Sonochemical route to create superconducting and superparamagnetic nanocomposites

by

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CHAPTER 1. INTRODUCTION

The purpose of this study is to demonstrate the capability of a single process, heterogenous sonochemistry, as a tool to produce two very different nanocomposites with tunable properties: a superconductor, MgB$_2$ with nano-inclusions, and iron/iron oxide (Fe/Fe$_2$O$_3$) in an alumina (Al$_2$O$_3$) matrix [for an explanation of sonochemistry and heterogenous sonochemistry see Section 1.1]. By modifying the sonochemical parameters, one is able to tune the magnetic properties and enhance the superconducting properties of MgB$_2$ and the superparamagnetic properties of the Fe/Al$_2$O$_3$ system. This is done through the ability of high intensity ultrasound to produce extreme environments where chemical and physical processes can occur due to acoustic cavitation.

Sonication is a term colloquially used to describe the process, or act, of irradiating a medium with sound energy, commonly in the form of exposure to ultrasound. Further, the term sonication is used in this work exclusively to mean irradiation with high intensity ultrasound. Sonication has been shown to reduce particle size, increase reactivity, act as a catalyst, and improve powder homogeneity. These are the effects of sonication which are exploited in this study.

For the MgB$_2$ study, B powder (both with and without dopants and inclusions) is sonicated in a decane solution before reaction with Mg to form MgB$_2$ nanocomposites. Sonication is used to homogenize dopants and inclusions, and is used to increase grain connectivity through reducing particle size. The dopants and inclusions act as pinning centers, thus preventing flux movement and increasing the critical current. However, adding too many pinning centers can increase phonon scattering and decrease the critical temperature. Also, clustered inclusions can disrupt the vortex lattice or create large normal regions inside the superconductor and
negatively affect the superconducting properties; sonication provides a way of creating small homogeneously dispersed inclusions. The samples are then encapsulated in minimally reactive pouches and exposed to Hot Isostatic Pressure, abbreviated HIP and discussed in section 2.3. HIP is used both as a means to react the B and Mg powders into MgB$_2$ and to reach near theoretical densities for the MgB$_2$ samples.

The superparamagnetic nanocomposite study utilized the catalytic and reactive nature of high-intensity ultrasound to create superparamagnetic nanocomposites by sonochemical irradiation of the carrier matrix material in the presence of a volatile organometallic precursor. During sonication, the volatile organometallic precursor, iron pentacarbonyl (Fe(CO)$_5$), forms mostly nanosized amorphous iron, which can then oxidize yielding iron oxide (Fe$_2$O$_3$ is used generically to describe any form of iron oxide). Sonication is used to produce and homogenize the nano-sized Fe and iron oxide particles throughout the Al$_2$O$_3$ matrix. The Al$_2$O$_3$ acts as a non-magnetic matrix providing stability and separation between the Fe and iron oxide particles. This is important as agglomeration of Fe particles will result in both domain formation and dissipation, which is undesirable. Sonication provides a single step process where Al$_2$O$_3$ and Fe(CO)$_5$ can be co-sonicated in decane to quickly and easily produce superparamagnetic samples. HIP is also used in these samples but instead is used to produce a structurally robust superparamagnetic ceramic that can be machined and processed for various applications.

This chapter is devoted to the discussion of the current state of knowledge on various subjects related to the thesis topic. Sonochemistry is reviewed in some detail before discussing type II superconductors and the properties of interest in this study. Superconducting nanocomposites are discussed with an emphasis on the difference between magnetic and nonmagnetic pinning in section 1.2.2. MgB$_2$ is highlighted with respect to the current state of research and the higher achievable values of $J_c$. Finally, the chapter concludes with a presentation of paramagnetism and superparamagnetism, and the advantages of using nanocomposites to make superparamagnetic samples.
1.1 Sonochemistry

Sonochemistry is the branch of chemistry that focuses on studying the effects of sound waves and sound properties on chemical reactions or systems, or simply the study of the chemical effects of high-intensity ultrasound. Sonochemistry can be further divided into the following subcategories, based on the type of reaction: homogeneous sonochemistry (liquids), heterogeneous sonochemistry (solid-liquid or liquid-liquid systems), and sonocatalysis (overlapping the first two). Sonochemical reactions must be carried out in a liquid phase for transmission of the sound waves and for cavitation to occur, which is why solid-solid or solid-gas systems are excluded. These types of reactions are excluded from the current study, as their use would be restricted to the materials modification only, and not to the synthesis of nanocomposites. Cavitation will be discussed in the upcoming section. My study focused on heterogeneous sonochemistry, therefore only one reaction type is discussed. For information on homogeneous or sonocatalysis, the reader can refer to [Einhorn et al., 1989], [Luche, 1996], [Pestman et al., 1994], and [Suslick, 1998].

Before proceeding, a brief look at the origin of sonochemistry should be presented. In 1894, Sir John I. Thornycroft and Sydney W. Barnaby noticed vibration in the testing of the first British destroyer propeller. They determined the vibration was caused by water pressure collapsing the bubbles created by the rotating propeller. Lord Rayleigh was commissioned by the british navy in 1917 to investigate the vibrations from the propeller and concluded it was due to the turbulence, heat, and pressure produced from the bubble collapse. Alfred L. Loomis was the first chemist to realize that intense sound waves could produce interesting chemical effects. It wasn’t until the 1980’s that sonochemistry really began to erupt as generators capable of high-intensity ultrasound became more reliable and inexpensive [Suslick, 1989].

Heterogeneous sonochemistry occurs between liquid-liquid systems or solid-liquid systems. This section, however, is focused on solid-liquid systems and the dynamics of these systems. Sonication, exposure to sound waves (In this work, sonication will exclusively mean irradiation of materials to high-intensity ultrasound), is used in many ways from cleaning to mixing to modification of powder shape, size, and morphology. Sonication with high-intensity ultrasound
provides access to an extreme environment for chemical reactions to occur with high pressure, short reaction times, and high energies through acoustic cavitation. Figure 1.1 shows a 3D representation of the different available methods for chemical processes in terms of energy, time, and pressure.

Figure 1.1: Graphical representation of some common chemical routes in terms of pressure, time, and energy. Sonochemistry is at the far end of this scale with high energy, high pressure, but short reaction times [Suslick, 1998, p. 527].

1.1.1 Cavitation and Bubble Collapse

Acoustic cavitation is the driving force of reaction processes during sonication. Sonication in liquid systems cause rapid and intense expansion and compression cycles. These cycles exert a negative pressure and positive pressure, respectively. During the expansion cycle, cavities can form if this negative pressure can overcome the tensile strength of the liquid. These cavities usually form where the tensile strength of the liquid is minimized, e.g. crevices, cracks, or small particles.
Once formed, these cavities "breath", expanding and contracting, with the subsequent expansion and compression cycles. The difference in surface area of the bubble leads to a faster expansion and a slower compression resulting in bubble growth from the competition of these two forces, surface tension and pressure, see figure 1.2. Eventually, the bubble reaches a resonant size where it absorbs a large amount of energy in a single expansion cycle and dramatically increases in size. During the next compression cycle the bubble cannot sustain this large surface area and an implosion occurs. However, a jet occurs when a bubble collapses near an extended surface causing high velocity particle collisions with the extended surface and erosion of the surface. This phenomena is responsible for degradation and erosion of propellers.

Figure 1.2: Graphical representation of bubble evolution and collapses.

Implosive collapse of these bubbles produces a release of the bubble’s absorbed energy and creates shock waves that are responsible for particle collisions. This release of energy can cause local heating, or hotspots, with temperatures of 5000 °C and a peak pressure of 1000 atmospheres, as measured from spectroscopic analysis [Suslick, 1998]. The resulting particle
collisions help to break up larger particles, weld smaller particles, and homogeneously mix all particles in the solution. Apart from welding similar particles, sonication can also result in coating of particles or the adhesion of one particle species onto another, e.g. FeO on MgB$_2$ [Prozorov et al., 2003]. Sonication also induces morphological changes; this is particularly interesting in bulk superconductors as grain connectivity and grain boundaries have important influences on the superconducting properties.

