ratio was achieved with a reaction time of 6 hours. This is a shorter reaction time than Li used, but our reaction was also performed differently; instead of reaction in a sealed autoclave, our syntheses were performed in hydrothermal bombs. In general it seems that the aspect ratio of a material will grow to a certain maximum point, around 6 hours, at which point the material will start to saturate, and favor a smaller aspect ratio. This is mostly consistent, the 9 hour reaction was likely an outlier.

In order to try and achieve a better aspect ratio, we attempted to seed these reactions, by adding some preformed Eu(OH)$_3$ nanowires in with the Eu(NO$_3$)$_3$ and NaOH reactants. The hope was to have the reactants grow on the pre-nucleated wires, along the same axis of growth,
increasing the aspect ratio. This was tried at both stages: before the material was put under hydrothermal conditions, and earlier, as the Eu(NO$_3$)$_3$ and NaOH were combined. This was tried multiple times, adding the product of a seeding reaction to a new reaction, and repeating this. Unfortunately a negligible changed was observed, so other conditions were varied.

The next advance in increasing aspect ratio was achieved when the isolation step was skipped, and the entire reaction volume of Eu(OH)$_3$ in excess base was put into the hydrothermal bomb. Through this, aspect ratios were improved to >8, and the final improvement was achieved by varying the [OH$^-$] level; the synthetic conditions used to get the results seen in Figure 7 are shown below in Table 2.

<table>
<thead>
<tr>
<th>Row</th>
<th>Eu (g)</th>
<th>[OH$^-$]</th>
<th>[OH$^-$]/Eu</th>
<th>L (nm)</th>
<th>W (nm)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.26</td>
<td>0.39</td>
<td>1.52</td>
<td>1360±572</td>
<td>723±84</td>
<td>2.0±0.6</td>
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<tr>
<td>2</td>
<td>0.25</td>
<td>0.78</td>
<td>3.16</td>
<td>447±160</td>
<td>129±29</td>
<td>3.6±1.7</td>
</tr>
<tr>
<td>3</td>
<td>0.26</td>
<td>1.05</td>
<td>4.01</td>
<td>313±146</td>
<td>49±20</td>
<td>6.6±2.5</td>
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<tr>
<td>4</td>
<td>0.25</td>
<td>1.55</td>
<td>6.30</td>
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<td>73±26</td>
<td>5.3±3.6</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>2.35*</td>
<td>8.87</td>
<td>691±300</td>
<td>73±25</td>
<td>10.0±4.0</td>
</tr>
<tr>
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<td>9.64</td>
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<td>72±27</td>
<td>15±9</td>
</tr>
<tr>
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<td>9.90</td>
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<td>369±137</td>
<td>129±33</td>
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<tr>
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<td>19.85</td>
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<tr>
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<td>4.67</td>
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<td>48±23</td>
<td>7.1±2.2</td>
</tr>
<tr>
<td>11</td>
<td>0.50</td>
<td>5.15</td>
<td>10.40</td>
<td>1289±782</td>
<td>105±42</td>
<td>13.4±7.7</td>
</tr>
</tbody>
</table>

Table 2. Results of varying reaction [OH$^-$] in Eu(OH)$_3$ nanowire synthesis. Table shows the amount of Eu(NO$_3$)$_3$ used (Eu), the concentration of base ([OH$^-$]), these concentration of base normalized to the amount of Eu(NO$_3$)$_3$ present ([OH$^-$]/Eu), the average wire length (L) and width (W) with standard deviation, and the resulting aspect ratio (R), with standard deviation. Light gray shading indicates use of NH$_4$OH, otherwise NaOH was used. * = NaCl added.

It was found that the aspect ratio was maximized by optimizing the [OH$^-$] level to a
certain point, at which point they begin to decrease again; this is shown in Figure 7. In general, in these reactions, the amount of Eu(NO$_3$)$_3$ used in the reaction was kept constant, and the [OH$^-$] level was varied, but the same result of increasing [OH$^-$] could be obtained from reducing the amount of europium starting material, seen by comparing rows 6 and 10. As a result of this, in order to see a stronger relationship between [OH$^-$] and aspect ratio, the [OH$^-$] level was normalized by dividing by the amount of [OH$^-$] used. The relationship between [OH$^-$]/Eu and the aspect ratio are shown below in Figure 8.

![Figure 8. Aspect ratios of Eu(OH)$_3$ nanowires as a function of the concentration of base, normalized to the amount of europium present.](image)

The cells shaded gray in Table 2, in rows 1, 2, and 4 indicate reactions done using NH$_4$OH instead of NaOH, and as can be seen, there is no observed effect on the aspect ratio. In row 5, NaCl was added to the reaction, with no effective change observed when compared to the reaction in row 6; the aspect ratio is somewhat smaller, but as is the [OH$^-$]/Eu level. Although we are now synthesizing nice wires with high aspect ratios, you can see by the standard deviations in
the lengths and widths that the material is somewhat poly-disperse. This isn't ideal, but unfortunately no variation in reaction conditions was found which increased monodispersity.

2.2.2 Eu$_2$O$_3$

Now that different Eu(OH)$_3$ morphologies were optimized based on [OH$^-$], reaction time and temperature, the conversion to Eu$_2$O$_3$ was studied:

$$2 \text{Eu(OH)}_3 \rightarrow \text{Eu}_2\text{O}_3 + 3 \text{H}_2\text{O}$$

Initial dehydrations to Eu$_2$O$_3$ were performed at temperatures of 800 °C, in air, for 3 hours. The TEM image below in Figure 9 shows that the material formed with these conditions did not effectively maintain the nanowire morphology.

![TEM image showing loss of morphology in Eu(OH)$_3$ nanorods dehydrated to Eu$_2$O$_3$ in air at 800 °C.](image)

The Ln(OH)$_3$ conversion to the Ln$_2$O$_3$ has been previously studied by TGA-DTA by Lito show a conversion from Ln(OH)$_3$ to LnOOH to Ln$_2$O$_3$, which is shown for the europium system in Figure 10. The material first loses one water molecule around 300 °C:
Eu(OH)$_3$ → EuOOH + H$_2$O

This water loss should give a theoretical value of 91.12%, very close to what we observed. Between 350 and 400 °C, another half molecule of water is lost:

EuOOH → ½ Eu$_2$O$_3$ + ½ H$_2$O

This final water loss should give a theoretical value of 86.69%, as we have seen. The TGA-DTA experiment is performed under flowing nitrogen; while not completely air-free, or under vacuum, the conditions are somewhat controlled.

![TGA-DTA thermogram showing dehydration of Eu(OH)$_3$ to Eu$_2$O$_3$. Performed under flowing N$_2$, the EuOOH intermediate is observed between 300-400 °C.](image)

Here we report a study by high-temperature PXRD in different environments. Shown below in Figure 11 are diffraction patterns as Eu(OH)$_3$ is heated from room temperature to 1200 °C.
°C in air. At 350 °C, the crystallinity of the material decreases, and converts to an amorphous phase. At 600 °C, the material becomes more crystalline, and can be indexed to Eu₂O₃.

Figure 11. PXRD patterns measured as Eu(OH)₃ was heated from room temperature to 1200 °C in air. The material goes through an amorphous transition starting at 350 °C, and becomes crystalline Eu₂O₃ at 600 °C.

In contrast, Figure 12 shows diffraction patterns of the same dehydration performed under dynamic vacuum; to compare, the material transitions at a lower temperature, 100 °C lower at 250 °C, and instead of going through an amorphous phase, peaks can be indexed to EuOOH. Crystalline Eu₂O₃ can be identified at a much lower temperature of 325 °C, versus 600 °C in air. The air environment must be too harshly oxidizing to go through the EuOOH intermediate observed under vacuum. As the EuOOH phase is observed in the TGA-DTA as well, showing the similarity of the conditions of dynamic vacuum and flowing N₂.
Figure 12. PXRD patterns measured as Eu(OH)$_3$ was heated from room temperature to 1200 °C under vacuum. The material goes through an EuOOH intermediate starting at 250 °C, and becomes crystalline Eu$_2$O$_3$ at 325 °C.

It is interesting to compare this with recent work done on the decomposition of La(OH)$_3$. Carvajal$^{24}$ has studied the dehydration of La(OH)$_3$ in air, and also does not see the LaOOH intermediate, which is unsurprising, since the decomposition was done in air, however they do see formation of lanthanum oxycarbonate, La$_2$O$_2$CO$_3$. It is possible that the amorphous phase that we pass through in Figure 11 under air is Eu$_2$O$_2$CO$_3$, but it more resembles Eu$_2$O$_3$. Eu$_2$O$_2$CO$_3$ is more typically formed by decomposition from europium acetate$^{25}$ or europium oxalate,$^{26}$ and has been used as a precursor to make nanostructures of Eu$_2$O$_3$.$^{27}$

As a result, dehydration of Eu(OH)$_3$ was done under dynamic vacuum in order to prevent agglomeration of material and better maintain morphology. At this stage, the reaction was optimized by varying the dehydration time and temperature to make sure the maximum aspect ratio was kept, giving the strongest control of morphology through the conversion to Eu$_2$O$_3$. As shown in the aspect ratios in Table 3, a greater loss of morphology occurs at high temperature,
which agrees with the TEM observed in Figure 9.

These results convey that it's important to balance a high enough temperature to achieve dehydration without going too high in temperatures to promote agglomeration. The best aspect ratio was obtained at 400 °C, but reactions were consistently done at 500 °C for 3 hours, to ensure a complete dehydration to Eu₂O₃, while still maintaining strong morphological control. The aspect ratios in Table 3 come from when the Eu(OH)₃ starting material were being synthesized as nanorods, rather than nanowires, so the aspect ratios should only be compared against one another.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 °C / 2 hr</td>
<td>N/A (EuOOH)</td>
</tr>
<tr>
<td>350 °C / 2 hr</td>
<td>4.78</td>
</tr>
<tr>
<td>400 °C / 2 hr</td>
<td>5.40</td>
</tr>
<tr>
<td>450 °C / 2 hr</td>
<td>4.53</td>
</tr>
<tr>
<td>500 °C / 2 hr</td>
<td>4.54</td>
</tr>
<tr>
<td>700 °C / 3 hr</td>
<td>3.88</td>
</tr>
</tbody>
</table>

*Table 3. Aspect ratios of Eu₂O₃ wires formed by dehydration under dynamic vacuum at increasing reaction temperature/time.*

2.2.3 EuS

Once good morphological control was be attained in the Eu₂O₃ wires, the next step was conversion to EuS by sulfurization with H₂S. Ideally we would find the minimum temperature at which EuS could be formed in order to maximize our chances of maintaining morphology. Initial reactions were not promising, and required very high temperatures to achieve complete reaction. In order to see phase-pure EuS, or even with minimal Eu₂O₂S impurity, temperatures of 800 °C were required. At 700 °C, even when significant Eu₂O₂S was still seen by PXRD, morphology
was still lost; significant agglomeration is seen in the SEM image of this material shown below in Figure 13.

![SEM image of Eu₂O₃ nanowires sulfurized at 700 °C without preheating under vacuum. PXRD shows ~50/50 mixture of EuS and Eu₂O₂S.](image)

After helpful discussions with Efrain Rodriguez at NIST, we found that by first heating the material under vacuum, followed by immediate sulfurization, the material could be converted to EuS at significantly lower temperatures. Rare earth oxides, including Eu₂O₃ can be very hygroscopic, absorbing water, as well as reacting with CO₂ to form carbonates on the surface. The presence of these materials on the Eu₂O₃ surface was reacting with the H₂S, first creating an outer shell of Eu₂O₂S before the Eu₂O₃ core has a chance to react. A TGA-DTA thermogram of Eu₂O₃ wires left in ambient conditions, shown below in Figure 14, shows that when the material is heated to 200 °C and held for a period of time, a small percentage, 1%, is lost. This is attributed to water, because when FT-IR studies were performed; the material did not show a strong carbonyl stretch, which would be very strong and sharp. Figure 14 shows that no
change is observed beyond ~20 minutes; the reaction was held for ~19 hours, without further change (only shown to ~90 minutes). To ensure full surface dehydration, the material was held under vacuum for 1 hour in all future sulfurizations.

![Figure 14. TGA-DTA thermogram of Eu₂O₃ nanowires losing adsorbed water at 200 °C.](image)

Furthermore, to ensure homogenous sulfurization, the Eu₂O₃ needs to be ground with a mortar and pestle to make a fine powder. Larger chunks of material give less surface area, and cause some portions of the material to be less available to react with H₂S. However, because we are trying to preserve the morphology, it was a concern that mechanical stress could destroy the morphology. To ensure this did not happen, SEM studies were performed to test the stability of the material during grinding. Eu(OH)₃ wires were ground with a mortar and pestle for 2 hours, periodically removing portions, and preparing SEM samples. Shown below in Figure 15 are these images, which shows that the material can be safely ground for 5 minutes without concern of destroying morphology, and by 40 minutes, morphology was completely destroyed. To be very conservative, samples were never ground more than 1 minute.
Once the surface material was dehydrated, it was observed that sulfurization to EuS could take place at significantly lower temperatures. Shown below in Figure 16 are SEM images of EuS formed from Eu$_2$O$_3$ nanowires. It was our hope that we could find a temperature at which we could synthesize EuS, but be low enough in temperature to avoid agglomeration, and preserve the nanowire morphology. As observed in material made at all temperatures, this was not achieved. Interesting though, EuS could be formed at significantly lower temperatures than normal; the leftmost image in Figure 16 shows EuS synthesized at 450 °C. Although this didn't maintain nanowire morphology, the fact that it was identified as EuS was significant, because higher temperatures are normally required, closer to 700 °C.29
2.2.4 Sodium-doped EuS

A closer examination of the PXRD pattern of the material synthesized at 450 °C is shown below in Figure 17. Although this material resembles EuS, the blue reference lines, labeled with their hkl faces indicate where the diffraction peaks should be seen. Looking at the lower diffraction angles, the (111) peak should appear at 25.9°, but appears at a higher angle, 26.9°. The same is observed at higher angles in the (420) peak, to a more significant degree, appearing at 74.1° versus 70.5°. This shift to greater 2θ values is indicative of a smaller unit cell; if the peak shift were a consistent value, it could be attributed to a zero point error, due to a difference in sample height on the instrument, however, that was not observed.
As was done with TmS, discussed in Chapter 1, the PXRD pattern in Figure 17 was analyzed by Rietveld refinement. A plot of the structural refinement for the EuS material synthesized at 450 °C is shown below in Figure 18.
Rietveld refinement gave the expected result that the lattice cell constant of the material was decreased; the literature value of EuS shrank from 5.969 Å to ~5.715(1) Å. This result was expected by the visual examination of the EuS pattern, however, an additional discovery was made that the calculated intensities for EuS did not match with the experimentally measured pattern. When the model was refined based on an increased occupancy of sulfur or decreased occupancy of europium, the refinement converged with a greater fit factor. Although there are layered materials where anion/cation excesses can exist as interstitial atoms, this is not likely in EuS because of its simple cubic structure.

Although the calculated pattern fit better with the experimental pattern better when a europium deficiency was applied to the model, the mechanism behind such a deficiency was
unclear. We propose that at lower synthetic temperatures it is possible that the trivalent europium might not be reduced to the divalent state, while still converting the material to the EuS structure, and replacing oxygens with sulfur. In order to maintain charge balance in this proposed structure, a formula such as $\text{Eu}^{3+}_{0.67}\text{S}$ could be possible. This phenomena was ascribed to effects from the nanoscale; when commercially available bulk $\text{Eu}_2\text{O}_3$ was sulfurized at 450 °C, only $\text{Eu}_2\text{O}_3$ and $\text{Eu}_2\text{O}_2\text{S}$ were observed in the resulting PXRD pattern; nothing like that observed in Figure 18.