1.1.2 Effects on Morphology, Reactivity, and Composition

Sonication has a profound effect on the morphology of powders and liquid-powder systems by smoothing particle surfaces. Metals with metal oxide coatings can be activated by sonication through stripping this coating and exposing the metallic surface, thereby increasing reactivity. Composition can also be affected through chemical reactions generated during the sonication process. This is particularly true when dealing with volatile organometallic compounds that are in liquid form, but upon reaction, form either solid-liquid or solid-gas yields. This is the case for Fe(CO)$_5$ and will be discussed in section 1.1.3.

![Image of morphological change in nickel powder before and after sonication](image)

Figure 1.3: Morphological change in nickle powder before and after sonication [Suslick, 1989, Figure 4 and 5].

Sonication effects on morphology is most remarkably seen in softer metals with low melting points. As shown in figure 1.3, Ni powder undergoes a drastic change in morphology resulting
from sonication [Suslick, 1989]. Figure 1.3a shows the Ni powder before sonication and a nonreactive crystalline coating is seen as the rough surface. Figure 1.3b shows the resulting powder after sonication where the nonreactive coating has been removed and the reactivity has been increased. This morphology change is attributed to shockwaves created by acoustic cavitation collapsing and causing high speed collisions between particles.

In the study aimed to determine the speeds of these particle collisions, the metal sonicated in the slurry was changed until neck-formations were not observed; The neck-formation is shown in figure 1.4. This figure shows two Zn grains that formed during an energetic collision resulting in the local melting and welding of the two grains. When irradiating slurries containing smaller grains, a collision can result in two particles merging into one without a visible neck-formation. The collision speeds estimated from this study suggest that particle collide with speeds $\sim 1/2\tilde{V}_{\text{sound}}$ [Doktycz and Suslick, 1990]. Alternatively, in processes involving two constituents (for instance MgB$_2$ and Fe(CO)$_5$), sonication can result in a change in surface morphology due to deposition of particles onto other grains or surfaces (iron oxide deposited on MgB$_2$ grains)[Prozorov et al., 2003].

Sonication can result in the “stripping” of particles from the surface of materials, particularly if it is an extended surface such as a metal sheet. This “stripping” of particles is a result of cavitation collapse on the surface, figure 1.5a, resulting in jets of particles colliding with the surface. This process is very similar to the idea of sand blasting, where high velocity particles collide with a surface and remove surface layers. This is very important as these newly exposed surfaces have a higher reactivity than the unsonicated sheets. Figure 1.5b, shows the destructive power of sonication and the reason why cavitation can cause problems for boat propellers. An increase in reactivity is not only achieved for extended surfaces, but can occur in powders as well [Suslick, 1998]. Glancing collisions in metal powders can result in the same “stripping” of powder surfaces, thereby increasing their reactivity.

The extreme environment created by cavitation collapse releases energy that can result in a change in composition and speed chemical reactions. Fe(CO)$_5$ is a yellowish-orange liquid, but after only a few seconds of sonication, it turns to a deep blackish brown precipitate. This
change is mostly attributed to the reaction $\text{Fe(CO)}_5 \rightarrow \text{Fe(CO)}_5-n + n\text{CO}$ ($n=1-5$), where amorphous iron can be produced when $n=5$ [Suslick et al., 1981]. Many other catalytic and compositional effects have been studied, but these are outside the scope of this thesis. Further discussion of the effect of sonication on $\text{Fe(CO)}_5$ can be found in the next section.

1.1.3 Effects of Ultrasound on $\text{Fe(CO)}_5$

The effects of high intensity ultrasound on $\text{Fe(CO)}_5$ through the use of a direct immersion sonication device have been reported for several different sonication media [Suslick et al., 1981]. Ultrasound has been used to produce amorphous iron [Suslick et al., 1991], hollow iron oxide nanospheres [Bang and Suslick, 2007], iron colloids [Suslick et al., 1996], and a variety of nano-sized materials. All of these products involve the sonication of $\text{Fe(CO)}_5$ and basically the same procedure, with the exception of sonication times, sonication media, additives in addition to $\text{Fe(CO)}_5$, and the way the post sonicated material was further processed and handled. Many different products, each used for very different applications, can be made from the same basic
process, thus making ultrasound a very powerful tool to produce iron and iron oxide composites, including nanocomposites.

The effects of sonication on Fe(CO)$_5$ alone were studied and the chemical process was reported [Suslick et al., 1981]. Sonication of Fe(CO)$_5$ yields Fe$_3$(CO)$_{12}$ and finely divided iron, but the concentration of Fe$_3$(CO)$_{12}$ was found to differ based on the sonication medium. The primary reaction of Fe(CO)$_5$ is reported to generally follow:

$$Fe(CO)_5 \xrightarrow{\text{ultrasound}} Fe(CO)_{5-n} + nCO \quad (n = 1 - 5)$$  \hspace{1cm} (1.1)

Equation 1.1 shows that Fe can be produced by the loss of all carbonyls from Fe(CO)$_5$, but this loss of carbonyls may also occur for Fe(CO)$_2$ and Fe(CO). However, the activation energy for both Fe(CO)$_2$ and Fe(CO) is much higher and therefore less likely to occur than that of Fe(CO)$_4$ and Fe(CO)$_3$ production. Suslick observed the expected relationship between the increased vapor pressure of the solvent, thus reducing the peak temperature of hot spots, and the yield amounts for iron. Any Fe(CO)$_4$ produced will react with the remaining Fe(CO)$_5$ as follows:

$$Fe(CO)_4 + Fe(CO)_5 \rightarrow Fe_2(CO)_9$$  \hspace{1cm} (1.2)
Suslick tested the sonication of Fe$_2$(CO)$_9$ in decalin in the presence of Fe(CO)$_5$ and without Fe(CO)$_5$, and found that both processes produce Fe(CO)$_5$ and finely divided iron. This means that Fe$_3$(CO)$_{12}$ is probably only produced from the reaction of Fe(CO)$_5$ that generates Fe(CO)$_3$ in the following way:

$$Fe(CO)_3 + Fe(CO)_5 \rightarrow Fe_2(CO)_8$$  \hspace{1cm} (1.3)

$$Fe_2(CO)_8 + Fe(CO)_5 \rightarrow Fe_3(CO)_{12} + CO$$  \hspace{1cm} (1.4)

Suslick also suggests that another possible route would be the dimerization of Fe(CO)$_4$, thus producing Fe$_2$(CO)$_8$, and then would continue through Equation 1.4 to produce Fe$_3$(CO)$_{12}$. Suslick reports that the relative yield using Fe(CO)$_5$ at a .10 M ratio with 1-pentene sonicated in decane yields approximately 2.4% Fe$_3$(CO)$_{12}$. One can infer that the remaining percentage is likely to be unreacted Fe(CO)$_5$ and a large portion of finely divided iron particles.

The sonication of Fe(CO)$_5$ results in mostly finely divided iron particles when sonicated in decane without other powder additives [Suslick et al., 1991]. When sonication occurs in the presence of another powder, the results can be the coating of this powder on the surface of the fine iron grains or can be the iron coating the surface of this other powder. The latter process, when carbon powder is used, can result in hollow nanospheres of iron since the post-sonicated product reacts the carbon due to the energy released during the oxidation of the iron surface, thus leaving only the hollow iron oxide sphere [Bang and Suslick, 2007]. Other additive powders result in iron or iron oxide grains attaching to the powder surface; this result is used to produce a non-magnetic matrix with isolated magnetic nanoparticles.

### 1.2 Type II Superconductors

Superconductivity was first discovered by Heike Kamerlingh Onnes in 1911 when he noticed that the electrical resistance of mercury abruptly dropped at a temperature of 4.2K [Onnes, 1911]. Several other pure metals were discovered to be superconducting and work began to determine the mechanism and define the characteristics of this newly discovered phenomena. In 1933 another interesting property emerged, Meissner and Ochsenfeld found that below the superconducting transition temperature, $T_c$, these materials expelled an applied
field, which is now known as the Meissner effect [Meissner and Ochsenfeld, 1933]. This effect in superconductors distinguishes superconductivity from being simply defined as “perfect conductivity”. In a perfect conductor, the penetrating field in the “normal” state would persist when the temperature was reduced below $T_c$; however, in a superconductor, the field is spontaneously expelled from the interior of the superconductor below $T_c$. While below $T_c$, the superconductor will return to the normal state by applying a high enough current, the critical current ($J_c$), or a high enough magnetic field, the critical field $H_c$.

In 1950, Ginzburg and Landau developed a mathematical theory that models superconductivity, but still didn’t offer an explanation of the mechanism [Ginzberg and Landau, 1950]. The Ginzburg-Landau (GL) theory did however introduce the two characteristic lengths that would later be used to divide superconductivity into two categories: type I and type II; these characteristic lengths being the coherence length $\xi$ and the penetration depth $\lambda$ given by:

$$\xi = \sqrt{\frac{h^2}{2m|\alpha|}}$$  \hspace{1cm} (1.5)

$$\lambda = \sqrt{\frac{m}{4\mu_0e^2\psi_0^2}}$$  \hspace{1cm} (1.6)

where $\psi_0^2$ is the GL order parameter in the absence of an electromagnetic field and $|\alpha|$ is a phenomenological parameter of the GL equations. The coherence length, $\xi$, is interpreted as the characteristic length over which $\psi$ deviates significantly from $\psi_\infty$, and the penetration depth, $\lambda$, is the length over which the field decays into the superconducting region. These length parameters are combined in a ratio known as the GL parameter $\kappa$, where $\kappa = \lambda/\xi$. Type I superconductors were defined as superconductors with $0 < \kappa < 1/\sqrt{2}$ and type II were defined as superconductors with $\kappa > 1/\sqrt{2}$.

In 1957, Alexei Abrikosov used the GL theory to show that in higher applied fields the field penetrates type II superconductor in quantized flux tubes, known as Abrikosov vortices to be discussed in section 1.2.2 [Abrikosov, 1957]. In this same year, Bardeen, Copper, and Schrieffer (BCS) proposed the microscopic theory of superconductivity and described the Cooper pair as the mechanism for superconductivity [Bardeen et al., 1957]. This provided yet another means of dividing superconductors into conventional, those following BCS theory, and unconventional,
those that do not fit the BCS theory. Later, as higher temperature superconductors were being
developed, the critical temperature ($T_c$) and the composing materials of the superconductor
became further categorical divisions.

The superconductors response to magnetic field penetration near $H_c$, the thermodynamic
critical field, is another defining property that separates type I and type II. Figure 1.6 shows a
graph of the flux penetration in both type I and type II superconductors. Type I has a single
critical field $H_c$ where the flux penetrates, but type II has two distinct fields: $H_{c1}$ where the
flux penetrates in the form of vortices entering what is known as the vortex state and $H_{c2}$
where the field fully penetrates and the material returns to the normal state. It can be seen
in figure 1.6 that type I superconductors undergo a first order phase transition at $H_c$, whereas
type II superconductors undergo a second order phase transition at $H_{c1}$ and $H_{c2}$. The vortex
state that arises in the region between $H_{c1}$ and $H_{c2}$ will be discussed further in section 1.2.2.

![Figure 1.6: Flux penetration in type I and type II superconductors](image)

1.2.1 Bulk Properties

The three major values generally associated with superconductors, mentioned previously,
are the three critical values of field, temperature, and current. Critical field and temperature
are examined in the present section with relation to impurities and defects, but the effect of impurities on critical current is reserved for section 1.2.2 where pinning is treated. A short description of critical current in the case of a pure superconductor with no pinning is presented at the end of this section.

With a GL parameter of $\kappa > 1/\sqrt{2}$, type II superconductors have very different magnetic properties over the type I superconductors, as well as generally higher critical temperatures and higher critical fields. This difference is generated from the consequences of $\xi < \lambda$. This results in a negative surface energy that makes it favorable for the material to be subdivided into domains until it is limited by the microscopic coherence length $\xi$. This was first theorized by Abrikosov in 1957 when he proposed that flux would enter and form a regular array of flux tubes, each tube carrying a quantized flux:

$$\Phi_0 = \frac{hc}{2e}$$

These tubes are composed of a normal core of size $\sim \xi$ surrounded by supercurrents that decay in the range of $\sim \lambda$. Since $\lambda > \xi$, the region of superconducting material to normal material remains large, thus allowing the superconductors to function even in higher fields. As the field is increased near $H_{c2}$, the flux lattice becomes more populated until eventually the supercurrent regions begin to overlap and it becomes energetically favorable for the material to return to the normal state above $H_{c2}$. The focus of section 1.2.2, will be the examination of the motion of the vortices due to applied currents and how the flux can be pinned in place by impurities, but first, the basic critical values are discussed in more detail.

### 1.2.1.1 Critical Fields in Type II Superconductors

Earlier $H_c$ was defined as the thermodynamic critical field and is related to the energy difference between the superconducting state and the normal state, $f_s - f_n = \frac{H^2}{8\pi}$, but this is only measurable when discussing type I superconductors. However, $H_{c1}$ and $H_{c2}$ (sometimes called the lower and upper critical fields, respectively) can be related in a type II superconductor
to a single thermodynamic critical field using the following equations:

\[
H_{c1} = \frac{4\pi}{\Phi_0} \epsilon_1 = \frac{H_c}{\sqrt{2\kappa \ln \kappa}}
\]  

(1.8)

\[
H_{c2} = \frac{\Phi_0}{2\pi \xi^2(T)} = \sqrt{2\kappa} H_c
\]  

(1.9)

where \(\epsilon_1\) is the vortex line tension or the free energy per unit length. From equation 1.9, one can see how \(H_{c2}\) can be affected by the addition of impurities and inclusions through the coherence length, \(\xi\), which is affected by the mean free path, \(\ell\). The mean free path is the average distance over which a charge carrier experiences scattering from collisions. Therefore by introducing impurities or inclusions into a clean superconductor, one can make the superconductor "dirty" and reduce the mean free path. To understand the effects these impurities will have on the superconducting properties, particularly \(H_{c2}\), one can calculate the effect of changing \(\ell\) on \(\xi\) and \(\lambda\). Using GL theory near \(T_c\) in the dirty limit, the equations for \(\xi\) and \(\lambda_{ef}\) can be written in a temperature dependent form related to the Pippard coherence length \(\xi_0\) and \(\ell\) as follows [Tinkham, 1996, pp. 118-120]:

\[
\xi(T) = 0.855 \frac{(\xi_0 \ell)^{1/2}}{(1 - t)^{1/2}}
\]  

(1.10)

\[
\lambda_{ef} = \lambda_L \left( \frac{\xi_0}{1.33 \ell} \right)^{1/2}
\]  

(1.11)

where \(t\) is the reduced temperature \(T/T_c\). Clearly, if \(\ell\) is decreased by the addition of more impurities, or inclusions, \(\xi\) is reduced and \(H_{c2}\) in equation 1.9 will be increased. This demonstrates how impurities and defects can increase the range of superconductivity in a magnetic field by increasing the upper critical field.

### 1.2.1.2 Critical Temperature and Impurity Effects

\(T_c\) is the temperature at which a transition occurs between the normal and the superconducting state. This transition occurs because at \(T_c\) the superconducting state has lower energy than the normal state. \(T_c\) is defined as the highest temperature for which a lower energy is given for \(n_s = |\psi|^2 \neq 0\) over that of \(|\psi|^2 = 0\), where \(n_s\) is the density of the superconducting electrons. From the GL theory, \(\alpha\) changes from positive to negative since \(|\psi_\infty|^2 \equiv -\frac{\alpha}{2}\) at
$T_c$. With $T_c$ now defined as the transition temperature, one might naturally wonder how to calculate $T_c$ from measurable quantities and also how $T_c$ is affected by things like impurities.