Generally, no occurrence of incomplete europium reduction is preceded in the literature, even in nanoscale material, with the increased surface area and associated strain. Because of the extraordinary stability of divalent europium based on the electron configuration, $\text{Eu}_2\text{S}_3$ is not a known phase. There is one reported europium sulfide phase, $\text{Eu}_3\text{S}_4$,\textsuperscript{31} which has a normal spinel-type structure, AB$_2$X$_4$, with divalent europium in the A site occupying tetrahedral holes, and trivalent europium in the B site occupying octahedral holes: $\text{Eu}^{2+}\text{Eu}^{3+}_2\text{S}_4$. $\text{Eu}_3\text{S}_4$ has a very different crystal structure than EuS; it is body-centered cubic, based on the Th$_3$P$_4$ structure, with the space group I-43d, and does not match with our obtained product, which is in a rock salt cubic structure, with space group Fm-3m. Based on this smaller, europium deficient material observed, the synthetic route was re-examined to determine where this shift in the cell lattice and change in europium occupancy could be originating from, shown below in Figure 19.

$\text{Eu(NO}_3\text{)}_3 + \text{NaOH} \rightarrow \text{Eu(OH)}_3 \rightarrow \text{vac} \rightarrow \text{Eu}_2\text{O}_3 \rightarrow \text{H}_2\text{S} \rightarrow \text{EuS}$

*Figure 19. EuS synthetic scheme.*

There are not a lot of different synthetic variables shown above. As conditions were changed, it was observed that with changes in the base, NaOH, that the lattice shift and europium
occupancy varied as well. When an alternative OH- source, KOH, was used, no cell lattice shift was observed at moderate synthetic temperatures of 650 °C. Based on this discovery, alternate sodium sources were used during synthesis. If Eu₂O₃, either in the bulk or nanoscale, was mixed with a sodium source; both NaOH and NaCl were utilized, the same changes in lattice parameter and europium occupancy were observed. This combination of factors, culminating with the reaction of Eu₂O₃ + NaCl + H₂S, led us to realize that the driving force behind lattice shift was sodium doping. Although sodium was not intentionally added as a reactant during the synthesis, adventitious sodium was present from this stage forward; if the Eu(OH)₃ nanowires were not thoroughly washed, sodium would be present, remaining from the addition of NaOH to Eu(NO₃)₃. When the PXRD pattern was refined based on sodium occupancy, with the Eu and Na occupancies constrained to total 1, the χ² fit value was even stronger, and could now be explained based on the given synthetic conditions.

The decrease in temperature required to synthesize EuS-like material was initially attributed to an effect of the nanoscale Eu₂O₃ wires being used, but once it was found that the presence of sodium was the driving force, we discovered sodium-doping was not limited to nanoscale material. If commercially available, bulk Eu₂O₃ was manually mixed with a sodium source, either NaCl or NaOH, the same shift in lattice constant was observed.

In addition to shifting the cell lattice and europium occupancy, as shown below in Figure 20, both of these factors vary systematically based on the synthetic temperature. At lower synthetic temperatures, greater amounts of sodium occupancy was observed in the PXRD patterns. In all of the syntheses represented in Figure 20, it is assumed that approximately the
same amount of sodium is present, because the same synthetic conditions were present in the syntheses and workup of the Eu(OH)$_3$ nanowires.

In all syntheses which showed Eu$_2$O$_3$ or Eu$_2$O$_2$S impurities, these were used as internal references, and their lattice constants were kept at literature values, so only the Eu$_{1-x}$Na$_x$S lattice constants were varied. To further verify the shift in lattice constant, electron diffraction images were obtained by performing selected-area electron diffraction using a transmission electron microscope; this images are shown below in Figure 21. Although electron diffraction is less accurate than x-ray diffraction, varying up to 3%, the trends are consistent, and show the same shift in lattice constant.

![Figure 20. Cell constant and sodium occupancy of europium sulfide synthesized at different temperatures.](image_url)
Figure 21. Selected-area electron diffraction images of materials synthesized at 450, 600, and 700 °C, having lattice constants of 5.711, 5.832, and 5.851 Å, respectively. Lattice shifts are consistent with those of the powder x-ray diffraction patterns.

To better understand the graph shown above in Figure 20, and the driving force behind sodium doping, three important things must be understood. First, there is a strong correlation between the cell lattice and the sodium occupancy; shown above in Figure 20, the red and blue data points representing the cell constant and sodium occupancy, respectively, always lie very close to one another. This can be further demonstrated below in Figure 22, where the cell lattice and sodium occupancy are plotted against one another, and show a strong linear correlation. Both values were refined independently from one another; the cell lattice is derived from peak position, and the occupancy from intensities. The linear correlation between cell constant and Na occupancy suggests the solid solution, Eu$_{1-x}$Na$_x$S obeys Vegard’s law.$^{32}$
Second, in terms of the shape of the curve, syntheses performed at 450 °C or below always gave a cell lattice of approximately 5.7 Å, and a sodium occupancy of approximately $x=0.5$. This is believed to be the minimum cell lattice, and the maximum sodium doping level; further discussion on this limit will follow.

Third, the two factors which govern the shape of the rest of the curve are the rate of europium reduction, and the rate of sodium diffusion. I propose that the rate of europium reduction varies with temperature to a stronger degree than the rate of sodium diffusion which can be essentially considered to be consistent. With these two mechanisms in place, let us compare three syntheses at different temperatures, with a small amount of sodium present (10 mol % Na, 90 mol % Eu):

**High temperature synthesis**: Eu$^{3+}$ reduces to Eu$^{2+}$ at fast rate, so some sodium diffuses into
structure as material goes into EuS crystal structure, but the material is still largely reduced.

Obtained product: $\text{Eu}_{0.9}\text{Na}_{0.1}\text{S}$.

**Moderate temperature synthesis:** Compared to the previous synthesis, Na diffuses into structure at faster rate, relative to Eu$^{3+}$ reduction, leaving some material without sodium. Obtained products: $\text{Eu}_{0.7}\text{Na}_{0.3}\text{S} + \text{Eu}_2\text{O}_2\text{S}$.

**Low temperature synthesis:** Maximum amount of sodium will diffuse into structure before Eu$^{3+}$ can reduce, leaving even more material to react with sodium. Obtained products: $\text{Eu}_{0.5}\text{Na}_{0.5}\text{S} + \text{Eu}_2\text{O}_2\text{S}$.

One of the important results to obtain from the three preceding example syntheses is that once the available amount of sodium has diffused into the structure and been sulfurized into EuS, any remaining $\text{Eu}_2\text{O}_3$ will only be reacted to $\text{Eu}_2\text{O}_2\text{S}$. This demonstrates that the presence of sodium is lowering the required synthetic temperature of the EuS structure. These examples exhibit the direct relationship of sodium and europium reduction.

Based on these syntheses and concepts, we put forward the proposed formula: $\text{Eu}^{2+}_{1.2}\text{Eu}^{3+}_{x}\text{Na}_x\text{S}$. This shows that if EuS is doped with sodium at $x=0.5$, none of the material will have reduced from Eu$^{3+}$ to Eu$^{2+}$. To further this point, if the moments of Eu$^{3+}$ and Na$^+$ are intrinsically connected, reducing Eu$^{3+}$ should remove Na$^+$ from the material as well. When $\text{Eu}_{0.5}\text{Na}_{0.5}\text{S}$ is reduced by reaction with europium vapor, we believe that the following occurs, with the sodium-doped and reduced PXRD patterns shown below in Figure 23, in green and blue, respectively:

$$\text{Eu}^{3+}_{0.5}\text{Na}^{+}_{0.5}\text{S} + \text{Eu}^0 + \text{Eu}^{3+}_{2}\text{O}_2\text{S} \rightarrow \text{Eu}^{2+}\text{S} + \text{Na}_2\text{O}$$
Although it was assumed this synthesis proceeded by the role of europium as a reductant, the same reaction was repeated without europium; Eu$_{0.5}$Na$_{0.5}$S was heated under dynamic vacuum in the same apparatus with the same reaction conditions; no change in material was observed. This reaction with europium strongly suggests that the sodium content and europium valency are intrinsically connected. To examine the valence state of europium more directly, studies were performed to probe to valency of europium in these materials through XPS and $^{151}$Eu Mössbauer spectroscopy.

XPS studies were performed on a series of materials with a range of doping levels (made at different synthetic temperatures from nanoscale material) to probe the relative concentration of Eu$^{3+}$ to Eu$^{2+}$, whose signals are well separated. Although it was difficult to quantify the exact ratio of Eu$^{2+}$ to Eu$^{3+}$, it is clear that decreasing sodium content (increasing temperature) corresponds to a higher Eu$^{2+}$/Eu$^{3+}$ ratio, shown in Figure 24. One complication in quantifying the
ratio is the observed increase in oxygen levels at low doping values. This creates ambiguity of the source of Eu$^{3+}$ as due to alkali metal doping versus the presence of small amounts of Eu$_2$O$_3$ and Eu$_2$O$_2$S impurities in these materials as seen in the PXRD patterns.

![Graph showing XPS data for the 4d Eu band; showing increase Eu$^{2+}$/Eu$^{3+}$ ratios at increased synthesis temperatures.](image)

**Figure 24.** XPS data for the 4d Eu band; showing increase Eu$^{2+}$/Eu$^{3+}$ ratios at increased synthesis temperatures.

Unfortunately, when the XPS spectra were being measured, it was not yet suspected that sodium-doping was present, so that region was not focused on. During XPS measurements, first a survey scan is taken over the whole energy range (0-1200 eV). Although it would be significantly stronger evidence if this region (Na 1s edge$^{33}$) was measured in greater detail with more scans at a lower speed, by zooming in on that region of the survey scan, shown below in Figure 25, it is still possible to see the increase in sodium content with decreased reaction temperature.
Figure 25. XPS spectra of Eu$_{1-x}$Na$_x$S material, demonstrating a moderate increased presence of Na in materials synthesized at lower temperatures.

The volume difference of Eu$^{2+}$ (ionic radii for 6 coordinate cation is 1.31 Å) and Eu$^{3+}$ ions (versus 1.02 Å), is often reflected in changes in lattice parameters, but this is complicated by the presence of Na$^+$ which is slightly larger than Eu$^{3+}$ (1.16 Å).\textsuperscript{34} In contrast, the Mössbauer effect is a local method and allows one to distinguish between valence states resulting from differences in a local Eu environment, even if randomly distributed over the sample. It is particularly feasible with $^{151}$Eu spectroscopy where the isomer shift differences for Eu$^{2+}$ and Eu$^{3+}$ states are distinctly pronounced over the resonance line width. The shift occurs as a result of the change of the 4f state population ($4f^7 \rightarrow 4f^6$, respectively) resulting in the change of $s(p)$ electron density at the nucleus. The $^{151}$Eu (21.6 keV) Mössbauer spectroscopy, is sensitive to the local environment, was applied to investigate the possible valence states of europium with a range of sodium doping level.

The spectra of samples prepared with different doping levels clearly show the presence of
absorption peaks at positions either characteristic to a trivalent europium with the isomer shift close to zero or to a divalent Eu state with very large negative value ($\sim -12$ mm/s) of the isomer shift – or both, but not ‘in-between’. Intermediate values would have indicated an intermediate-valence state, which is understood as the dynamic process of fluctuation between the two valence states at the rate larger than set by the observation method, of the order of $10^8$ s$^{-1}$ (see Figure 26).

The spectrum of the sample prepared at 350 °C, which based on Rietveld refinement of x-ray diffraction data is $\text{Eu}_{0.5}\text{Na}_{0.5}\text{S}$, consists of a single absorption peak originating from trivalent europium ions, based on the peak position. This data excludes the presence of the crystallographically proper EuS phase which should contain only divalent europium. The inability to fit the data well with a single Lorentzian line, is most likely due to the presence of a small amount of $\text{Eu}_2\text{O}_3$ impurity, as revealed in the powder x-ray diffraction. The top spectrum in Figure 26 shows the result of fitting with an additional separate component accounting for the europium oxide impurity (at the level of about 10%). The parameters of this impurity line were constrained to the literature values.$^{35}$ It is important to note that in general, due to limitations set by the resolution, it is not possible to identify different phases which contain $\text{Eu}^{3+}$ ions.

The higher temperature of synthesis ($650$ °C), with mid-range dopant, $\text{Eu}_{1-x}\text{Na}_x\text{S}$ for $x$ between 0.5 and 0, clearly exhibits divalent europium as expected for EuS phase. In addition, the $^{151}\text{Eu}$ Mössbauer spectrum reveals the presence of a large amount of trivalent europium in addition to the expected divalent component, shown in the second spectrum Figure 26. The absorption line related to $\text{Eu}^{3+}$ contributes to $42(2)$% of the total absorption spectrum area, and is described by the values of parameters which may be compared to those for the Lorentz line.
obtained for the spectrum of the Eu$_{0.5}$Na$_{0.5}$S (formed at 350 °C). While the value of line-width parameter, FWHM = 3.2(1) mm/s, agrees quite well with the value obtained in the case of the Eu$_{0.5}$Na$_{0.5}$S (350 °C sample), the line position, IS = -0.02(10), differs beyond the quoted statistical errors (see Table 4). It should be pointed that the description of the absorption profile with the single Lorentz line should be considered as effective, due to inability to resolve contributions from individual local environments of the europium ions (which, nevertheless preserve their valence state with $4f^6$ occupancy).

<table>
<thead>
<tr>
<th>Sample</th>
<th>IS [mm/s]</th>
<th>FWHM [mm/s]</th>
<th>Contr. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{3+}$</td>
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<td>3.6(2)</td>
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<tr>
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<td></td>
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<td>3.3(1)</td>
</tr>
</tbody>
</table>

Table 4. Values of parameters resulting for a single Lorentzian fit of the absorption peaks in the $^{151}$Eu Mössbauer spectra. Relative contributions (Contr.) of divalent and trivalent components are calculated as a respective fraction of the surface (area) under the resonance lines. The value may be used as an estimation of the abundance of europium in a given valence state if one neglects the differences in the magnitudes of the Mössbauer-Lamb factors.

The Mössbauer spectrum of the sample synthesized with lower doping values clearly demonstrates that the most dominant fraction (85%) represents divalent europium, but still some amount of trivalent ions can still be observed, seen in the bottom spectrum in Figure 26. It is possible there is Eu$^{3+}$ present as oxidized material that is not crystalline enough for observation by x-ray powder diffraction. The energy difference between Eu$^{2+}$ and Eu$^{3+}$ states in EuS is small and thus the local environment may easily influence the valence description of europium. 36
Eu Mössbauer spectra showing the oxidation state of europium compared to the synthetic temperature.

Figure 26. $^{151}$Eu Mössbauer spectra showing the oxidation state of europium compared to the synthetic temperature.