BCS theory gives a means of calculating $T_c$ from finding when the temperature dependent energy gap $\Delta(T) \to 0$; this is given by:

$$\frac{\Delta(0)}{kT_c} = \frac{2}{1.13} = 1.764$$

(1.12)

This is true for conventional superconductors, following the BCS theory, but experimental values for $2\Delta$ can range between $3.0kT_c$ and $4.5kT_c$, with most clustering near the BCS value $3.5kT_c$ [Tinkham, 1996]. Further, it is also known that $T_c$ as well as $H_c$ is expected to follow what is called the isotope effect where $T_c \sim M^{-\alpha}$, $\alpha = \frac{1}{2}$ for BCS superconductors [Maxwell, 1950, Reynolds et al., 1950]. It has been shown that this value of $\alpha$ is not always $\frac{1}{2}$, and is affected by other properties of the specific material, like Coulomb interactions [Bill et al., 1998].

When impurities or defects are added to the superconducting material, the $T_c$ of the material can be reduced due to scattering off the additional defects as well as from magnetic effects. The effects of impurities on $T_c$ can be divided into two categories: magnetic and non-magnetic impurities. With magnetic defects, the local spin of the impurity interacts with the electron spin of the Cooper pair ($\sim -2J S_s$) and can result in the pair breaking of the Cooper pair, and thus the lowering of $T_c$. The pair breaking formula in the Abrikosov-Gorkov theory with paramagnetic impurities is:

$$\alpha \equiv \tau_s^{-1} = \frac{n}{h} \left[ \frac{N(E_F)}{2k_B} \right] J^2 D(R)$$

(1.13)

where $N(E_F)$ is the density of states at the Fermi level, $n$ is the impurity concentration, $J$ is the exchange energy, and $D(R)$ is the DeGennes factor. Further, the theory predicts a universal form for the decrease in the transition temperature in terms of the pair breaking parameter $\alpha$,

$$\ln \left( \frac{T}{T_{c0}} \right) = \psi \left( \frac{1}{2} \right) - \psi \left( \frac{1}{2} + 0.14 \frac{\alpha T_{c0}}{\alpha_{cr}} \right)$$

(1.14)

where $\psi$ here is the digamma function and $\alpha_{cr}$ corresponds to the destruction of superconductivity at all temperatures. Since $\alpha$ is proportional to $n$, $\alpha_{cr}$ is similarly proportional to
a critical impurity density $n_{cr}$ for which the superconductivity will be destroyed. The initial reduction in $T_c$ with increasing rare earth impurities from the Abrikosov-Gorkov is given by:

$$\left(\frac{dT_c}{dn}\right)_{n=0} = -\left[\frac{\pi^2 N(E_F)}{2k_B}\right] J^2 D(R)$$

(1.15)

The results of both equation 1.14 and 1.15 demonstrate how the initial addition of magnetic impurities can reduce the critical temperature and, at some critical limit, the superconductivity will be completely destroyed with the addition of too many magnetic impurities through the breaking of the Cooper pair [Bennemann and Ketterson, 2008, p. 645].

Non-magnetic impurities also act to break Cooper pairs by introducing additional scattering sites. Using the BCS model, the change in $T_c$ can be attributed to the effect the impurity has on the general properties of the superconductor and also the reduction of the anisotropy energy through the reduction of the mean free path. When $\ell = \infty$, the superconductor is said to be pure without any scattering. As impurities and defects are added $\ell$ is reduced and when $\ell < \xi_0$, the superconductor is said to be in the “dirty” limit. This is important as the region $\ell \sim \xi$ is the theoretical separation between the dominate effect in the change of $T_c$ with the addition of more impurities. The initial introduction of impurities results in a reduction of $T_c$ that is nearly linear and is effected heavily by $\ell$, and thus is named the “mean-free-path” region. However at $\ell \sim \xi_0$, the effect is determined by the impurity itself and the way the impurity effects the properties of the system, and is known as the “valence” region [Markowitz and Kadanoff, 1963].

The basic BCS formula for $T_c$, $kT_c = 1.14 \omega_D \exp[-1/VN(0)]$, can be used to get a very general understanding of how impurities would affect $T_c$, but this is far from theoretically rigorous. It is important to note that $V$ in the BSC formula is the interaction potential and not volume. The full theoretical derivation of the subsequent formulas can be found in the paper by Markowitz referenced above. The results come from treating the anisotropy effect as a correction to $V$ in the “mean-free-path” region and using a linear term, $K^i$, that accounts for any corrections in the “valence” region. The formula for the effect of non-magnetic impurities
on $T_c$ is:

$$\delta T_c(\chi) = K^i \chi + \langle a^2 \rangle T_c I_c(\chi),$$

where $I_c(\chi) = \int_0^{2\beta_c \omega_D / \chi} \frac{dy \tanh(\frac{1}{4} \chi y)}{y \left(1 + y^2\right)}$, (1.16)

where $\langle a^2 \rangle$ is the angular average of the square of the anisotropy interaction, and $\chi = (kT_c \tau_a)$

where $\tau_a$ is the collision time equal to $\ell / v_F$. This shows that with the initial introduction of impurities the $T_c$ will in fact decrease, but then as $\ell \sim \xi_0$ the change in $T_c$ will become linearly dependent on the term $K^i$ which will change with the selection of the impurity. With both $H_c$ and $T_c$ accounted for, $J_c$ is the last of the three major values to examine.

### 1.2.1.3 Description of Critical Current

$J_c$ is the critical current, or the maximum current for which superconductivity can still occur. This is trivial to define in the case of a type I superconductor as it is related directly to $H_c$ through Ampere's Law. For this approach, the formula for $J_c$ takes the simple form of:

$$J_c = \frac{c}{4\pi} \frac{H_c}{\lambda}.$$  (1.17)

This is easy to understand as this current will produce a field equal to that of the critical field and therefore result in the return to the normal state. However, in type II superconductors this formulation of $J_c$ offers little practical applicability as flux penetrates at $H_{c1}$. $J_c$ is still defined as the maximum current that can be applied before a finite resistance develops, but the formulation is more complex. In order to calculate $J_c$ “properly” for a type II superconductor, the effect of applied current on vortex motion and pinning needs to be addressed. Without providing any formalism, it is useful to define $J_c$ for type II superconductors as the maximum current that can be applied before the onset of power dissipation.

### 1.2.2 Vortices, Flux Motion, and Pinning

A previous section, 1.2, described how flux can penetrate type II superconductors at a field $H_{c1}$ up to a field of $H_{c2}$ where the material then becomes normal. Once flux enters, it forms a regular array inside the sample due to the mutual repulsion of each vortex which was first described by Abrikosov [Abrikosov, 1957]. Abrikosov’s calculations suggested a regular
square shaped flux lattice as the stable lattice, but later calculations revealed that a lower energy state was the triangular array lattice. Ten years later, the first direct observation of the Abrikosov lattice were published and can be seen in figure 1.7a. Also, figure 1.7b shows the flux lattice with defects from holes and lattice distortions. Other types of defects include stacking faults and point defects (interstitials and vacancies) [Essmann and Träuble, 1967]. These defects introduce an energy barrier that can trap or hinder flux motion, and when this occurs the vortex is said to be pinned.