Europium sulfide has been doped with lanthanides, but to our knowledge there are no examples of doping with alkali or alkaline earth metals. By contrast, binary alkaline earth sulfides (MgS, CaS, SrS, BaS) with the same rock salt structure have been doped with Eu$^{2+}$ (or Ce$^{3+}$) and are well known to luminesce. These materials have been extensively studied for thin film electroluminescent phosphors. Beyond doped materials, there are very few ternary alkali metal lanthanide sulfide (A-Ln-S) phases known. The most commonly reported material has the composition ALnS$_2$ (A = alkali metal and Ln = lanthanide), in which the lanthanide is in the
trivalent oxidation state. Lanthanide reactions in alkali metal-polychalcogenide fluxes expanded this to include NaLnS$_3$ for Ln = La and Ce, which is relatively modest given the wide number of interesting new materials discovered in this solvent system.$^{39}$

Another class of compounds of interest for display materials are phosphors based on the lanthanide oxysulfides, Ln$_2$O$_2$S, which are difficult to prepare and frequently have poor nanostructured morphology.$^{40-42}$ Interestingly, Eu$_2$O$_2$S can be prepared using the same precursors for EuS nanoparticles (dtc complexes) but under an oxygen, rather than inert, atmosphere.$^{43}$ Recently it was discovered that well-defined nanostructures of Ln$_2$O$_2$S could be prepared as long as sodium doping was present.$^{44}$ Regardless of morphology, the authors were unable to form Ln$_2$O$_2$S nanomaterials unless sodium was incorporated. The role of Na$^+$ doping was ascribed to differences in the hard/soft nature of the cations in forming either the hard oxide (La$_2$O$_3$) or ‘soft’ oxysulfide (La$_2$O$_2$S) material. The high doping level (~10%) results in the formation of anion vacancies.

The material we have identified as Eu$_{0.5}$Na$_{0.5}$S, is the same composition as the previously reported NaEuS$_2$.\textsuperscript{45} The ALnS$_2$ material can exhibit two structure types: a cubic rock salt with disordered cations, or a hexagonal $\alpha$-NaFeO$_2$ material. The $\alpha$-NaFeO$_2$ structure has the same anion packing as the rock salt but with segregation of the monovalent and trivalent cations into alternating layers. Cation ordering is frequently observed when the charge between the two cations differs by more than one unit.$^{46}$ Previously, NaEuS$_2$ has been reported only in the cation-ordered hexagonal structure, and not the disordered cubic structure as we observe here. It seems reasonable that this is due to the low reaction temperatures where the highly charged Eu$^{3+}$ is
likely to have low diffusivity. It is interesting to note that in a comparison of the cell constants for the ALnS$_2$ series (Ln = Sm-Yb), the hexagonal $a$ parameter linearly decreases across the lanthanide series reflecting the lanthanide contraction of the Ln$^{3+}$ ions, but the cell constant for NaEuS$_2$ is off the trend line. The increased cell constant for the europium material may reflect the presence of some divalent europium.$^{34}$ By contrast, compared with the lanthanides that form the cubic materials NaLaS$_2$ (5.868 Å), NaCeS$_2$ (5.819 Å), NaNdS$_2$ (5.767 Å), the cubic NaEuS$_2$ cell constant (5.72 Å) reported here is consistent with trivalent europium.

At 350 °C without sodium, the europium sesquioxide is not reduced; only Eu$_2$O$_3$ is observed in the x-ray powder diffraction suggesting that Eu$^{2+}$ is not thermodynamically favored at this temperature. In the presence of sodium, the cubic rock salt material is formed, but always as Eu$_{0.5}$Na$_{0.5}$S even under a range of NaOH:Eu$_2$O$_3$ ratios. The oxidation state of the europium in the 1:1 metal ratio is purely trivalent, again suggesting the conditions are not reducing enough. The excess europium appears as Eu$_2$O$_3$ even under repeated sulfurization or extended reaction times.

Magnetic studies were performed on materials synthesized at different temperatures, determining the Curie-Weiss constant, $\theta$, and the strength of the magnetic moment, $\mu_{\text{eff}}$, using Curie-Weiss $1/\chi$ vs. $T$ plots, and when possible, the Curie temperature, $T_C$, using Arrott plots. The results are shown below in Table 5. These studies provide insight into both the europium valence (based on the magnetic moment, $\mu_{\text{eff}}$) as well as the ferromagnetic coupling.

$\mu_{\text{eff}}$ is a measure of the effective magnetic moment of a material. This relates to the calculation of magnetic spin, with:
\[ \mu_{\text{eff}} = 2 \sqrt{S(S+1)} \]

\(\mu_{\text{eff}}\) can be determined from the Curie constant, C, taken from the Curie-Weiss law:

\[ \mu_{\text{eff}} = \sqrt{\frac{C \cdot 3 k_B}{\mu_0 N_A \mu_B^2}} \]

<table>
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<th>(a (\text{Å}))</th>
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</tbody>
</table>

Table 5. Magnetic properties of \(\text{Eu}_{1-x}\text{Na}_x\text{S}\) at various doping levels. For each sample, the lattice constant, \(a\), and europium occupancy, \(x\), give the properties of the material. The Weiss constant, \(\theta\) gives the ferromagnetic ordering temperature, and the corresponding \(R^2\) value for its determination. \(\mu_{\text{eff}}\) gives the effective magnetic moment, and \(T_C\), the ferromagnetic ordering temperature determined by Arrott plots. For \(T_C\), N/A indicates a \(T_C\) could not be determined because of insufficient ferromagnetic ordering, and blank rows were measurements taken at Virginia Tech, where only a Curie-Weiss plot was measured.

Magnetic studies suggest that the ferromagnetic coupling in \(\text{Eu}_{1-x}\text{Na}_x\text{S}\) decreases with increasing doping levels (lower \(T_C\) and reduced ferromagnetic ordering temperatures, \(\theta\)). The loss of magnetic ordering is consistent with the replacement of the magnetic europium by non-magnetic sodium, resulting in disruption of the europium-europium magnetic communication.

What is interesting is the strength of the anti-ferromagnetic coupling, as observed in the large negative Weiss constants. One would expect the non-magnetic ion to disrupt any ferromagnetic coupling. Using the Curie-Weiss plots, it was found that the reduced magnetic moment (\(\mu_{\text{eff}}\))...
decreases with increasing sodium doping. The high $\mu_{\text{eff}}$ value found in stoichiometric EuS is consistent with the spin only value ($S = 7/2$) found for Eu$^{2+}$. As the sodium level increases, the concentration of Eu$^{3+}$ (with $S = 3$) increases, causing a reduction in $\mu_{\text{eff}}$.

At low enough temperature, below 450 °C, Eu$_2$O$_3$ (without sodium) will not react at all, and starting at 450 °C, Eu$_2$O$_3$ reacts to form Eu$_2$O$_2$S. For this reason, at low synthetic temperatures, the impurity phase is seen to be Eu$_2$O$_3$, and at higher temperatures, Eu$_2$O$_2$S. In studying the formation of Eu$_2$O$_2$S, we have also shown that Eu$_2$O$_3$ can react with EuS to give Eu$_2$O$_2$S:

$$\text{Eu}_2\text{O}_3 + 2 \text{EuS} \rightarrow 2 \text{Eu}_2\text{O}_2\text{S}$$

This reaction has been studied as a function of time and temperature, shown below in Table 6. Heating at lower temperatures, at 350 °C didn't yield any reaction, which isn't very surprising, given that Eu$_2$O$_3$ and H$_2$S don't react at that temperature either. At 800 °C, the reaction went to completion, showing only EuS by PXRD. At an intermediate temperature of 500 °C, a partial reaction was seen, showing a mixture of all three materials. This was run again for 5 hours instead of 2, but still showed starting materials. The two reactions at 500 °C were refined by Rietveld analysis, but it was ambiguous as to the relative amounts; it is difficult to get quantitative data on percent composition because of different crystallinities of materials.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>PXRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 °C</td>
<td>2 hr</td>
<td>Eu$_2$O$_3$ / EuS</td>
</tr>
<tr>
<td>500 °C</td>
<td>2 hr</td>
<td>Eu$_2$O$_3$ / Eu$_2$O$_2$S / EuS</td>
</tr>
<tr>
<td>500 °C</td>
<td>5 hr</td>
<td>Eu$_2$O$_3$ / Eu$_2$O$_2$S / EuS</td>
</tr>
<tr>
<td>800 °C</td>
<td>2 hr</td>
<td>Eu$_2$O$_2$S</td>
</tr>
</tbody>
</table>

_Table 6. Reaction of Eu$_2$O$_3$ and EuS to form Eu$_2$O$_2$S at varying reaction temperatures and times._
Because Eu₂O₃ and H₂S do not react at low temperatures (350 °C), but do so in the presence of sodium, this is a good technique to examine the ability of other materials to dope into the EuS structure. Although not yet extensively studied, both calcium and lithium are shown to dope into EuS, effectively observed through the similar lattice shift, observed by PXRD. Less understood are the products formed when using potassium or magnesium.

2.2.5 Other dopants in EuS

Reaction with KOH yields an unknown product, the PXRD pattern is shown below in Figure 27. No peaks in the pattern can be indexed to any known phases in the PDF-2 database. Results from varying the synthetic conditions in this reaction are shown below in Table 7. In the sodium system, the same sodium-doped product was obtained using sodium hydroxide or sodium chloride; this is not observed in the potassium system. If potassium bromide is used instead of potassium hydroxide at 350 °C, no reaction occurs. It is possible to solve the crystal structure of a material based on powder diffraction rather than the standard single-crystal structure determination approach, but this is typically done with high quality synchrotron data, with the availability of intense high angle reflections.⁴⁸
Table 7. Products obtained by reaction of Eu$_2$O$_3$, KOH, and H$_2$S under various reaction conditions.

To try and get a better understanding of the material, high-temperature PXRD studies were performed by heating the material on the hot stage of the diffractometer and studying its decomposition. The resulting diffraction patterns are shown below in Figure 28. The material undergoes three phase transitions; at 500, 700, and 1000 °C. At 500 °C, Eu$_2$O$_2$S is observed and some of the peaks from the unknown pattern disappear, suggesting that it could be multiple phases, as many of the peaks remain the same. It is still unclear what changes at 700 °C, but at 1000 °C, the only material remaining is Eu$_2$O$_3$, both the cubic and monoclinic phases (the
monoclinic phase is discussed in more detail in Chapter 3). The peaks which remain the same in all patterns correspond to the platinum sample holder, from the (111), (200), and (220) reflections at 39.8, 46.2, and 67.6°, respectively.

Reaction with magnesium chloride at higher temperatures (650 °C) gives EuS (no lattice shift observed in PXRD patterns) and MgS, however, at lower temperatures, 450 °C, Eu₃S₄ is observed. Depending on the synthetic temperature used, some mixture of Eu₂O₃, EuS, Eu₃S₄, MgS, and an unknown phase are obtained; these results are shown below in Table 8. Shown below in Figure 29 is the PXRD pattern of material synthesized at 450 °C, a mixture of EuS and Eu₃S₄ and an unidentified phase. As with the potassium system, these results are presented, but not explained in greater detail, as this system is not yet understood.

Figure 28. PXRD patterns of the material formed by reaction of Eu₂O₃, KOH, and H₂S, as the material is heated to 1200 °C under dynamic vacuum.
Table 8. Results of reactions of Eu₂O₃ + MgCl₂ + H₂S.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>PXRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 °C</td>
<td>Eu₂O₃ + Eu₃S₄ + EuS + ?</td>
</tr>
<tr>
<td>450 °C</td>
<td>Eu₃S₄ + EuS + ?</td>
</tr>
<tr>
<td>500 °C</td>
<td>MgS + EuS + ?</td>
</tr>
<tr>
<td>550 °C</td>
<td>MgS + Eu₂O₃ + EuS + ?</td>
</tr>
<tr>
<td>650 °C</td>
<td>MgS + EuS</td>
</tr>
<tr>
<td>800 °C</td>
<td>MgS + EuS</td>
</tr>
</tbody>
</table>

2.2.6 Gadolinium-doped EuS

Finally, as discussed in Chapter 1, there is strong motivation for doping EuS with trivalent lanthanides such as gadolinium, in order to strengthen magnetic communication, increasing the ferromagnetic ordering temperature. By starting with Eu₁₋ₓGdₓ(OH)₃ nanowires, we should hopefully be able to maintain the gadolinium level through the chemical conversions, and obtain Eu₁₋ₓGdₓS nanocrystals. Given the difficulty in maintaining morphology during the
sulfurization of Eu$_2$O$_3$, they may not remain as nanowires, but there is still strong motivation for this approach, to make any sort of nanoscale material.

Synthesizing Eu$_{1-x}$Gd$_x$S from the dtc precursors in the solid-state and in solution both have disadvantages. Solution synthesis has shown significant oxidation and loss of magnetic communication; furthermore no good approach has been discovered for shape control. Solid-state synthesis with the lanthanide dtc complexes leaves behind a significant amount of carbon and is a messier synthesis with a lot of organic byproducts.

Returning to the synthesis of the Ln(OH)$_3$ nanowires; Li's synthesis, shown below in Figure 30, starts from Ln$_2$O$_3$, dissolving the material in nitric acid to form the nitrate, then subsequent reaction with a hydroxide source in order to precipitate Ln(OH)$_3$. Starting from the oxide has two main advantages; lanthanides are often difficult to obtain with high-purity; because of the similarities in the lanthanides, they generally occur together in nature, and have similar reactivities so can be hard to separate. Lanthanide oxides are generally the purest sources, in terms of metal-content percentage, and secondly, the oxides are the most economic source.

$$\text{Ln}_2\text{O}_3 + \text{HNO}_3 \rightarrow \text{Ln(NO}_3)_3 + \text{NaOH} \rightarrow \text{Ln(OH)}_3$$

*Figure 30. Scheme of Ln(OH)$_3$ synthesis used by Li.*

Unfortunately, when trying to adapt Li's synthesis$^{21}$ to form Eu$_{1-x}$Gd$_x$(OH)$_3$ nanowires, it was discovered that Eu$_2$O$_3$ and Gd$_2$O$_3$ have different solubilities in nitric acid, which could make targeting a specific doping-level more difficult. In order to bypass this, we have started with the nitrates, as seen below in the scheme in Figure 31, which are both of which are extremely soluble in water.
Eu(NO$_3$)$_3$ + Gd(NO$_3$)$_3$ + NaOH $\rightarrow$ Eu$_{1-x}$Gd$_x$(OH)$_3$

*Figure 31. Scheme of Eu$_{1-x}$Gd$_x$(OH)$_3$ synthesis.*

Material was successfully made by this route which was indexed by PXRD to Eu(OH)$_3$. Starting with these gadolinium-doped materials, they were converted to the sesquioxide and sulfide through the methods presented earlier. These conversions were performed targeting three different doping levels, and in order to verify that the true doping level corresponds with the starting mixture of Eu:Gd(OH)$_3$, ICP-MS was used to measure the ratio of Eu to Gd, just as was done with the dtc precursor method. The results were very consistently close to the targeted doping level, which are shown below in Figure 32.