![Figure 1.7: Surface of Pb-4at% In rod at 1.1K. The black dots consist of cobalt particles which have been stripped from the surface with a carbon replica. The right image shows a high density of defects in the flux lattice. (A: Hole B:Flux line dislocations.)](Essmann and Träuble, 1967, Figure 1 and 2)

### 1.2.2.1 Flux Motion due to Applied Current

As shown earlier, the vortex is comprised of a normal core that decays into the superconducting space. These normal cores allow for flux to penetrate and can cause problems for applications requiring applied currents. With both applied current and flux penetration, the Lorentz force begins to act on these flux lines and can cause flux flow if the flux lines are not pinned in place by some other force, e.g. a pinning force. The Lorentz force equation is written
\[ \mathbf{F}_L = J_i \times \frac{\mathbf{B}}{c}, \quad (1.18) \]

where \( J_i \) can be any current in the sample. The Lorentz force can be used to show that the regular triangle array results from the mutual repulsion felt between a set of two vortices. For this situation, one would use the current density produced by the shielding currents of one vortex at the location of the other vortex’s flux center. However for applied currents, the Lorentz force equation can be used to show that without some opposing force the vortex lattice will begin to flow resulting in flux motion.

Equation 1.18 shows how the interaction of an applied current, \( J_a \), present in the superconductor and the flux, \( B \), inside the vortex core act to generate a force on the vortex causing vortex motion. This force, assuming no other forces, causes the flux line to move transverse to the current at a velocity \( v \), which causes an electric field parallel to the current following the equation:

\[ \mathbf{E} = \mathbf{B} \times \frac{v}{c} \quad (1.19) \]

This electric field created by the flux motion in the presence of the parallel applied field becomes a source of power dissipation. Although this is not a theoretically rigorous approach, it demonstrates how the Lorentz force motivates flux flow and power dissipation in the absence of pinned vortices.

In order to prevent this electric field and power dissipation, one needs to introduce some form of pinning force that prevents these flux lines from flowing. This pinning force is introduced through the addition of pinning centers or defects that act to add a potential well where the vortices will become pinned. Without pinning, there is a small viscous drag associated with the flux motion, but this force is not significant enough to slow or stop the flux motion and other pinning is needed. Pinning is inherent in any bulk sample since bulk samples cannot be produced free from defects, but pinning centers on the scale of \( \xi \) and \( \lambda \) are the most effective. Pinning comes in the form of any inhomogeneity in the material such as: impurities, grain boundaries, or voids. These voids can be introduced through doping and artificially introducing impurities.
1.2.2.2 Pinning Force from Non-Magnetic and Magnetic Inclusions

The concept of a pinning center acting as a potential well was briefly mentioned earlier, and this idea is now expanded to formulate a limiting value at which a pinning center will be ineffective. A pinning center is considered ineffective if instability in the vortex lattice is caused rather than providing a point of stability where the vortex is held. A dilute system of pinning centers allows one to consider the effect on a single vortex. For this case, the pinning force, \( p \), at the origin results in a displacement \( u_0 = \frac{p}{4\pi\mu_e\beta(\phi_0/B)^{1/2}} \) of the vortex. Therefore, at some point \( \frac{dp}{dx} > 4\pi\mu_e\beta(\phi_0/B)^{1/2} \) must be reached in order for stability. This is known as the pinning threshold and indicates that the curvature of the potential well must meet this threshold value in order for the inclusion to have a stabilizing effect.

In this thesis, the pinning force is not being calculated directly and therefore a more general approach can be taken in terms of how the pinning force is calculated. The vortex lattice forms a regular array due to the mutual repulsion of neighboring vortices. If a portion of the lattice is pinned by randomly distributed pinning centers, the entire vortex lattice is considered to be held in place by an average pinning force. The total pinning is then \( P_v = Np_m \) where \( N \) is the number of active pinning centers in the sample and \( p_m \) is the average pinning force for one such pinning center binding one vortex.

For the purposes of this thesis, the theoretical derivation of the pinning force will not be presented, but if the reader is interested Campbell and Evetts offer many theoretical approaches for estimating the pinning force in various situations [Campbell and Evetts, 1972]. Also, the formulas that follow are obtained from this same reference and further discussion of their limitations and applicability can be found in section 7.2 Pinning Interactions in a Stress-Free Material of [Campbell and Evetts, 1972]. For non-magnetic pinning, the maximum pinning force is estimated for small particles of radius \( q \ll \xi \) as:

\[
p_m = \frac{\mu_0^{3/2} H_0^{5/2}}{\kappa^2(\phi_0)^{1/2}} \left( \frac{4}{3} \pi q^2 \right) \tag{1.20}
\]

where \( \mu_0 \) is the shear modulus for the vortex lattice. This result comes from considering the energy necessary to drive the electrons normal in the core when the core is moving away from the pinning center. This approach shows that the pinning force \( p_m \) on a single vortex
is proportional to the volume of the pinning center. However, it should be noted that this formulation becomes inaccurate if the particle size is increased such that the size affects the material properties such as when \( q \gg \xi \). Since nanocomposites are being considered, this estimation remains valid so long as the impurity size stays below the region of \( \xi \), for MgB\(_2\) this means \( q \ll 3\text{-}12\text{nm} \).

The pinning force is considered to be long ranged for magnetic defects as the magnetization of the particle interacts with the supercurrents surrounding the vortex core. This interaction allows the magnetic pinning centers to act on a range of the order \( \lambda \) rather than in the range of the vortex core, \( \xi \). Magnetic pinning was theoretically considered as a surface or near surface effect only, but recently bulk magnetic pinning was treated theoretically and experimentally [Snezhko et al., 2005]. The magnitude of the force is affected by the particle size, orientation of the magnetization vector, and the magnetization value. The presence of the magnetic particle induces a supercurrent and the pinning force is written with respect to this induced supercurrent density, \( \tilde{j}(\rho_v, \theta_v) \), at the vortex core in spherical coordinates as:

\[
\tilde{F} = \int [\tilde{j}(\rho_v, \theta_v) \times \tilde{\phi}_0] \, dl,
\]

where \( dl \) is the flux line element, the integration is over the entire flux line, and \( \tilde{j}(\rho_v, \theta_v) \) is given by:

\[
\tilde{j}(\rho_v, \theta_v) = -\frac{MR}{[1 + 3(\lambda/R) + 3(\lambda/R)^2]} \left( \frac{1 + \rho/\lambda}{\rho^2/\lambda^2} \right) \exp \left( -\frac{\rho - R}{\lambda} \right) \sin \theta. \tag{1.22}
\]

Snezhko uses this calculation to show that for \( \rho - R > \lambda \) the magnetic force magnitude is proportional to \( \exp[-(\rho - R)/\lambda] \) justifying the claim that the force acts on a range farther than \( \lambda \). This force will be attractive for angles \( 0 < \alpha < \pi/2 \) and repulsive for \( \pi/2 < \alpha < \pi \). However assuming a random distribution of particles, the force being attractive or repulsive is immaterial and the vortex still experiences a bulk pinning effect. A more meaningful treatment of \( J_c \) is now presented that discusses the effect of pinning in the critical state model.
1.2.2.3 Critical Current in the Critical State and Bean Model

Section 1.2.1.3 defined $J_c$ as the maximum current permitted without resistance. Without pinning, any currents would produce a Lorentz force and cause dissipation; therefore, $J_c = 0$. With the introduction of pinning, a current is able to flow up to a maximum value such that the pinning force can compensate for the Lorentz force, thus maintaining the stable vortex equilibrium. However as the pinning has a maximum value, $p_m$, this indicates that there must also be a maximum point where increasing the current any further results in $F_L > F_v$ and dissipation occurs; this current is $J_c$. This leads to the idea of a state in which the stability of the vortex lattice is dependent on these critical phenomena, the critical state. Naturally, the limit of the critical state is represented by the formula:

$$B \times \text{Curl } H = B \times J_c = P_v(B).$$

In the simple case where current and flux are perpendicular, this equation reduces to simply $J_c = P_v/B$. This $J_c$ is the typical $J_c$ associated with experimental measurements when dealing with type II superconductors.