*Figure 32. PXRD patterns of gadolinium-doped Eu(OH)$_3$ wires through their conversion to Eu$_2$O$_3$ and EuS. The graph on the right shows that the doping-level remains consistent between conversions.*

Despite successful synthesis of different doping levels of Eu$_{1-x}$Gd$_x$S, preliminary magnetic results were not promising, shown below in Table 9. These syntheses and measurements were performed before the risk of sodium-doping was known, so just as magnetic
communication was disrupted in Table 5 with Eu$_{1-x}$Na$_x$S material, it is likely here as well, due to trace sodium-doping.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.006</td>
<td>18.89 K</td>
</tr>
<tr>
<td>0.01</td>
<td>18.80 K</td>
</tr>
<tr>
<td>0.1</td>
<td>16.24 K</td>
</tr>
</tbody>
</table>

*Table 9. Early magnetic results from Eu$_{1-x}$Gd$_x$S samples.*

Since the discovery of sodium-doping in EuS, this project has been revisited, with assistance from Haydee Dalafu, Natasha Khatri, and Nicholas Rosa, with preliminary results shown below in Table 10. In these syntheses, Eu$_{1-x}$Gd$_x$(OH)$_3$ wires were thoroughly washed before dehydration, to eliminate the possibility of sodium-doping. Initially, increases in magnetic ordering temperatures were not observed at any doping-level. Europium oxysulfide was observed in some PXRD patterns, and because of our experiences with oxidized material disrupting magnetic communication, these materials were annealed in H$_2$S. Still, no increases in magnetic ordering resulting from gadolinium-doping were observed, so as a final attempt at eliminating any possible oxidation, the material was annealed in europium vapor, which has shown promise.
Table 10. Magnetic results for Eu$_{1-x}$Gd$_x$S nanocrystals. $\theta/T_C$ ordering temperatures given in K. Initial materials were made by sulfurization of (Eu$_{1-x}$Gd$_x$)$_2$O$_3$. The 2nd and 3rd sets of data show results after annealing in H$_2$S and europium vapor, respectively.

As of late, downtime of SQUID instruments has impeded progress on continuing to examine these materials, but increases in ordering temperatures, both $T_C$ and $\theta$, at doping levels, $x=0.05$ and $x=0.09$, once annealed in Eu vapor, indicate proof of concept, shown in Table 10 above and we expect to see improvements on the data obtained as compared to the $\theta$ vs. $x$ results from Chapter 1, from the dtc precursor thermolysis.

Recent development of the sulfurization of Eu$_2$O$_3$ nanowires has shown that it is possible to obtain wire-like structures in EuS by reaction at high temperatures and short reaction times. Shown below in Figure 33 is material which indexes to EuS by PXRD, and whose SEM image clearly show wire-like morphology; these were formed at 800 °C with H$_2$S, reacted only for 10 minutes. This is in stark contrast to material shown in Figure 16:
In order to achieve this morphology, the synthesis was changed; the old and new syntheses are shown below.

Old synthesis:

1. Apply dynamic vacuum, heat to 200 °C, hold 1 hour
2. Remove vacuum, activate H₂S flow, increase to 800 °C, hold 2 hours
3. Remove from heat, once at room temperature, close H₂S flow

Change to synthesis:

2. Heat to 800 °C, remove vacuum, activate H₂S flow, hold 10 minutes

Additionally, the apparatus was improved so that the setup was not opened to air in between the vacuum and H₂S steps.

EuS shown in Figure 33 appears to be of a wire-like morphology, however there does appear to be some minor agglomeration, so it was doubtful that the material has remained single-
crystalline, as can be seen below in Figure 34, shown by high resolution TEM. Further changes in the synthetic conditions may further improve this morphological control, but a single-crystalline product is not likely.

![Figure 34. HRTEM image of EuS nanowires.](image)

Work by Könenkamp has been done in sulfurizing ZnO nanowires to ZnS;\(^{11}\) it was shown that reaction with sulfur vapor gave a cleaner morphology than H\(_2\)S, shown below in Figure 35. Previously, using sulfur vapor in our synthesis would have proved difficult to maintain for 2 hours, both to provide a sufficient reservoir of reagent, and more difficulty, to avoid clogging the apparatus. H\(_2\)S has the advantages of being commercially available in gas cylinders, and eliminates the possibility of solidified sulfur clogging the apparatus. Recent developments reducing the synthetic time from 2 hours to 10 minutes make using sulfur vapor more feasible. However, reaction of ZnO to ZnS only requires anion-exchange, whereas Eu\(_2\)O\(_3\) to EuS also
requires reduction of Eu$^{3+}$, which may be more difficult with sulfur vapor, when compared to the more strongly reducing H$_2$S.

Figure 35. SEM images of ZnO nanowires (left) converted to ZnS with H$_2$S (center) and sulfur vapor (right). Used without permission from Könenkamp.11

Preliminary attempts at the synthesis of Eu$_{1-x}$Na$_x$S under these quicker synthetic conditions do not exhibit sodium-doping. When NaOH was mixed with Eu$_2$O$_3$ wires and heated in H$_2$S, no shift in the cell lattice of the products was observed by PXRD. This could have two explanations; the shorter reaction time may not be enough time for sodium to diffuse into the lattice; Eu$_{1-x}$Na$_x$S could be the thermodynamically favored product. This is unlikely however; in a control experiment where EuS and NaOH were mixed together and heated, no sodium-doping is observed, only when sodium is added during the sulfurization process.

A more likely explanation is loss of NaOH during the heating to 800 °C under vacuum. Shown below in Figure 36 is a TGA-DTA thermogram of Eu$_2$O$_3$ nanowires with remnant NaOH present, from the Eu(OH)$_3$ synthesis, being heated to 1000 °C. Loss of water, around 1% is observed by 200 °C, as in Figure 14, but at higher temperatures, weight loss continues, and is likely due to loss of remnant NaOH by hydrolysis. This further explains why Eu$_{1-x}$Na$_x$S was never observed previously in our lab, when synthesis of Eu$_2$O$_3$ by dehydration of Eu(OH)$_3$ was
performed at higher temperatures in air.

Figure 36. TGA-DTA thermogram of Eu$_2$O$_3$ nanowires, with remnant NaOH, heated to 1000 °C.

2.3 Experimental.

**General information.** Europium(III) nitrate hexahydrate and europium(III) oxide were obtained from Strem. Gadolinium(III) nitrate hexahydrate, sodium hydroxide, and sodium chloride were obtained from Sigma. Europium metal was obtained from Alfa Aesar. All chemicals were used as received. Thermal analysis was performed on an SDT Q600 TA instrument. Simultaneous TGA-DTA data were studied from samples in an alumina pan from 25-1000 °C under a N$_2$ flow of 20 mL/min, with a heating rate of 10 °C/min. Elemental analysis was performed on a Perkin Elmer 2400 Series II CHN/O analyzer.
Electron microscopy. Selected-area electron diffraction images were taken with a JEOL JEM 2100F Field Emission Gun Transmission Electron Microscope, at 200 kV. SEM images were taken with a Zeiss SUPRA 55-VP scanning electron microscope, at an acceleration voltage of 20 kV with an in-lens detector. High resolution TEM and selected-area electron diffraction were performed with a JEOL JEM 2100F Field Emission Gun Transmission Electron Microscope, at 200 kV, at the University of Maryland Nanoscale Imaging Spectroscopy and Imaging Laboratory. Lower resolution TEM images were taken on a JEOL JEM 1200 EXII TEM operated at 80 keV using a high resolution Tietz F224 camera at Villanova University.

X-ray diffraction. Powder x-ray diffraction patterns were obtained using a Rigaku Ultima IV X-ray powder diffractometer with CuKα radiation at 40 kV and 44 mA with a D/teX silicon strip detector. For high-temperature PXRD studies, material was loaded on a platinum sample plate, which was heated according to the specifications of the experiment. For example, Figure 12 was generated with the following conditions: the heating rate was set to 10 °C/min, with 2 minute equilibration steps, followed by an x-ray measurement, all performed under dynamic vacuum. These steps were performed at 25, 50, 100, 150, 200, 250, 275, 300, 325, 350, 375, 400, 450, 500, 600, 700, 800, 900, 1000 and 1200 °C. Rietveld refinement was performed using GSAS, through the EXPGUI interface. As appropriate, the parameters which were refined were cell lattice constants, thermal parameters (for each phase, all atoms were constrained to give the same parameter), site occupancy, background, zero-point error, phase fractions, and GW, LY, and asym profile parameters.

ICP-MS. Europium-gadolinium ratios were determined by laser ablation inductively coupled
plasma mass spectrometry (LA-ICPMS). Samples were ablated using a 213 nm wavelength ultraviolet laser (New Wave UP213) and ratios measured using a ThermoFinnigan Element 2 magnetic sector, single collector ICP-MS. Samples were ablated with a 15 µm spot and a photon flux between 2 and 3 J/cm$^2$ and a laser repetition rate of 7 Hz. A mixture of both spots and lines were used for measurement, with no discernible difference in the results. Ablation was into a stream of helium, with downstream mixing into the Ar flow for introduction into the plasma. NIST610 (a synthetic glass doped with lithophile trace elements) was ablated under matching conditions (though with a larger spot size) for standardization. Both Eu isotopes (151 and 153) were measured as were all 7 Gd isotopes (152, 154, 155, 156, 156, 158 and 160). All were measured in analog mode due to the high Eu and Gd concentrations, but $^{152}$Gd and $^{154}$Gd were not usefully determined due to their low natural abundance. The other five Gd isotopes were used for elemental ratio determination. Other rare earths were measured, but remained largely below detection. Elemental ratios were determined using LAMTRACE software, with an assumed Eu abundance – hence ratio determination rather than absolute abundances. Both Eu and the abundant Gd isotopes gave internally consistent results and isotopic ratios with the expected natural abundances. Samples were mounted on double sided tape, with the fine powders pressed into the tape with a clean spatula to ensure adherence to the surface. Based on the Eu:Gd ratio, the composition for the polycrystalline samples was determined from ICP-MS.

**Magnetic measurements.** Magnetic measurements were made on a Quantum Design MPMS SQUID from 5 K to 300 K in a 10 kOe field, performed either at George Washington University
or Virginia Polytechnic Institute. Crystalline, powdered samples containing ~10 mg of material were loaded into a gelatin capsule. The sample was positioned within a plastic straw for analysis. The diamagnetic correction of the sample was calculated using \( \chi_d = (-184.03/2) \times 10^{-6} \) emu/mole, and was subtracted. The ferromagnetic ordering temperature, \( \theta \), was determined using \( 1/\chi \) versus \( T \) plots. The plots were fit using a linear regression. Arrott plots were obtained by calculating isotherms from 13 to 23 K. For each field, 500, 1000, 2000, and 5000 Oe, the magnetization was squared (emu²/mol²) and plotted as a function of H/M (Oe g/mol). The values of \( M_S^2 \) where H/M is zero (for each isotherm) were then graphed as a function of temperature. The \( M_S^2 \) vs T plot where \( M_S^2 \) goes to zero was used to determine the Curie temperature, \( T_C \), based on a linear regression. This is depicted in Figures 5 and 6 in Chapter 1.

**X-ray Photoelectron Spectroscopy (XPS).** XPS analysis was performed using a PHI 5400 XPS system (base pressure < 5 x 10⁻⁸ Torr) and samples were analyzed using Mg Kα X-rays (1253.6 eV). Samples were prepared by pressing a small quantity (~5 mg) of Eu powder onto double sided copper tape (1 x 1 cm²) so that no copper was visible through the powder. Photoelectrons ejected from each sample were measured with a precision high energy electron analyzer operating at constant pass-energy. Survey scans performed to determine elemental composition were completed using a pass-energy of 178.95 eV at a scan rate of 0.250 eV/step. The regions containing the desired elements of interest were swept using higher-resolution scans completed using a pass-energy of 89.45 eV at a scan rate 0.125 eV/step. Spectra were processed with commercially available software (CasaXPS), and atomic concentrations were quantified by integration of the relevant photoelectron peaks.⁵²
**Eu Mössbauer studies.** $^{151}\text{Eu}$ (21.6 keV) Mössbauer spectroscopy was applied to investigate the possible valence states of europium with a range of sodium-doping levels. Measurements were carried out at room temperature with the radiation parent nuclide $^{151}\text{Sm}$ in a $\text{Sm}_2\text{O}_3$ matrix. Due to the unresolved quadrupole splitting, this source gives a broadened emission ‘single-line’ with a half-width of about 1.4 mm/s. The data were fitted with a single Lorentzian line for each separate absorption peak which is described by the full width at half maximum (FWHM) and the line position (isomer shift – IS) relative to the source in the form of $(^{151}\text{Eu})\text{Sm}_2\text{O}_3$. This simple approach is justified for the purpose of simply identifying and characterizing the valence states of europium.

**Eu$_{1-x}$Gd$_x$(OH)$_3$ nanowires.** Generally, $\text{Eu(NO}_3)_3\cdot6\text{H}_2\text{O}$ (0.25 g, 0.56 mmol) was dissolved in 5 mL $\text{H}_2\text{O}$. For Gd-doped samples ($x \neq 0$), a solution of $\text{Gd(NO}_3)_3\cdot6\text{H}_2\text{O}$ in water was added, to achieved targeted doping level. 1 g NaOH was added to make a 5 M solution, which was stirred for 20 minutes; a white, flocculent precipitate formed immediately. The solution was put into a 20 mL Teflon lined Parr Bomb and heated at 180 °C for 6 hours. Once cooled to room temperature, the supernatant was decanted and discarded. The vessel was filled to 10 mL with $\text{H}_2\text{O}$, and the resulting solution was centrifuged for 10 minutes. The supernatant was decanted and discarded. This was repeated with 10 mL ethanol. The precipitate was dried under vacuum for 1 hour, and the material was lightly ground with a mortar and pestle to increase surface area. Percent yield: 88%. Reagent amounts and reaction time and temperatures varied when changing nanowire aspect ratio. Powder x-ray diffraction patterns matched that of $\text{Eu(OH}_3$, PDF 00-017-0781 (ICDD, 1979).
(Eu$_{1-x}$Gd$_x$)$_2$O$_3$ nanowires. 200 mg Eu$_{1-x}$Gd$_x$(OH)$_3$ nanowires were heated in a quartz tube in a Lindberg/Blue M horizontal tube furnace at 500 °C for 3 hours under dynamic vacuum. Percent yield: 83%. Powder x-ray diffraction patterns matched that of the cubic phase of Eu$_2$O$_3$, PDF 00-034-0392 (ICDD, 1984).

Eu$_{1-x}$Gd$_x$S nanocrystals. (Eu$_{1-x}$Gd$_x$)$_2$O$_3$ nanowires were heated on a graphite boat in a quartz tube in a Lindberg/Blue M horizontal tube furnace at 200 °C for 1 hour under dynamic vacuum. A mixture of 5% H$_2$S, 95% N$_2$ was then flowed through the quartz tube over the material, and the furnace was set to 800 °C for 2 hours. After heating, the tube was removed from the furnace, and once cooled to room temperature, the stopcocks and valves were closed, and the flow of gas was ceased. Percent yield: 90%. Obtained powder x-ray diffraction patterns could be indexed to EuS, PDF 00-026-1419 (ICDD, 1974).

Eu$_{1-x}$Gd$_x$S annealing. Materials were first annealed in 5% H$_2$S, 95% N$_2$; on a graphite boat in a quartz tube, H$_2$S flow was initiated, and the furnace was heated to 200 °C. After 1 hour at 200 °C, the temperature was increased to 800 °C for 2 hours, at which point the tube was removed from the furnace. When the tube cooled to near room temperature, H$_2$S flow was stopped. Materials were then re-characterized by PXRD and SQUID. In a nitrogen atmosphere glovebox, material was placed on top of ~100 mg Eu foil (0.1 mm thick) on a graphite boat in a quartz tube. The closed tube was taken out of the glovebox and heated in a Lindberg/Blue M horizontal tube furnace at 700 °C for 3 hours under dynamic vacuum. In both cases, a powder x-ray diffraction pattern was matched with that of EuS, PDF 00-026-1419 (ICDD, 1974).

EuS nanowires. Eu$_2$O$_3$ nanowires were heated on a graphite boat in a quartz tube in a
Lindberg/Blue M horizontal tube furnace at 200 °C for 1 hour under dynamic vacuum, and then 
the temperature was increased to 800 °C. A mixture of 5% H₂S, 95% N₂ was then flowed through 
the quartz tube over the material for 10 minutes. After heating, the tube was removed from the 
furnace, and once cooled to room temperature, the stopcocks and valves were closed, and the 
flow of gas was ceased. Percent yield: 96%. Obtained powder x-ray diffraction patterns could be 
indexed to EuS, PDF 00-026-1419 (ICDD, 1974).

**Eu₁₋ₓNaₓS nanocrystals.** Eu₂O₃ (either nanowires as synthesized, or bulk material) was ground 
with a mortar and pestle to increase surface area and homogenize the sodium distribution. 
Initially, nanowires containing remnant NaOH were used, later, more thoroughly washed 
nanowires were used, and NaOH or NaCl was manually loaded, and ground with the material. 
Sample material was heated on a graphite boat in a quartz tube in a Lindberg/Blue M horizontal 
tube furnace at 200 °C for 1 hour under dynamic vacuum. A mixture of 5% H₂S, 95% N₂ was 
then flowed through the quartz tube over the material, and the furnace was set to a temperature 
between 350 and 900 °C, that varied with the experiment, for 2 hours. After heating, the tube was 
removed from the furnace, and once cooled to room temperature, the stopcocks and valves were 
closed, and the flow of gas was ceased. Obtained powder x-ray diffraction patterns could be 
indexed using EuS, PDF 00-026-1419 (ICDD, 1974), with differences in peak position and 
intensity due to a shift in the lattice constant and europium occupancy, as analyzed by Rietveld 
refinement. Other dopants were tested through the same technique.

**EuₓNa₁₋ₓS reduction.** In a nitrogen atmosphere glovebox, 10 mg Eu₁₋ₓNaₓS nanocrystals were 
placed on top of Eu foil (100 mg, 0.1 mm thick) on a graphite boat in a quartz tube. The tube was
taken out of the glovebox and heated in a Lindberg/Blue M horizontal tube furnace at 700 °C for 3 hours under dynamic vacuum. Percent yield: 78%. A powder x-ray diffraction pattern was matched with that of EuS, PDF 00-026-1419 (ICDD, 1974).

References


Chapter 3

SOLID-STATE SYNTHESIS OF EUROPIUM OXIDE

3.1 Introduction

Europium monoxide, EuO, has a $T_C$ of 69 K,\(^1\) compared to the lower $T_C$ for EuS of 16 K. This difference can be explained by examining their electronic structures. Shown below in Figure 1 are the band structures for the europium chalcogenides, EuO through EuTe, and their corresponding electronic band gaps, $E_g$, and magnetic ordering temperatures, $T_C$ and $T_N$. A band diagram can be thought of as a molecular orbital diagram with broadened orbitals; because we are looking at a bulk picture of the material, there are Avogadro's number of energy states present.

These band diagrams in Figure 1 are mostly what you would expect for a normal semiconductor, with the filled $p$ orbital acting as the valence band, which is the equivalent of the highest occupied molecular orbital, HOMO, in a molecular orbital diagram, and the unfilled $d$ orbital as the equivalent of the lowest unoccupied molecular orbital, LUMO. Normally, $E_g$ is calculated by the difference between the valence and conduction bands, but the difference in the europium chalcogenides is the presence of the $f$ orbitals. As these orbitals are non-degenerate and do not participate in bonding, they are narrow and unbroadeened, but are filled with electrons, so $E_g$ is smaller, only the difference between the $f$ orbital and the conduction band. Typical $E_g$ values are $<1$ eV for a metal, 1-3 eV for a semiconductor, and $>3$ eV for an insulator.
The relationship between $E_g$ and the magnetic ordering temperatures can be seen that as $E_g$ increases, the magnetic communication becomes weaker and the ordering temperatures decrease. This is logical based on a decreased number of electrons in the conduction band, which as we know from electron doping studies, is responsible for the magnetic communication and ordering.

Going further down the series, EuSe demonstrates even weaker ordering, with a $T_C$ of only 7 K. As shown, EuSe also has a $T_N$ of 4.6 K; EuSe is known as metamagnetic, because it can demonstrate either ferromagnetic or antiferromagnetic ordering, depending on the strength of the applied magnetic field. In a weak magnetic field, the moments will antiferromagnetically

- **EuO**
  - $T_C = 69$ K
  - $E_g = 1.12$ eV
- **EuS**
  - $T_C = 16$ K
  - $E_g = 1.65$ eV
- **EuSe**
  - $T_C = 7$ K
  - $T_N = 4.6$ K
  - $E_g = 1.8$ eV
- **EuTe**
  - $T_N = 9$ K
  - $E_g = 2.05$ eV

Figure 1. Electronic band structures of the europium chalcogenides, EuO through EuTe, along with their electronic band gaps, $E_g$ and magnetic ordering temperatures. Altered for clarity from Wachter\textsuperscript{35} without permission.
align, but as the magnetic field is strengthened, the moments will be induced to
ferromagnetically order, which is a stronger form of magnetic order. EuTe is also
antiferromagnetic, but with a lower $T_N$, indicating weaker magnetic communication, due to fewer
electrons in the conduction band.

Because of the smaller $E_g$ in EuO, it displays stronger magnetic communication and a
correspondingly higher $T_C$, but can be increased even further with gadolinium-doping, to 170 K,$^2$ as discussed in Chapter 1, or even higher to ~200 K with lanthanum-doping.$^3$ Despite the
advantages of EuO's magnetic properties compared to those of EuS, EuO is a more difficult
system to synthesize, especially on the nanoscale. Most of the work done with EuO has been
with thin-films,$^4$–$^6$ as CVD, and other thin-film methods allow extremely fine synthetic control,
resulting in carefully controlled stoichiometry and homogeneity.

The difficulty in synthesizing EuO is that europium is very sensitive to oxygen; EuO
contains divalent europium, and must be reacted with some source of oxygen, while avoiding
oxidation to Eu$^{3+}$. Most of the work on nanoscale EuO has been performed by Hasegawa, who
has utilized a variety of interesting synthetic methods in order to overcome the synthetic
difficulties. Shown below are nanocrystals of EuO synthesized by reaction of dilute oxygen with
europium metal in liquid ammonia.$^7$
Another approach to EuO nanocrystals is through photo-reduction of Eu$^{3+}$ by UV-irradiation,\textsuperscript{8} or more effectively, through reduction with an ArF-laser.\textsuperscript{9} Synthesis by laser irradiation gives small particles, with a 4.7 nm particle size, but also of a single-crystalline nature.

Work has been done by Jin on synthesizing nanorods of EuO.\textsuperscript{10} In this work, he starts with polycrystalline Eu(OH)$_3$ nanorods and dehydrates them to Eu$_2$O$_3$, and reacts this material with europium vapor to reduce the Eu$_2$O$_3$ to EuO. As you would expect, the product is polycrystalline as well; this synthesis is shown below in Figure 3.
Figure 3. Scheme showing the synthesis of polycrystalline EuO nanorods, shown are SEM and SAED images.

It is based on Jin's synthetic approach that we will synthesize EuO nanowires. A point which has not yet been stressed is the fact that the Eu(OH)$_3$ nanowire starting material is single-crystalline. There isn't precedent for single-crystal nanowires having enhanced magnetic properties, but there has been shown to be enhanced electrical properties; because of the intrinsic connection between electricity and magnetism, it is easy to imagine magnetic enhancements from single-crystallinity.

3.2 Results and discussion

3.2.1 Europium oxide synthesis

When Eu(OH)$_3$ nanowires are dehydrated to Eu$_2$O$_3$, not only is the nanowire morphology preserved, but single-crystal material is obtained, maintaining the crystallinity during the reaction. This is demonstrated through high resolution TEM images and SAED as shown below in Figure 4.
Figure 4. High resolution TEM images showing the single-crystal nature of the Eu$_2$O$_3$ wires. Lattice fringes and reflections in the electron diffraction can both be indexed to Eu$_2$O$_3$.

Because of the single-crystal nature of these conversions, we should be able to improve on Jin's synthesis of EuO not only through better control of aspect ratio, but even more significantly by synthesizing single-crystal EuO nanowires, as long as the final step remains as a single-crystal transformation.

As was done by Jin, EuO is commonly synthesized in the solid-state by the reduction of Eu$_2$O$_3$ with Eu metal,$^{11}$ shown below:

\[ \text{Eu}^{3+} \text{O}_3 + \text{Eu}^0 \rightarrow 3 \text{Eu}^{2+} \text{O} \]

This must be done at high enough temperatures in order to sublime the europium metal, which happens at 700 °C,$^{12}$ but as we are trying to maintain the morphology of our Eu$_2$O$_3$ nanowires, finding balanced conditions to achieve this is important. This reaction has the
advantage of the reducing agent being part of the products, so there are no issues with contamination. This is unlike lanthanum metal, which can be used for reduction as well, resulting in the sublimation of EuO. Shown below in Figure 5 is an SEM image of the product of Eu₂O₃ nanowires and Eu reacted at 800 °C for 3 hours:

![SEM image of material formed by reaction of Eu₂O₃ with Eu metal at 800 °C for 3 hours.](image)

This material indexes by PXRD to EuO, but it is clear that 800 °C for 3 hours are not the optimal reaction conditions, given the significant amount of agglomeration seen in Figure 5. By changing the conditions slightly, the wire-like morphology was successfully maintained, when reacted at 750 °C, for 4 hours; a TEM image of the material is shown below in Figure 6.
This synthesis was thought to be extremely successful; the PXRD pattern was indexed to EuO, TEM images showed preservation of the nanowire morphology, and SAED showed discrete spots rather than rings, showing the single-crystalline nature. Unfortunately, upon closer analysis of the SAED images, the reflections were indexed to cubic Eu$_2$O$_3$, which was not observed in the x-ray diffraction patterns. This outcome was observed repeatedly on many different wires within multiple samples, and no electron diffraction patterns in any sample could be indexed to EuO. These results are shown below in Figure 7.
3.2.2 Reaction with electron beam

It was ambiguous as to the source of Eu$_2$O$_3$; its presence could be either due unreacted starting material, or EuO could have oxidized or otherwise reacted to form Eu$_2$O$_3$. Oxidation was first suspected, because of the oxophilic nature of europium. More TEM measurements were performed, with samples prepared and delivered under air-free conditions, only being exposed to air very briefly upon loading the sample into the instrument.

Theoretical studies have been performed, showing the possibility of the high-energy electron beam of a TEM reacting material and causing a phase transition.$^{14,15}$ In an attempt to slow or arrest this transition, using a low temperature sample holder, TEM measurements were taken at liquid nitrogen temperatures.

Even at very low temperature (~100 K), the material was visibly reacting in the presence of the electron beam. After a portion of the material was studied in the electron beam for a period of time, it would appear more polycrystalline than upon initial imaging. This reaction with the

---

*Figure 7. PXRD pattern and selected area electron diffraction image, indexed to EuO and Eu$_2$O$_3$, respectively.*
beam is shown by TEM images below in Figure 8.

![TEM images showing a nanowire becoming more polycrystalline by reaction with the electron beam.](image)

**Figure 8. TEM image showing a nanowire becoming more polycrystalline by reaction with the electron beam.**

As a result, it is unclear if the material is single-crystal as synthesized, which would show that the single-crystalline nature can be maintained from the synthesis of the Eu(OH)$_3$ and chemical transformation to Eu$_2$O$_3$ and finally EuO. It is unclear why the EuO material was oxidized to Eu$_2$O$_3$ in the presence of the electron beam in our material, when this was not reported in the nanocrystal system by Hasegawa,$^9$ or in nanowires by Jin.$^{10}$ This does call into question the identity of the material he reported; because no scale bars are shown in his electron diffraction images, we cannot index the reflections, as both EuO and Eu$_2$O$_3$ are cubic materials.

Other possibilities remain though; the nanowires we have synthesized are thinner than those made by Jin, ~50 nm vs. ~300 nm in diameter, so it is possible that the smaller scale, and correspondingly increased surface area makes the material more susceptible to reaction with the beam. This idea is supported by the idea that a lot of the thin film work with EuO is
characterized by low-energy electron diffraction, LEED\textsuperscript{5,16} which being of lower energy would be less likely cause the reaction to Eu\textsubscript{2}O\textsubscript{3}.

Ideally, in order to verify this claim, we would take a material which indexes by PXRD to EuO, expose it to the electron beam, where it reacts and is indexed to Eu\textsubscript{2}O\textsubscript{3}, and take that same material and re-examine it by PXRD to see newly formed Eu\textsubscript{2}O\textsubscript{3}. Unfortunately this isn't straightforward, as the amount of material measured with TEM is microscopic, and that same amount of material is not sufficient to obtain a PXRD pattern. We have attempted to simulate this through exposure to the electron beam in an SEM, with which a greater amount of sample can be examined, but this did not prove successful. Electron diffraction cannot be performed by SEM, and when the material was re-examined by PXRD, it was still indexed to EuO. The intensity of the electron beam is much higher, using a voltage of 200 kV, compared to the maximum voltage on our SEM instrument of 30 kV.

3.2.3 Monoclinic Eu\textsubscript{2}O\textsubscript{3}

During the EuO synthesis, it is important that no trace amounts of water remain in the material, or else the monoclinic Eu\textsubscript{2}O\textsubscript{3} phase is formed as an unwanted side product. The monoclinic phase of Eu\textsubscript{2}O\textsubscript{3} is a high-temperature phase; the cubic to monoclinic phase transition takes place around 1075 °C.\textsuperscript{17} This transition has been highly studied because of the application of Eu\textsubscript{2}O\textsubscript{3} as neutron absorbers in nuclear reactors,\textsuperscript{18} and the different thermal expansion properties of the cubic and monoclinic phases. Despite being such a high temperature transition, it is observed at the lower synthetic temperatures used in our EuO syntheses around 750 °C.

It has been shown that this transition can take place at lower temperatures in nanoscale
materials due to the increased surface area, and the associated strain on the crystal structure, from the Gibbs-Thomson effect.\textsuperscript{19} Additionally, the presence of water affects the thermodynamics of the transition, again, vastly lowering the transition temperature, shown in the analogous Y\textsubscript{2}O\textsubscript{3} system.\textsuperscript{20}

Because of its appearance in our syntheses, we wanted to better understand the monoclinic Eu\textsubscript{2}O\textsubscript{3} phase, and its formation. A better understanding could help us to avoid it during synthesis of EuO and other materials, however, if we could synthesis phase-pure monoclinic Eu\textsubscript{2}O\textsubscript{3} with any sort of morphological control, it would be interesting to study any difference in reactivity, and possibly use it as an alternative route for chemical transformations. Because of the high temperature of this transition, we don't expect to be able to synthesize material with good nanowire morphology by heating cubic Eu\textsubscript{2}O\textsubscript{3} wires to \textasciitilde1200 °C.