The critical state is used to describe how the magnetic field and critical currents penetrate into the superconductor. As small fields are applied, the field begins to penetrate the exterior of the sample, but at some internal distance the field will be zero. Critical current flows in the region where the field penetrates, but is zero in the region where the internal field is zero. As the external field increases, the internal field and current penetrate further into the sample. Many models offer a relationship between the critical current and the internal field, but none is more simple or more widely used than the Bean Model. In 1962, C. P. Bean publishes a paper where he makes a simple approximation to deal with magnetization and flux penetration inside of a cylindrical type II superconducting sample [Bean, 1962]. The resulting model is called the Bean model or the critical state model.

The purpose of Bean’s paper was to theoretically calculate the magnetization of hard superconductors. However, his paper is better known for the model that he used to arrive at his results. Bean assumes that the sample is only capable of sustaining a lossless macroscopic current up to a maximum current, $J_c$, and the currents flow to this full amount for a depth
necessary to compensate for the penetrating flux. Using the Bean model one can construct a
one dimensional flux density profile to help understand hysteresis in type II superconductors;
figure 1.8 is one such profile.

![Bean model interpretation of flux entrance into type II superconductor](image)

Figure 1.8: Bean model interpretation of flux entrance into type II superconductor

Figure 1.8 shows how this flux density profile would look for a applied field in the $\hat{z}$ direction
and therefore the current $J$ in the $\hat{y}$ direction. The slope of the lines given by the gradient
dB/dx can be related to the current through Ampere’s Law, $\nabla \times B = \mu_0 J$, which reduces
to $-dB/dx = \mu_0 J$ in one dimension. As the field is increased, the current penetrates further
into the sample until the value $H^*$ where the maximum field is screened and the maximum
current flows throughout the sample. As the field is raised above $H^*$, the flux increases in
the sample, but $J_c$ is unaffected. Figure 1.8b shows that as the field is decreased the flux
density gradient must remain constant and flux can become trapped inside the sample. This
is most obvious when returning to no applied field, $H=0$, as indicated in Figure 1.8b. Once $H = -\frac{1}{2}H^*$ is reached, one sees a canceling of flux densities. It is clear from the figure that type II
superconductors are hysteretic (meaning they retain a “memory” of their magnetic history),
and are therefore irreversible which limits their use in ac applications.

The Bean model can also be used to calculate $J_c$ from the hysteretic or irreversible part of a magnetization loop. This means that the hysteresis loop can be decomposed into reversible and irreversible parts. By then taking the difference in the heights of the irreversible loop $2\Delta M_{irr}$ and multiplying them by a factor based on the samples geometry and dimensions, the magnetic data can be converted to $J_c$. This is done through the use of calculating the total magnetic moment for the shapes specific geometry using a Bean model approach, meaning $j(r)$ is constant across the entire sample [Charles P. Poole et al., 2007, p. 396]. The total magnetic moment is given by the general formula:

$$M = \frac{1}{2} \int_V [r \times j(r)] d^3r.$$  \hspace{1cm} (1.24)

Using the sample geometry of a slab of rectangular cross section with sides $2w$ and $2b$ ($w \leq b$) and thickness $2d$, the exact formula can be reached as:

$$M = \frac{J_c w}{20} \left( 1 - \frac{w}{3b} \right) V, \text{ where } V = 8wbd.$$  \hspace{1cm} (1.25)

Further, the strength of the pinning force in the material can be estimated by taking this $J_c$ and multiplying by the applied field which uses the critical state equation, equation 1.23. Equation 1.23 and 1.25 are used later in the data analysis of MgB$_2$ to convert the magnetization measurements into both $J_c$ and the corresponding pinning force.

### 1.3 MgB$_2$

MgB$_2$ has been produced since the early 1950’s, and was widely available from commercial sources well before 2001. It was announced that MgB$_2$ was superconducting with an unusually high transition temperature of 39 K by Akimitsu at a symposium on “Transitional Metal Oxides” on January 10, 2001 in Sendai, Japan. After this announcement, experimentalists scrambled to verify this discovery and theorists rushed to explain how this simple binary system was offering such a high $T_c$. Studies began focusing on understanding the origin of this high transition temperature, and other detailed studies of MgB$_2$’s superconducting properties began. By July alone, more than 260 studies had been performed with a majority being posted
to the e-prints archive at http://xxx.lanl.gov/. As this thesis is only concerned with the effects on $H_c$ and $J_c$ due to sonication and additives, the specifics on the theory of the superconducting properties will not be presented; however, some properties will be referenced.

MgB$_2$ is popular because of its unusually high transition temperature among simple binary compounds and also its high $H_c$ and $J_c$ values, which makes it an excellent candidate for high current and field applications. The conventional models could not accurately predict the data coming from isotope substitution and specific heat measurements. Initial assumptions by some researchers were that this high $T_c$ indicated an exotic superconducting mechanism. As MgB$_2$ was studied, the complexity of this physically simple and easily produced compound became apparent.

By late 2001, Choi et al. presented the origin for the anomalous behavior of MgB$_2$ from first principles [Choi et al., 2002]. Others had already theorized two gaps [Liu et al., 2001, Golubov et al., 2002] or presented evidence of MgB$_2$ being two-gapped but no calculations were done from first principles. By late 2002, MgB$_2$ was well studied and there was a general consensus on the superconducting properties and the superconducting mechanism, which was not exotic, but was interesting. In 2003, a Physica C issue was devoted to reviewing the normal and superconducting properties of MgB$_2$ (Volume 385, Issue 1-2, March 2003).

MgB$_2$ is now accepted as a two-gap superconductor following BCS phonon mediated s-wave behavior by the majority of the physics community. These two gaps are the pi-band gap and the sigma-band gap, having the values: $\Delta_\pi \approx 2.8$ meV and $\Delta_\sigma \approx 6.8$ meV. MgB$_2$ has the AlB$_2$ hexagonal structure where B and Mg are arranged in alternating layers as can be seen in figure 1.9. The physical properties can be seen in table 1.1 as reproduced from [Charles P. Poole et al., 2007, Table 9.2]. Poole notes that some of these values are averages and were not arrived at using a two gap model. Section 1.3.2 takes a closer look at the specific $H_c$ and $J_c$ values for certain samples produced during research.
1.3.1 Doping: Substitution and Nanoparticle Inclusions

The doping of MgB$_2$ with various compounds and elements has produced samples with improved magnetic and transport properties. In literature, doping is generically used to describe the introduction of any “foreign” constituent to the MgB$_2$ matrix which might have some magnetic or electrical effect. Doping can produce two outcomes, a substitution or an inclusion. A substitution (also known as substitutional chemistry) can be defined as doping with an additive that replaces either the Mg site or B site on the atomic scale and acts similarly to the Mg or B atoms. Substitutions are generally represented by either the formula (Mg$_{1-x}$A$_x$)B$_2$ or Mg(B$_{2-x}$A$_x$), where A is the additive and x is relative amount of substitution. Inclusions, or nanoparticle inclusions, are defined as any small, or nanosized, impurities (being larger than a single atomic unit) trapped inside the sample during the formation of the MgB$_2$. These inclusions act as pinning centers and add strength to the pinning force restricting flux movement. Although these particles may replace Mg or B sites, the nanoparticles act as voids or impurities rather than acting similarly to Mg or B.