Since hydration affects the thermodynamics of the formation of monoclinic Eu\textsubscript{2}O\textsubscript{3}, we refluxed our starting cubic Eu\textsubscript{2}O\textsubscript{3} nanowires in water to see if monoclinic Eu\textsubscript{2}O\textsubscript{3} would form. Instead of either phase of Eu\textsubscript{2}O\textsubscript{3}, we observed a mixture of two phases: Eu(OH)\textsubscript{3}, and a phase which we assigned as EuOOH. Because of these products, we that Eu\textsubscript{2}O\textsubscript{3} was re-hydrolyzing to the starting material:

\[
\text{Eu}_2\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 2 \text{Eu(OH)}_3
\]

This was an interesting result, but even more interesting was an SEM image of the material which resulted, demonstrating that nanowire morphology is still maintained in this reverse reaction, as shown below in Figure 9.
In the initial reaction, cubic Eu$_2$O$_3$ was refluxed for 2 hours. We repeated the experiment with varying reaction times in order to try and obtain phase-pure materials; by reacting for a longer time, just Eu(OH)$_3$, and a shorter time, just EuOOH. Upon a closer result of the PXRD patterns from these reactions, and the initial reaction, we found that the phase which we indexed to EuOOH was a close match, but didn't match with every diffraction peak. However, this phase did resemble the cubic phase of Eu$_2$O$_3$, but with shifted peaks.

Rietveld refinement was performed on this material, and it refined to something close to Eu$_2$O$_3$, but with a larger unit cell; 11.352(3), larger than the Eu$_2$O$_3$ cell of 10.859. Additionally, the intensities were not at their expected values; when the two europium sites were allowed to refine freely, they resulted in values of 1.66(3) and 0.76(1); the LIVEPLOT view from Rietveld refinement is shown below in Figure 10.
In order to better our understanding of this reaction, we expanded the scope of the synthesis, by instead of refluxing the cubic Eu$_2$O$_3$ nanowires in water, heating them under hydrothermal conditions at 180 °C for 17 hours. This material was indexed to phase-pure Eu(OH)$_3$ and SEM showed that the morphology was wire-like, but appeared fuzzier than those just refluxed in water, as shown below in Figure. It is not yet clear the mechanisms in this system.

*Figure 10. LIVEPLOT view from Rietveld refinement of the hydrolysis of Eu$_2$O$_3$ nanowires.*
3.2.4 Europium oxyhalides

As we were having trouble ascertaining the phase formed during this synthesis of EuO from Eu₂O₃, because of the discrepancy between the x-ray and electron diffraction, we investigated alternate syntheses of EuO. Work by Bärnighausen showed that a solid-state reaction under vacuum between europium oxyhalides and lithium hydride yielded single-crystals of EuO:

$$\text{EuOX}(s) + \text{LiH}(s) \rightarrow \text{EuO}(s) + \text{LiX}(g) + \frac{1}{2} \text{H}_2(g) \ (X = \text{F, Cl, Br})$$

Based on this, we investigated reactions which could give us EuOX; there have been solution-based syntheses of lanthanide halides, LnOX from the lanthanide trihaloacetates, Ln(CX₃COO)₃. These have been used in the synthesis of nanoplates and nanowires of LaOCl, EuOCl, and LaOCl:Eu. Alternatively, LnOF has been made through solid-state reactions of Ln₂O₃ with polytrifluoroethylene, or thin films by chemical vapor deposition. The most promising synthesis was work by Vary, where Eu₂O₃ was reacted with ammonium halides and
yielded the europium oxyhalides:

\[
\text{Eu}_2\text{O}_3 (s) + 2 \text{NH}_4\text{X} (s) \rightarrow 2 \text{EuOX} (s) + \text{H}_2\text{O} (g) + 2\text{NH}_3 (g) \quad (X = \text{F, Cl, Br})
\]

Adapting this synthesis to start with our Eu$_2$O$_3$ nanowires gave successful synthesis of EuOF, EuOCl, and EuOBr nanowires; PXRD patterns confirm the identity of the material formed, and are shown below in Figure 12. SEM images showing the wire-like morphology are shown below in Figure 13.

**Figure 12. PXRD patterns of EuOF, EuOCl, and EuOBr, respectively.**

**Figure 13. SEM images of EuOF, EuOCl, and EuOBr nanowires, respectively.**

Despite being able to maintain the wire-like morphology, unfortunately the material was
determined by TEM to be polycrystalline; this is shown below in Figure 14. Because of this, even if we could synthesize EuO from this route, the material would not likely be single-crystalline.

![TEM image of EuOCl nanowires, showing the polycrystalline nature of the material.](image)

Furthermore, reaction with LiH unfortunately has not yielded EuO; the product is identified by PXRD to be the monoclinic phase of Eu₂O₃, shown below in Figure 15; just as is found as impurity in the previous reaction with Eu metal. To further demonstrate the stability of this phase, monoclinic Eu₂O₃ can also obtained during synthesis of the europium oxyhalides if the materials are not sufficiently dried; even at the significantly lower temperature of 400 °C.
Figure 15. PXRD pattern of material formed with reaction of EuOCl nanowires with LiH; this pattern is indexed to the monoclinic phase of Eu₂O₃.

Even if they cannot be used as a precursor for EuO, the lanthanide oxyhalides have other uses; like the oxides, LnOX materials are used as phosphors, and EuOF has been synthesized on the nanoscale with interesting luminescent properties. Samarium oxychloride, SmOCl, is an effective catalyst for the formation of propylene carbonate from propylene oxide and carbon dioxide.

During the synthesis of EuOF, a wide variety of fluorine chemistry was discovered in this system. When used stoichiometrically, the EuOF phase is isolated, however, if an excess of NH₄F is used during the synthesis, a range of other europium fluoride structures are observed. Initially, another oxyfluoride phase was observed, Eu₂O₂F₄, containing more fluorine per atom than in EuOF. Other pure fluoride phases were seen; Eu₂.₄, Eu₂.₄₄, and EuF₃. In the case of europium trifluoride, EuF₃, multiple phases could be made, a hexagonal and orthogonal phase. By changing the synthetic conditions, these two structures were able to be made phase-pure, with their PXRD patterns shown below in Figure 16. Work by Sun demonstrated control between the
EuOF and EuF$_3$ phases by the choice of capping ligand during synthesis.

Unfortunately with these syntheses, morphology could not be maintained, as shown by the SEM images in Figure 17. This is somewhat surprising, given that EuOF nanowires could be made, and the hexagonal phase of EuF$_3$ was made at an even lower temperature, 300 °C. If the same conditions, heating 400 °C for 2 hours as was used for the synthesis of EuOF, but with a larger excess of NH$_4$F, a mixture of the two EuF$_3$ phases is observed by PXRD. Because in this case, there is no wire-like morphology, unlike in the case of EuOF, we don't expect that tweaking the synthetic conditions for EuF$_3$ that nanowires could be made. The different syntheses of Eu(O)X material are summarized below in Table 1.

Figure 16. PXRD patterns of the orthogonal and hexagonal phases of EuF$_3$. 

[Graph showing PXRD patterns of orthogonal and hexagonal phases of EuF$_3$.]
Figure 17. SEM images of the orthogonal and hexagonal phases of EuF$_3$, respectively, which show no wire-like morphology.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temp. (°C)</th>
<th>Equiv. NH$_4$X</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuOCl</td>
<td>400</td>
<td>1.2</td>
<td>wires</td>
</tr>
<tr>
<td>EuOBr</td>
<td>400</td>
<td>1.2</td>
<td>wires</td>
</tr>
<tr>
<td>EuOF</td>
<td>400</td>
<td>1.2</td>
<td>wires</td>
</tr>
<tr>
<td>EuF$_3$ (hex.)</td>
<td>300</td>
<td>5.5</td>
<td>agglom.</td>
</tr>
<tr>
<td>EuF$_3$ (ortho.)</td>
<td>600</td>
<td>10</td>
<td>agglom.</td>
</tr>
</tbody>
</table>

Table 1: Summary of synthesis conditions and resulting morphology for different Eu(O)X phases.

The destruction of morphology in the EuF$_3$ phases brings up another point which has not been stressed in any of the chemical transformations we have studied yet, that there must be a degree of similarity in the crystal structures of the starting material and products in order to maintain morphology. It seems that too much atomic rearrangement causes a loss in the overall morphology. With this, I propose that there are two classes of chemical transformation:

1) Single-crystal to crystal transformations

2) Morphological templating

In examples which were presented earlier, the topotactic reaction of Te nanowires into Ag$_2$Te and subsequent cation exchange to CdTe, ZnTe, and PbTe$^{33}$ the single-crystalline nature
of the materials were preserved. These are examples which I will call single-crystal to crystal transformations; reactions which involve similar crystal structures in the starting material and product. In these transformations, the overall structure is preserved, so the starting morphology can be maintained, as well as the single-crystal nature.

With the morphological templated reactions there is some structural similarity, but not enough to fully maintain the crystal structure during a topotactic reaction. In these conversions, the larger morphology, such as a nanowire will be somewhat preserved, but there is too much atomic movement breaking up the crystal lattice, and the material will become polycrystalline, even with a single-crystal starting material.

A common theme in studying which transformations are true single-crystal to crystal transformations versus morphological templates is the anionic backbone. The most common single-crystal to crystal transformation is that of cation exchange, in which the anionic structure of a material stays intact, and cations diffuse in and out of the structure. Breaking up this anionic backbone seems to lead to deformation of a crystalline structure, and in more extreme cases, the larger morphology of the nanostructure.

This is demonstrated in the comparison of the successful single-crystal to crystal dehydration of Eu(OH)$_3$ to Eu$_2$O$_3$, compared with reaction of Eu$_2$O$_3$ to EuS, or any of the (oxy)halides. In formation of EuS, the entire anionic backbone of oxygen atoms must be replaced by sulfurs, and in the case of EuOX, oxygen atoms are replaced by halides. This is the likely reason for complete loss of structure in the synthesis of the two different phases of EuF$_3$, where all oxygen atoms are replaced by fluorines. It is unclear as to the single-crystal nature of EuO
formed by reduction of Eu$_2$O$_3$ with europium metal, because of the reaction with the electron beam under TEM. It does seem as though it's possible that it could be a single-crystal to crystal transformation, as the primary change is reduction of trivalent europium, with the anionic backbone staying mostly intact. However, this theory is brought into question with recent developments in the quick, high-temperature reaction of Eu$_2$O$_3$ to EuS which seems to maintain at least some degree of morphology. In the least, it could be said with strong certainty that anion-exchange is more difficult and delicate than cation-exchange.

In order to try and find more use for these materials, EuOCl was reacted with H$_2$S to see if more interesting materials could form, or if we would just make EuS, as was studied in Chapter 2. No interesting results came of this; at high temperatures, EuS was formed, also with a loss in morphology, and when reacted at 350 °C, no reaction was observed, just as was the case with Eu$_2$O$_3$.

Furthermore, EuOCl was studied by high-temperature PXRD with uninteresting results: EuOCl was stable until 100 °C. At 150 °C, Eu$_2$O$_3$ was observed, and by 200 °C, only Eu$_2$O$_3$ was present.

Through the reaction of Eu$_2$O$_3$ + NH$_4$X, three of the europium oxyhalides were synthesized, but this did not seem to work in the case of EuOI. It is unclear what is formed during this synthesis; the obtained PXRD pattern could not be indexed to anything in the ICDD database. Although EuOI is not a reported pattern in the ICDD or ICSD databases, its tetragonal cell parameters are reported in the abstract of a paper by Baernighausen, and did not match. Energy dispersive spectroscopy (EDS) was performed on the material formed, shown below in
Figure 18 along with the corresponding SEM image, and iodine was found.

Figure 18. EDX and SEM image of material formed by synthesis of Eu₂O₃ and NH₄I, which cannot be indexed by PXRD.

EuOI seems to be more difficult to synthesize than the other oxyhalides; as of the time of this writing, a search in SciFinder scholar gives 56, 69, and 37 references for the other europium oxyhalides, the oxyfluoride, oxychloride, and oxybromide respectively, whereas a search for europium oxyiodide only gives 10 references.

3.3 Experimental.

**General information.** Europium(III) nitrate hexahydrate was obtained from Strem. Sodium hydroxide, ammonium chloride, ammonium iodide, and ammonium fluoride were obtained from Sigma. Ammonium bromide was obtained from Merck. Europium metal was obtained from Alfa Aesar. All chemicals were used as received. Selected-area electron diffraction images were taken with a JEOL JEM 2100F Field Emission Gun Transmission Electron Microscope, at 200 kV. SEM images were taken with a Zeiss SUPRA 55-VP scanning electron microscope, at an acceleration voltage of 20 kV with an in-lens detector. EDX was performed with an Oxford Instruments X-Max Silicon Drift Detector.

**X-ray diffraction.** Powder x-ray diffraction patterns were obtained using a Rigaku Ultima IV X-
ray powder diffractometer with CuKα radiation at 40 kV and 44 mA with a D/teX silicon strip detector.

**Eu(OH)$_3$ nanowires.** Eu(NO$_3$)$_3$·6 H$_2$O (0.25 g, 0.56 mmol) was dissolved in 5 mL H$_2$O. 0.5 g NaOH was added to make a 2.5 M solution, which was stirred for 20 minutes; a white, flocculent precipitate formed immediately. The solution was put into a 20 mL Teflon lined Parr Bomb and heated at 180 °C for 6 hours. Once cooled to room temperature, the supernatant was decanted and discarded. The vessel was filled to 10 mL with H$_2$O, and the resulting solution was centrifuged for 10 minutes. The supernatant was decanted and discarded. This was repeated with 10 mL ethanol. The precipitate was dried under vacuum for 1 hour, and the material was lightly ground with a mortar and pestle to increase surface area. Percent yield: 88%. Powder x-ray diffraction patterns matched that of Eu(OH)$_3$, PDF 00-017-0781 (ICDD, 1979).

**Eu$_2$O$_3$ nanowires.** 200 mg Eu(OH)$_3$ nanowires were heated in a quartz tube in a Lindberg/Blue M horizontal tube furnace at 500 °C for 3 hours under dynamic vacuum. Percent yield: 83%. Powder x-ray diffraction patterns matched that of the cubic phase of Eu$_2$O$_3$, PDF 00-034-0392 (ICDD, 1984).

**EuO nanowires.** In a nitrogen atmosphere glovebox, 10 mg Eu$_2$O$_3$ nanowires were placed on top of 100 mg Eu foil (0.1 mm thick) on a graphite boat in a quartz tube. The tube was taken out of the glovebox and heated in a Lindberg/Blue M horizontal tube furnace at 750 °C for 4 hours under dynamic vacuum. Percent yield: 78 %. A powder x-ray diffraction pattern was matched with that of EuO, PDF 00-015-0886 (ICDD, 1965).

**EuOBr nanowires.** Eu$_2$O$_3$ nanowires (22 mg, 0.06 mmol) were lightly ground in a mortar and
pestle with excess NH₄Br (14 mg, 0.15 mmol) and dried in an oven at 120 °C for 2 hours in a graphite cup. In a glovebox, this was loaded into a flame-dried quartz tube and put under vacuum briefly, for approximately 2 seconds, and then left under static vacuum. The material was heated at 400 °C for 2 hours. Percent yield: 97%. A powder x-ray diffraction pattern was matched with that of EuOBr, PDF 00-016-0785 (ICDD).

**EuOCl nanowires.** Eu₂O₃ nanowires (20 mg, 0.06 mmol) were lightly ground in a mortar and pestle with excess NH₄Cl (10 mg, 0.19 mmol) and dried in an oven at 120 °C for 2 hours in a graphite cup. In a glovebox, this was loaded into a flame-dried quartz tube and put under vacuum briefly, for approximately 2 seconds, and then left under static vacuum. The material was heated at 400 °C for 2 hours. Percent yield: 96%. A powder x-ray diffraction pattern was matched with that of EuOCl, PDF 00-012-0163 (ICDD).

**EuOF nanowires.** Eu₂O₃ nanowires (20 mg, 0.06 mmol) were lightly ground in a mortar and pestle with excess NH₄F (5 mg, 0.14 mmol) and dried in an oven at 120 °C for 2 hours in a graphite cup. In a glovebox, this was loaded into a flame-dried quartz tube and put under vacuum briefly, for approximately 2 seconds, and then left under static vacuum. The material was heated at 400 °C for 2 hours. Percent yield: 88%. A powder x-ray diffraction pattern was matched with that of the low temperature rhombohedral phase of EuOF, PDF 00-026-0636 (ICDD).

**hexagonal EuF₃ nanocrystals.** Eu₂O₃ nanowires (24 mg, 0.07 mmol) were lightly ground in a mortar and pestle with a large excess of NH₄F (28 mg, 0.75 mmol) and dried in an oven at 120 °C for 2 hours in a graphite cup. In a glovebox, this was loaded into a flame-dried quartz tube
and put under vacuum briefly, for approximately 2 seconds, and then left under static vacuum. The material was heated at 300 °C for 2 hours. Percent yield: 86%. A powder x-ray diffraction pattern was matched with that of the hexagonal phase of EuF$_3$, PDF 00-032-0373 (ICDD, 1976).

**orthogonal EuF$_3$ nanocrystals.** Eu$_2$O$_3$ nanowires (27 mg, 0.08 mmol) were lightly ground in a mortar and pestle with a large excess of NH$_4$F (57 mg, 1.54 mmol) and dried in an oven at 120 °C for 2 hours in a graphite cup. In a glovebox, this was loaded into a flame-dried quartz tube and put under vacuum briefly, for approximately 2 seconds, and then left under static vacuum. The material was heated at 600 °C for 2 hours. Percent yield: 86%. A powder x-ray diffraction pattern was matched with that of the low temperature rhombohedral phase of EuOF, PDF 00-026-0636 (ICDD, 1976).

**References**


19, 2677–2681.

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Appendix

RIETVELD REFINEMENT

Introduction

Developed by Hugo Rietveld,¹ the technique of Rietveld refinement allows different aspects of a powder diffraction pattern (from either or x-rays or neutrons) to be modeled, creating a calculated pattern, generated from a series of properties of a crystalline material.

With this technique, an experimental diffraction powder pattern is input, and by refining a model based on different variables, such as lattice size, atomic positions, thermal parameters, and a range of Gaussian and Lorentzian factors governing peak shape can be calculated. By allowing the calculated and experimental powder patterns to converge, structural information can be determined about the material. Rietveld refinement was performed using the program General Structure Analysis System (GSAS),² developed at Los Alamos National Lab, using the user interface EXPGUI,³ (named as the graphical user interface, GUI, used for the .exp files in GSAS) developed by Brian Toby.

Getting started

In order to perform Rietveld refinement, you can use Windows, Mac, or Linux. EXPGUI is the program which acts as interface and helps you to run separate programs such as POWPREF, GENLES, and LIVEPLOT, in the GSAS suite of software, which allow you to perform Rietveld refinement, and whose functions will be explained in greater detail soon.

ConvX allows you to convert your experimental diffraction data from the output of your instrument to a variety of other formats, including GSAS, but is for Windows only. CMPR is another alternative which can be run from Windows, Mac, or Linux. All of these are free, and can be downloaded from the following locations:
EXPGUI: http://www.ccp14.ac.uk/solution/gsas/
ConvX: http://www.ccp14.ac.uk/ccp/web-mirrors/convx/#ConvX
CMPR: https://subversion.xor.aps.anl.gov/trac/CMPR/wiki

EXPGUI will need to be installed to your computer, and you should leave the installation location as the default (C:\gsas\). This is important, because EXPGUI has been written to tie a lot of different programs together, many of which are written ages ago, when filenames could only be of a certain length, and only include a few types of characters. Installing EXPGUI to a location such as a C:\Program Files\gsas\ can cause problems because 'Program Files' is relatively long, and includes a space. This will be repeated many times throughout this guide, but remember to save all files with relatively short and simple filenames such as wlb132, etc.

The files which you will need are the PXRD pattern files you wish to refine, from your diffractometer, the instrument parameter file (*.prm), and ideally, crystallographic information files (CIF) (*.cif) for the crystal structures you are refining based on. Experimental files should be used without any cleanup; do not first perform any background subtraction, for example. You should be able to obtain the instrument parameter file from the person in charge of operating your instrument, or you can email the manufacturer directly. CIFs are generally created based on single-crystal x-ray diffraction, and can be obtained from sources such as the Cambridge Structural Database (CSD) or the Inorganic Chemistry Structural Database (ICSD).

It is possible to refine a structure without having full crystallographic information, just having some basic structural information, such as the structure type, and a rough idea of the cell parameters, but this makes the process significantly more difficult. Solving the crystal structure of a material based on powder diffraction rather than the standard single-crystal structure determination approach is possible, but this is typically done with high quality synchrotron data, with the availability of intense high angle reflections, and using other software.
In order to demonstrate Rietveld refinement, I will be providing two sample files. The first of which is a simple PXRD pattern of EuS, in order to make you familiar with the process of Rietveld refinement. The second is a material from Chapter 2 of this thesis, a sodium-doped EuS sample, \( \text{Eu}_{1-x}\text{Na}_x\text{S} \), which will show you more advanced skills such as refining lattice parameters, site occupancy, and including multiple phases. If this is your first time using GSAS, especially if the refinement you will be attempting is complicated, it will be easier to learn with these first.

You should have the following files:

- EuS.txt: Experimental diffraction pattern of EuS.
- EuNaS.txt: Experimental diffraction pattern of \( \text{Eu}_{1-x}\text{Na}_x\text{S} \).
- UltimaIV.prm: Instrument parameter file for the diffractometer used, a Rigaku Ultima IV.
- EuS.cif: CIF for EuS. Used as basis for both refinements.
- NaCl.cif: CIF for NaCl; impurity phase found in \( \text{Eu}_{1-x}\text{Na}_x\text{S} \) refinement.

These files should be accompanied with the electronic copy of my thesis, found somewhere in the Stoll lab, or else are available at: https://www.dropbox.com/sh/6dpfdtb0xw8p8se/PX-DcmeKf1. If you cannot find these, please contact me at wlb6@georgetown.edu.

**Tutorial 1: EuS**

1. Convert file for GSAS

The first step is to prepare your diffraction pattern, and convert it into the GSAS format. First create a folder for your refinement. For this example, use C:\gsas\MyWork\EuS. Place all of the example files in here.

ConvX:

ConvX.exe is a standalone file which can be run from anywhere without actually being installed on to your computer. Just be sure that the experimental files you output also contain short, simple
filenames. Open ConvX.exe, and you will see the following window:

![ConvX software window](image)

*Figure 1. ConvX, used to convert your diffraction pattern into the GSAS format.*

First, in the 'File(s) to convert' section, select the file type of your pattern. The files which I have provided are ASCII files, generated by JADE, so in our case, we will select ASCII 2theta,I as the type. To the right, select your file, EuS.txt. When you hit open, in order to see EuS.txt, you will need to set 'Files of type' to all files. Under 'Output parameters', select the radiation source used for your diffractometer. This will typically be copper (Cu), but this can vary. Under 'Output file details' select GSAS as the file type, with a .raw extension. Convert the file using 'Do That Convert Thang !!' and hopefully you will see a message pop up saying 1 file converted.

2. Create EXPGUI file

Open, EXPGUI, and then your EuS folder. The folder will appear blank, type in EuS, and hit read. You will see the following message appear:
It cannot find your EXPGUI file, since you have not yet created one, and it prompts you to create the file. Do so by hitting 'Create'. It will then ask you for an experiment title; do so however you want, I used: 'EuS tutorial'.

3. Add EuS phase

The first step of refinement is to add the phase of material you are refining based on. In the phase tab, click 'Add phase', and you will see the following:
Next to 'Import phase from:', click on 'PowderCell .CEL file' and change to Crystallographic Information File (CIF). Select EuS.cif, and the different boxes will be populated with the EuS crystal information. I generally change the Phase title to something simpler, such as EuS, but it's not necessary. Click add when ready, and another box will pop up, asking you to verify the symmetry operators, just hit continue.

The next step of this is to add the atoms within the structure. These will be generated from the CIF, and you will see the following:
Generally all of the information will be correctly generated from the CIF. The atom types given list the atom and the charge, for example Eu+2 and S-2. EXPGUI is not programmed to handle charges, so delete those, leaving just Eu and S. The other columns shouldn't need any change, but so you know what they mean:

- **Atom name**: Just a name for the atom to be used during refinement.
- **x, y, z**: Atomic coordinates.
- **Occ**: Occupancy; for a stoichiometric structure, this will always be 1.
- **Uiso**: Isotropic thermal parameters: essentially quantifying the thermal vibration of the atom.

Depending on how the single-crystal was solved and refined, the Uiso values may come out differently; it's a good idea to set all of these to 0.025. When ready, click 'Add atoms'.

**4. Add diffraction pattern**

Once you have added in the initial starting phase, you can add in your experimental diffraction pattern. Click on the powder tab, and at the bottom, click 'Add New Histogram', and you will see the
5. Initial refinement and liveplot

Now you have your initial phase, which will form the basis of the calculated model, and your experimental data loaded into EXPGUI. We will now do an initial refinement, and visualize and quantify how our refinement is so far.

From the top bar, select POWPREF. POWPREF will update the file with what information is to be refined. You will see the following:
This is a screen you will be seeing often, the only thing to verify is that the statement successfully executed, this is shown above, circled in red. Once you see this, hit any key. In the event you don't see this, something has gone wrong; consult the troubleshooting section at the end of this appendix. You will now see this screen:
After you have exited POWPREF, you'll be returned to EXPGUI, and you will be asked if you want to adopt any changes made. If on the previous screen (shown in Figure 6), no errors were seen, and you're satisfied with the changes made, click 'Load new', and that will update your file. If anything went wrong, click 'Continue with old', and any changes made with an external program such as POWPREF will be discarded. This is another screen which will appear a lot.

Now that we have the file set with POWPREF, we can do our initial refinement, done with GENLES. When GENLES is run, it will perform refinements on your calculated model. You will see this screen:
Figure 8. Screen seen once GENLES is finished.

There are two things to check for on the screen, once GENLES is run; these are circled above in Figure 8. The most important thing is the bottom item circled, which tells you the result of the refinement. There are three options:

1) Convergence was achieved: This is the best result. Your refinement has taken into consideration all of the factors you selected to refine, and found the best values which caused the calculated model to best fit the experimental.

2) ***** System of equations is diverging *****: Things went wrong. When refining, GENLES was unable to find an acceptable result, and ended up going off course.

3) Neither. If neither of those messages appear, GENLES is still in the process of refining, and more refinement cycles are needed.

Assuming the system did not diverge, the other portion of the screen to look at is the 'Reduced CHI**2 value'. This is the $\chi^2$ goodness of fit value. As the model is refined, this value will decrease, a
perfect fit would give you a $\chi^2$ value of 1. It is up to you when to determine you are done refining, but you generally want a $\chi^2$ value of less than 2.

When you press any key to exit that screen, the screen from Figure 7 will appear again. If the result of GENLES was divergence, hit 'continue with old' to discard those results. If there was convergence, or more refinement is needed, accept the results with 'Load new'. Now that GENLES has been run, the refinements can be visualized with LIVEPLOT. This look as follows:

![Figure 9. LIVEPLOT results, visualizing the results of refinement.](image)

In the above screen, there are 5 elements displayed in the legend on the right. On the top of the screen, the black Xs show the experimental pattern, the green line is the background, the purple vertical lines show where the phase should have peaks, and the red line is the calculated model. The blue line at the bottom shows the difference between the experimental and calculated model; ideally, with a perfect model, this would be a completely flat line. LIVEPLOT may be left open in the background, or on another screen, or can be closed and run again after any GENLES run. If left open, it will update after GENLES is run.
6. Refining the background, selecting a range

The easiest first step is to refine the background. In the powder tab, click 'Edit background'. On
the next screen, click 'Fit background graphically'. By first showing the program where we think the
background is, we are providing an initial background, to make it easier to refine on. Under 'mouse
click action', click add. This will allow us to manually add in background points. Click along the
background of the pattern, adding points from the beginning to the end. Where it says 'Fit with 2 terms',
click on 2, and set that to the highest number shown. Then click on Fit. A simulated background will
appear. If this does not appear correct, add or delete background points and Fit the background again. It
doesn't have to be perfect, you will be refining the background more later. Once you are satisfied, click
'Save in EXP file & Exit'. A refined background is shown below:
Accept the changes with 'Load new'. As you can see, there are no peaks which appear at lower angle, and there is just background. This can be left as is, and the background will be mostly ignored, however it can also be removed from the refinement. In the powder tab, click 'Set Data Limits & Excluded Regions'. From here, you can observe that no peaks appear below 20°, so this region will be ignored. To do so, in the lower left corner, in the excluded regions section, click on '<0.000'; this indicates that no data is being excluded, as there is nothing below 0°. You can now update this with a value of 20, indicating that data below 20° will be ignored. In this case, we have a peak right at the
edge of the high angle region, but otherwise, a similar approach could be taken. Click 'Save & Finish', and follow the usual steps of running POWPREF and GENLES, and accepting the changes in both cases.

Now it is time to begin manually refining different aspects of our model. In the EXPGUI interface, if a variable is set to refine, the corresponding checkbox will be marked. Depending on how you defined your background, it may not be ideal, so check 'Refine background' and run POWPREF and GENLES. Hopefully, if you compare the LIVEPLOT views before and after, you will see a smoother background, and a reduced $\chi^2$ value.

7. Determining what to refine next

From this point, it is important to determine what to refine next, by looking at the LIVEPLOT and seeing where the biggest differences in the model are. There generally four main areas to be refined: peak position, shape, intensity, and multiple phases.

a. Peak position. If the pattern looks generally correct, but the peaks are shifted from where they are expected to be, peak position should be corrected. This can be done through a zero-point error, or a change in cell lattice. The cell lattice should only be refined with good reason; if larger angle peaks are shifted to a greater degree than those of small angle peaks, something may have caused the cell lattice to shift. Examples include if the measurement was performed at non-ambient conditions; change in temperature or pressure will result in a change in cell parameters, or if the stoichiometry of the material is different, different sized dopants can result in a shift due to Vegard's law. Otherwise, a zero-point error will often need to be corrected for, in the event the sample position was slightly misaligned.

b. Peak shape. The shape of the peaks will generally need to be refined according to a set of Gaussian and Lorentzian factors, as well as thermal parameters. Factors which affect peak shape and width include crystallite size, and the crystallinity of the material.

c. Peak intensity. If after correcting for the shape of the peak, the intensities do not appear correct, and
the background appears to be in the right position, one of two factors may be need to be accounted for; preferred orientation or site occupancy. Preferred orientation may arise from a heterogeneous distribution of crystal alignment, especially if the crystals are needle or plate-like, certain crystallographic faces may be over expressed in the diffraction pattern. The easiest way to test for this is to grind the sample with a mortar and pestle in an attempt to homogenize the sample, and re-collect the pattern. This can be accounted for during refinement as well. Alternatively, site occupancy may need to be adjusted, either due to vacancies in the material, or maybe other atoms may be doped into the structure.

d. Multiple phases. Finally, if there are peaks which are unaccounted for, other phases may be present in your sample. These can be added in separately, and refined independently. Alternatively, it is possible that the space group selected for your sample is incorrect, and a lower symmetry space group would be more appropriate.