The importance of using nanosized particles can be seen in equations 1.20 and 1.16. With
Table 1.1: Basic physical properties of the superconductor MgB$_2$. Some parameters are anisotropic with only average values listed here and are not achieved using a two gap model.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superconducting transition temperature $T_c$</td>
<td>39 K*</td>
</tr>
<tr>
<td>Coherence length $\xi_0$</td>
<td>5 nm*</td>
</tr>
<tr>
<td>Penetration depth $\lambda$</td>
<td>140 nm*</td>
</tr>
<tr>
<td>Ginzberg-Landau parameter $\kappa$</td>
<td>$\approx$ 25</td>
</tr>
<tr>
<td>Electron mean free path $\ell$</td>
<td>$\approx$ 60 nm*</td>
</tr>
<tr>
<td>Residual resistivity ratio RRR = $\rho(300K)/\rho(42K)$</td>
<td>$\approx$ 20</td>
</tr>
<tr>
<td>Debye temperature $\Theta_D$</td>
<td>340 K</td>
</tr>
<tr>
<td>Fermi surface electron velocity $V_F$</td>
<td>$4.8 \times 10^5$ m/sec*</td>
</tr>
<tr>
<td>Isotope effect constant $\alpha$</td>
<td>0.32</td>
</tr>
<tr>
<td>Upper critical field $B_{c2}$, clean sample ($\ell \gg \xi_0$)</td>
<td>16 T*</td>
</tr>
<tr>
<td>dirty sample ($\ell \ll \xi_0$)</td>
<td>30 T*</td>
</tr>
<tr>
<td>Irreversibility field $B_{irr}$, clean sample</td>
<td>7 T*</td>
</tr>
<tr>
<td>dirty sample</td>
<td>15 T*</td>
</tr>
<tr>
<td>Thermodynamic critical field $B_c$</td>
<td>0.43 T</td>
</tr>
<tr>
<td>Lower critical field $B_{cl}$</td>
<td>30 mT</td>
</tr>
<tr>
<td>Critical current density $J_c$</td>
<td>$\approx 4 \times 10^5$ A/cm$^2$*</td>
</tr>
</tbody>
</table>

*Values obtained from [Canfield et al., 2003].

large or agglomerated (meaning many nanoparticles clustered together) particles, the scattering cross section becomes large and $T_c$ will be significantly reduced. Also, larger particles begin to negatively affect the superconducting properties by preventing flux from entering a stable configuration in the superconductor. In order to establish effective pinning the pinning centers need to be weak enough to allow flux entrance and stabilization, but strong enough to prevent the flux motion once it has penetrated the superconductor. Since the purpose of this thesis is to enhance the superconducting properties, preserving the native properties while enhancing pinning through the addition of pinning centers becomes the primary concern. This means adding inclusions that enhance both $J_c$ and $H_{c2}$ without having a significant negative effect on $T_c$. This is achieved through using both magnetic and non-magnetic nanoscaled (on the order of $\xi$) inclusions which have a large effect on $J_c$ and $H_{c2}$ without adding significantly to the phonon scattering effects which act to reduce $T_c$. However, the reader is reminded that the linear term in equation 1.16 is affected by the physical and chemical effects of the ion chosen to act as the inclusion. Therefore, size is not the only factor which needs to be considered and
a wide range of impurities should be attempted.

Before the end of 2001, several elements were already being tried to determine their effect on the superconducting properties of MgB$_2$; including Zn, Be, Cu, Ti, Nb, Si, Li, Ni, Fe, Al, C, Co, and Mn [Buzea and Yamashita, 2001]. Most of these additions do little more than lower the transition temperature while providing insignificant improvements to $H_c$ and $J_c$ values. Zn was reported as the only element that had resulted in a 1° increase in $T_c$, although there was no agreement on the doping level that resulted in this increase [Moritomo and Xu, 2001, Kazakov et al., 2001]. Most attempts to maximize MgB$_2$ have been through the effective use of elements and compounds to act as pinning sites to restrict vortex motion, in which case a homogenous distribution is important.

Some of the most successful additions have been C doping [Ma et al., 2006] and SiC doping [Dou et al., 2002, Jung et al., 2009, Kovac et al., 2009]. Single element doping with C results in both substitution of B and also some C particle inclusion. The effects of C-substitution is believed to be a result of electron doping, or band filling, and of the increase of carrier scattering [Tajima et al., 2007]. C doping does however causes a significant drop in the $T_c$ value, by $\sim$ 7-10K. Co-doping of Si and C is believed to reduce this negative effect on $T_c$ because of the co-substitution’s atomic radii being closer to B [Dou et al., 2002]. These two additives are resulting in the highest $J_c$ values at higher applied fields among all additives currently tested.

This leads to the use of heterogeneous sonochemistry as a natural choice to beneficially modify MgB$_2$. The attractiveness of sonication is in the ability to uniformly and homogeneously mix impurities throughout the superconductor in a single step process. Also, the process can break down chemical bonds and can allow the decomposition of volatile organometallics to add extremely pure metal pinning centers inside the superconducting matrix. This is hard to achieve with standard metal powder inclusions which contain significant oxide phases due to the large surface area.
1.3.2 Bulk, Tape, Wire and Thin Film Properties

The superconducting properties of MgB$_2$ vary depending on how the MgB$_2$ is formed and the type of sample being measured, such as bulk (powder or pellet), thin film, tape, or wire. It should be mentioned that all the samples produced for this thesis are classified as pellets, but the other types are presented for comparison. Most MgB$_2$ samples, including bulk samples, are largely produced by a powder-in-tube (PIT) method, meaning that stoichiometric amount of powder are placed in a closed tube and reacted at a set temperature. Thin-films are typically produced through a pulsed laser deposition process on various reacting and non-reacting substrates. Tapes can be produced in a number of ways but a PIT method followed by drawing into wires or tapes is very common. Some tapes are stabilized by a sheath material that is typically non-reacting with MgB$_2$. Of these sheath materials, Fe seems to be the a typical choice showing little reaction with MgB$_2$, but recently Ti and Nb have shown to be more effective choices [Kovac et al., 2009]. Wires, however, were first produced by exposing boron filaments to a Mg vapor diffusion process in a closed cell [Canfield et al., 2001]. Alternatively, wires have been recently produced from MgB$_2$ encased in a metal tube which is drawn or rolled into smaller diameters. This produces a densely packed wire while providing additional reinforcement for typically hard and brittle MgB$_2$ wires.

Table 1.2 shows several values of $J_c$ for each type of sample preparation method. It is hard to compare the values between thin films and bulk samples at the same field and temperature. Thin films may have a greater $J_c$ at very small fields, but these values drop off pretty rapidly due to the lack of effective pinning which makes bulk samples so magnetically robust. In this way, each sample type has it’s own specialize application and purpose. Thin films are designed for high current applications which require little to no field and the extremely high currents of $\sim 10^8$ A/cm$^2$ are only achieved in very narrow bridges on the order of 100’s of nanometers. Bulk samples, tapes, and wires can possess more pinning sites because of their larger dimensions and therefore are generally more magnetically robust. The values shown in table 1.2 reflect some of the highest $J_c$ values achieved to date.
Table 1.2: Jc values for different types of MgB$_2$ samples produced from bulk, tape, wires and thin films

<table>
<thead>
<tr>
<th>Sample type</th>
<th>$J_c$ (A/cm$^2$)</th>
<th>Temp (K)</th>
<th>Applied Field (T)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>$10^5$</td>
<td>20</td>
<td>3</td>
<td>[Dou et al., 2004]</td>
</tr>
<tr>
<td>Tape</td>
<td>$1.85 \times 10^4$</td>
<td>4.2</td>
<td>10</td>
<td>[Ma et al., 2006]</td>
</tr>
<tr>
<td>Wire</td>
<td>$1.33 \times 10^5$</td>
<td>5</td>
<td>4.5</td>
<td>[Dou et al., 2002]</td>
</tr>
<tr>
<td>Wire</td>
<td>$1.08 \times 10^5$</td>
<td>2</td>
<td>20</td>
<td>[Dou et al., 2002]</td>
</tr>
<tr>
<td>Thin Film</td>
<td>$1.60 \times 10^8$</td>
<td>2</td>
<td>0</td>
<td>[Zhuang et al., 2008]</td>
</tr>
<tr>
<td>Thin Film</td>
<td>$2.30 \times 10^8$</td>
<td>5</td>
<td>0</td>
<td>[Zhuang et al., 2008]</td>
</tr>
<tr>
<td>Thin Film</td>
<td>$6.70 \times 10^7$</td>
<td>25</td>
<td>0</td>
<td>[Zhuang et al., 2008]</td>
</tr>
</tbody>
</table>

1.4 Paramagnetism and Superparamagnetism

A detailed treatment of diamagnetism and paramagnetism can be found in many solid state physics textbooks, such as [Ashcroft and Mermin, 1976, Kittel, 1996]. In this section, the very basic theory is treated in conjunction with domain theory to explain how paramagnetism and superparamagnetism arises. This section contains both a discussion of the origin of paramagnetism as well as how domains form in order to minimize the energy of a sample. Superparamagnetism can be viewed as a special case of paramagnetism in which individual ferromagnetic particles are too small to allow the formation of domain walls, hence the material behaves as a paramagnet. The section will conclude with a brief description of how these nanocomposites, magnetic particles in a non-magnetic matrix, can be used and the advantages of using nanocomposites over typical composites.