This is the order in which I generally perform Rietveld refinement, but you may do so in any order, going back and forth to further refine the model. It is best to refine these individually and not turn on many variables, as GENLES is much more likely to diverge. This is especially true when refining different variables which are accounting for the same thing, such as refining the cell lattice and the zero-point error simultaneously. Later in the refinement, when the model is very close, more variables can be turned at once; the final goal will be to have all variables which you are refining activated at the same time, and achieve convergence.

In this example, we will only need to refine based on peak position and shape.

8. Refining peak position

In order to adjust the peak position, it is important to determine which variables should be refined. As you can see in the LIVEPLOT, there is not a significant peak shift, and it doesn't appear to vary different amounts at high vs. low angles. As such, we will choose to refine based on the zero-point
error. This is done in the powder tab, by checking the 'Refine zero' box. Be sure that the variables in the
other tabs are unchecked. The only exception to this is 'Scale factor' in the scaling tab, which should
generally be left checked at all times; this section will be discussed more in our second example. Now
perform POWPREF and GENLES.

You may find that one iteration of GENLES is insufficient to achieve convergence. This can be
fixed either by simply running GENLES multiple times until convergence is achieved, or by changing
the number of cycles per GENLES refinement. Also, remember that POWPREF only needs to be run
when you have changed any variables in EXPGUI; if you are only further refining to achieve
convergence, you can just click GENLES more as needed. In order to increase the number of
refinement cycles in a GENLES run, go to the 'LS Controls' tab. The number of cycles is 3 by default,
but this can be adjusted; I generally choose 20. With a slower computer you may want fewer cycles per
run, so it stalls less.

9. Refining peak shape

Once the peaks appear where they are calculated to be, the shape of the peaks should be refined.
This is done in the Profile tab. At the top, you should see 'Hist 1 -- Phase 1 (type 2)'. If a different type
is shown, change the type by clicking 'Change type' and setting the function type to 2. We will be
refining GW, LY, and asym (which will appear once you have refined GW once). As usual, first verify
that all other variables (except scale factor) are unchecked.

Check the GW box, which will be refining based on a Gaussian shape, then run POWPREF and
GENLES. Uncheck GW, and repeat the process for LY, which will refine based on a Lorentzian shape.
Again, uncheck LY, and repeat the process for asym, which will refine based on asymmetry, primarily
in low-angle peaks. Once you have refined these individually, you may refine more of them at once; in
general it is best to add variables one at a time, refining at each step then adding another.

Once these profile factors have been refined, we should refine the thermal parameters. First turn
off GW, LY, and asym, and go to the phase tab. If you click on a row with an atom in it, start with Eu, you will see more options available to you at the bottom of the screen. The refinement flags X, U, and F correspond to atomic position, (isotropic) thermal parameters, and site occupancy, respectively. Check the box for U, and do the same for the S atom. Alternatively, if you drag your mouse along multiple atom rows, these can be checked at the same time. You will see in the atomic rows, that when a parameter is being refined, its corresponding letter will appear. You should see '0 U0 0' in the ref/damp column for both atomic rows now.

Before we refine these, we want to add a constraint to keep them locked together. With higher quality synchrotron data, we could reliably determine the thermal parameters independently, however, with data from a normal benchtop diffractometer, there is not enough data for these to be considered reliable. In order to add this constraint, go to the Re/Constraints tab. At the bottom, click 'New Constraint'. Select both atoms by dragging your mouse over both rows, then select the variable UISO. Hit save, and you have now added the constraint, and can refine based on thermal parameters. It's important to note that in order for the rules of the constraint to be applied, both of the atoms' thermal parameters must always be refined together. Now you can go back and re-refine the profile parameters, and once you are comfortable, refine on all of the peak fitting variables at once.

10. Final refinements

Now you have refined on each aspect of the model individually and can start refining multiple aspects together in order to obtain the best fit possible. Remember that if the refinement diverges at any point, you should hit 'Continue with old' instead of 'Load new' and then turn off some variables before continuing. Shown below is the LIVEPLOT from my final refinement of this model, with a $\chi^2$ value of 4.958. This is clearly not a perfect refinement, but is still very good.
Tutorial 2: Eu_{1-x}Na_{x}S

1. Introduction/Getting started

Now that you have practiced some of the more basic refinement methods on a simple diffraction pattern, we will do a more complicated example which utilizes more techniques such as site occupancy. This tutorial will assume you have read through Tutorial 1, and will refer only briefly as to how to perform certain techniques. If you're having trouble following, re-read Tutorial 1, and refer to the glossary at the end of this appendix.

Follow the same techniques from Tutorial 1, in order to create a folder, EuNaS, and convert EuNaS.txt to the GSAS format. Then setup your GSAS file, EUNAS.EXP, and we can get started.

2. Adding a modified phase

The phase which we are refining on is a sample of EuS which has had some Eu atoms doped with Na atoms, Eu_{1-x}Na_{x}S (see Chapter 2 for more details). Because this phase is structurally similar to,
and based on that of EuS, we will start by adding the EuS phase. Begin to add the phase as normal, however, when adding the atoms in, and removing their charges, we will do an additional step. In the bottom right, click 'More atom boxes', and a blank row will appear. We are going to add in the Na atom, and give it the same coordinates as Eu, but set its occupancy to 0. It should appear as it does below:

![Figure 12. Adding in Na atom to EuS phase.](image)

Once this phase has been added, create the histogram with the experimental pattern (EuNaS.raw) and instrument parameter file (UltimaIV.prm), just as we did in Tutorial 1. Similarly, remove the data below 25° (after removing the data below 20°, you see that there is still unnecessary background, so more can be removed) and refine the background. After this, the LIVEPLOT should look something like this:
It should be apparent that the purple vertical lines representing the EuS phase are shifted from where they should be. Because the shift is not the same at all angles, a change in lattice parameter should be suspected.

3. Refining lattice parameters

In the phase tab, on the right hand side, check 'Refine cell'. You will notice that GENLES has not changed the EuS lattice parameters to match with the shifted peaks. This is because it is a very dramatic shift, and Rietveld refinement is generally done by inducing small local changes to arrive at the best calculated model. In order to refine these lattice parameters, we need to give it a better starting point. We should be able to visually determine that there is now a smaller lattice, so let's manually change that. In the phase tab, click 'Edit Cell'. Adjust this value to 5.8 as a starting point. As shown below, you are only allowed to change one value of the lattice parameters. Because the phase is set to $F \text{m} \cdot 3 \text{~m}$, which is a cubic cell, the parameters are locked in as $a=b=c$, and $\alpha=90^\circ$. 

Figure 13. LIVEPLOT of EuNaS after background refinement.
Figure 14. Manually adjusting the unit cell parameter.

Now rerun GENLES and you will see that we had a closer starting point, it was able to refine the cell parameter to about 5.812, and the LIVEPLOT looks much better. Turn off the cell refinement, and you can adjust the zero-point error. Similar to how we refined the different factors contributing to peak shape in Tutorial 1, once you have refined both the cell parameter, and the zero-point error individually a few times, we can turn both on and perform a refinement.

4. Refining site occupancy

It should hopefully be apparent from the LIVEPLOT that there is an issue with the intensities, especially if you look at the low-angle peak at 26.5°. Because we know that there is sodium doped into the EuS structure, let's now refine based on that. The structure of this material is Eu_{1-x}Na_xS, so we want to make it so the occupancy of Eu and Na sum to 1. To do this, we go back to the Re/Constraints tab, and again select 'New Constraint'.

For this constraint, add a second column by clicking 'New Column'. In one column, select Eu, and in the other, select Na. Set one of the variables to FRAC, and the other will update automatically. In one column, set the Multiplier to -1, and now save the constraint. This is telling GENLES that
whenever it increases the occupancy of one atom, it should decrease the other by the same amount.

This constraint should appear as below:

![Figure 15. Adding a constraint to link the Eu and Na site occupancies.](image)

With this in place, return to the phase tab, and set both the Eu and Na atoms to refine based on site occupancy, F. It is important to note, just as with the thermal parameters, that you must always have these set to refine together, or else the rules of the constraint will not be followed. Perform GENLES, and you should see the Eu and Na occupancies change to around 0.64 and 0.36, respectively.

5. Finish refining the 1st phase.

Now that we have added in the additional atom, and refined upon its occupancy, finish refining this phase the same way as we did in Tutorial 1; refine peak shape based on the profile parameters and thermal occupancies (remember to constraint all 3 atoms together), and try and refine everything together to get the phase as close as you can. My LIVEPLOT looked as shown below, with a $\chi^2$ value of 5.042.
6. Adding a second phase

As you can see, there are peaks which are unaccounted for. Because I know these to be sodium chloride, NaCl, we will add this phase in as well. The process for this is exactly the same, just use NaCl.cif and delete the charges as usual. Follow the same basic refinement procedures which we performed in the first Eu$_{1-x}$Na$_x$S phase, and in Tutorial 1. It's important to remember what to refine on. Because we have no reason to suspect NaCl would have a different unit cell, we want to make sure to not refine that variable. Furthermore, NaCl can act as an internal standard, in order to help get a more accurate determination of what the cell lattice of Eu$_{1-x}$Na$_x$S is, by further separating the zero-point error and lattice constants.

Finally, in order to determine the different relative amounts of the phases in the system, scale factors must be applied. In the Scaling tab, check the boxes to refine both Phase 1 and 2, as shown below.
Figure 17. Refining the relative amount of each phase.

Now it is just a matter of applying the same refinement principles we have learned, to get the best possible fit for our model. The ideal situation would be to refine all of the variables which we have refined, at the same time. For this system, I have done so, and gotten a $\chi^2$ value of 1.695. In order to see the second phase, you will need to reload LIVEPLOT. The final LIVEPLOT result is shown below:
7. Miscellanea/final notes

In order to determine some final information from your refinement, click on lstview in the top menu. From here, you can see an expanded view of the results of your refinement. There is a lot of information here for you to look through, but I will just point out one important result below:
As you can see, a sigma is given for every refined parameter, shown above is the sigma for the cell lattice parameter, so you can determine a margin of error for your result. That could be reported as $5.801(1)$ (the 1 in parentheses indicating that the last digit is plus or minus 1). It is important to note that only variables which were refined in the last genles run will be given here, so this is good to do last, once you have been able to refine everything simultaneously.

At any point during your refinement, when you are looking at the LIVEPLOT view, you can determine the hkl value of a peak. Hold your mouse over the position of a peak, and hit the 'h' button on your keyboard. You will see a box pop up, identifying the peak, as shown below. If there are multiple peaks in the area of your mouse, they will all be shown.
Glossary

Button 3: GENLES

This initiates refinement of the model based on selected variables. This should follow POWPREF.

Button 4: POWPREF

Whenever changes to the refinement are made (when you turn on/off variables to be refined) this should be run to save the file.

Button 6: LSTVIEW

After the model has been completely refined, this will allow you to view the results of the refinement in one file, including sigma errors.

Button 7: LIVEPLOT

This will allow you to visualize the progress of refinement.

Tab 1: LS Controls

Figure 20. LIVEPLOT showing the hkl values of a peak, done by hitting 'h' on your keyboard, while mousing over a peak.
• Number of cycles: Adjust number of cycles of refinement per GENLES run.

**Tab 2: Phase**

• Add phase: This is how your phase is initially input. Best to do from a .cif file, but can be manually input as well.

• Edit cell: Edit cell parameters. Will only allow editing of allowed parameters based on symmetry.

• Refine cell: Will refine cell parameters during GENLES.

• Atomic rows: When a row is selected, you may manually adjust atomic coordinates, site occupancy, or thermal parameters. These can also be refined with GENLES by checking X, U, or F, respectively. Atomic coordinates were not discussed in these two tutorials, because they are not important in a cubic system, but can be in other systems.

**Tab 3: Powder**

• Phase flags: Only phases which are checked will be refined. Generally leave all checked.

• Background: Edit background will allow you to edit the background. Within this, it is good to fit the background graphically initially, so the refinement has a good starting point. The different background types are just different ways the background line is calculated; this isn't very important.

• Diffractometer constants: These are constants from the instrument, and should not be changed, except for the zero-point offset, as that can arise from variations in sample height.

• Add new histogram: This is how the experimental diffraction pattern is initially added.

• Set data limits & excluded regions: From here you can adjust the portions of the diffraction pattern which are used. Good for ignoring large portions of background.

**Tab 4: Scaling**
• Scale factor: This is a mathematical constant to make the numbers of all refined variables worked out. This has no physical meaning, and should generally be left on.

• Phase fractions: If you are refining a system with multiple phases, these values will tell you the relative amounts in the diffraction pattern. This should not be taken with too much weight, as there are many factors which determine the relative intensities of different phases.

Tab 5: Profile

• GU/GV/GW: These are factors which determine the Gaussian contribution to the shape of each peak.

• LX/LY: These are factors which determine the Lorentzian contribution to the shape of each peak.

• Asym: A factor to compensate for asymmetry, primarily in low-angle peaks.

Tab 6: Re/Constraints

• New constraint: From here, you can add different constraints on the refinement. Examples which were discussed in the tutorials were keeping the thermal parameters of atoms the same as one another, and keeping the site occupancies of atoms within a doped system constrained to one another.

Troubleshooting

In the event something has gone wrong, it is easiest to catch it right away and select 'Continue with old' to avoid these changes from entering the file. If you miss this opportunity, either by accident, or because you didn't realize something was wrong, you're still safe.

In the top menu, click File, then Open. If you check 'Include Archived Files', you can go back to any iteration of your refinement, as shown in the image below. Also select to sort .exp files by 'Mod. Date', so you can see your history chronologically. When you click on a file, in the lower right, you will
see some information about your file, such as the current $\chi^2$ value, how many variables you were refining on, and how many times you had run GENLES so far. Click through these files and select the one you want to go back to. Once you hit Read, it will ask you whether you want to 'Use New Name', which will have you save this as a new .exp file to work with, or 'Continue with current', which will overwrite your current .exp file with the archived file.

![Image of an archived file](image)

**Figure 21. Opening an archived file.**

This is the easiest way in order to fix your file; essentially by undoing all changes in your file since things went wrong. Alternatively, you can look through the values for each refinement, and if you see something wrong, adjust it manually, but there isn't much advantage to this approach.

**Final notes**

You should now be able to do many aspects of Rietveld refinement. This is a very powerful technique, which can do much more than is listed here. The CCP14 website ([http://www.ccp14.ac.uk/whatsnew_history.html](http://www.ccp14.ac.uk/whatsnew_history.html)), although no longer updated, is a good resource for single-crystal/powder x-ray diffraction analysis, including a lot of GSAS resources. APS (Advanced
Photon Source @ Argonne) has put out a good guide as well:

http://www.aps.anl.gov/Xray_Science_Division/Powder_Diffraction_Crystallography/5ParametersRecipes/5ParametersRecipes.pdf

Obviously there is a lot more that GSAS is capable of, but here I have presented to you what I am most familiar with. Much of what I have learned is a result of Mark Green's crystallography class, for which I am very thankful. The rest has come from experimentation, and searching the internet. Please feel free to contact me if you have any questions, and I will do my best to help you out.

Will Boncher, wlb6@georgetown.edu.

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