1.4.1 Paramagnetic Properties

The basic property that identifies a sample as paramagnetic is the response of the magnetic moment aligning with the field resulting in a positive value for the magnetic susceptibility, $\chi$ (per unit volume) defined as

$$\chi = \frac{M}{H}$$

where $M$ is the magnetization or magnetic moment per unit volume and $H$ is the strength of the magnetic field. Conversely, a diamagnetic sample would exhibit a negative susceptibility.
The magnetic moment has three principle components that contribute to paramagnetism and diamagnetism. The paramagnetic contributions come from the intrinsic spin of each electron and the angular orbital motion around the nucleus. The diamagnetic contributions come from the response of the change in the orbital motion with an applied field [Kittel, 1996, p. 417].

One can use the quantum theory of paramagnetism to reach a formula for the magnetization of an atom in an applied field. The magnetization can be calculated for an atom of angular momentum quantum number J as,

\[ M = NgJ\mu_B B_J(x), \] (1.27)

where \( x = gJ\mu_B B/k_BT \) and \( B_J(x) \) is the Brillouin function given by:

\[ B_J(x) = \frac{2J + 1}{2J} \coth\left(\frac{2J + 1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right) \] (1.28)

In the classical limit, the Brillouin function is replaced by the Langevin function, \( L(x) \)

\[ L(x) = \coth(x) - \frac{1}{x}, \] (1.29)

because the value of \( J \) is now continuous. The magnetization then becomes

\[ M = N\mu_B L(x) = N\mu_B \left[ \coth\left(\frac{\mu B}{k_BT}\right) - \left(\frac{k_BT}{\mu B}\right)\right], \] (1.30)

where \( N \) is the number of atoms per unit volume, \( \mu_B \) is the magnetic moment of the atom, and \( B \) is the applied field. Figure 1.10 shows magnetization loops for paramagnetic, ferromagnetic, and superparamagnetic samples. Paramagnetic samples have no remnant magnetization, \( M_R = 0 \), when \( H = 0 \), but the saturation magnetization, \( M_s \), occurs at higher fields than in superparamagnetic samples. The thermal energy keeps the spins randomized, but as the field increases, the spins begin to align with the field, and then at saturation the spins are fully aligned.

A ferromagnetic sample will exhibit some level of hysteresis, but even a soft ferromagnetic material (meaning the coercive field is very low) has a small amount of dissipation and makes ferromagnetic material undesirable for certain applications. Figure 1.10 shows a hard ferromagnetic magnetization curve with significant hysteresis, and the coercive field, \( \pm H_c \) (not
Figure 1.10: ferromagnetic, F; paramagnetic, P; and superparamagnetic, SP, magnetization versus field. $M_R$ indicates the remnant magnetization which is the remaining magnetization upon returning to $H=0$ from some field $H \neq 0$. Both paramagnetic and superparamagnetic sample show no remnant magnetization, but the superparamagnetic samples show much higher saturation magnetization. A fairly hard ferromagnetic curve is shown, but even for soft ferromagnetic, $M_R \neq 0$, and therefore hysteresis and dissipation will occur in cycling the magnetic field.

to be confused with the critical field in superconductors) is the field at which $M$ transitions from positive to negative and vice versa. The last of the curves in figure 1.10, which is the superparamagnetic curve, shows a large saturation magnetization with little to no hysteresis meaning $M \sim H_c \sim 0$. This is attractive for applications where using a small field to switch the sense of the magnetization (taking $+M_s$ to $-M_s$) without dissipative losses is needed, e.g. hard drives, transformers, etc. The next section demonstrates what makes these “paramagnetic” samples so “super” and how this phenomena originates.
1.4.1.1 Superparamagnetic Properties

Figure 1.10 shows the magnetization of a superparamagnetic sample, but the reason for this response is still unaddressed. In a paramagnetic sample with no applied field, the spin direction of each atom is randomly distributed in all direction to minimize the energy and therefore the magnetization is zero. However, increasing the field raises the magnetization because the spin of each atom tends to align with the magnetic field and when all the spins align the sample has reached saturation, the maximum magnetization. Similarly, for a superparamagnetic sample, large clusters of atoms act as one large spin and align with the applied field creating the “super”-paramagnetic response. In this way, superparamagnetic particles follow the same form as the magnetization formula for a paramagnet, but with a change in the value of the moment. Superparamagnetic magnetization is given by the formula:

\[ M = N \mu L(x) = N \mu \left[ \coth \left( \frac{\mu H}{k_B T} \right) - \left( \frac{k_B T}{\mu H} \right) \right] \]

where \( \mu \) is now the moment per particle, and \( N \) is the number of particles per unit volume. This is the same form as equation 1.30, but \( \mu_B \), a single atomic moment, is replace by \( \mu \) which is a collection of atomic moments, where \( \mu \) can be \( > 1000\mu_B \). Therefore, small fields can create large magnetization differences since the moments easily orient with the field. This property makes superparamagnetic samples very attractive for application which require large changes in magnetization for very low applied fields. In order to understand what separates a sample from being superparamagnetic versus just paramagnetic requires the presentation of domain energies.

1.4.2 Domains in Paramagnetic Material and the Superparamagnetic Threshold

A domain is defined as a region of oriented magnetic moments within a sample, and a domain wall, or Bloch wall, is a very small transitional region between domains where the moments rotate from one orientation to another. Domains and domain walls form in ferro- or ferrimagnetic materials in order to minimize the magnetic dipolar energy produced by aligned magnetic moments. The sample forms these domains in such a way as to minimize the overall
total energy of the system. Each additional domain costs additional energy in the form of the domain wall between the domains, but by increasing the number of domains, the sample is able to reduce its overall dipolar energy. This results in a balancing competition between the reduction in the dipolar energy and the added cost of the domain walls. A graphically represented domain and domain wall can be seen in Figure 1.11.

Figure 1.11: The arrows represent the orientation of the magnetic moments, with the arrow tip representing the north pole, forming the domains and the interior lines separating these regions represent domain walls. The dipolar energy can be reduced by breaking into two domains (center) over a single domain (left) and can be broken into four domains (right) to further reduce the dipolar energy. The domain wall (below) is the region of transition between domains, and the bottom picture shows the moments with the north pole rotating toward the reader until being directed out of the page in the center and then continuing to rotate until the moment has flipped to the other orientation.

As domain walls are transitional regions, a very thin domain wall requires an enormous amount of energy compared to a larger transitional region. Therefore, as the size of the particle is reduced, one also reduces the available size of the domain wall. Below a certain limiting size, determined by the material, domain walls are no longer able to form as the associated energy cost is too great and the entire particle acts as one huge moment. In this way, paramagnetism is seen as a multi-domain response but superparamagnetism is a single domain response. The
The size limit below which a particle contains a single domain is given by finding where the single domain energy is lower than the wall energy. This critical size threshold is calculated from:

\[
\frac{1}{2} \left( \frac{4\pi}{3} \right)^2 R_c^3 M_s^2 = \left( \frac{\pi J R_c}{a} \right) \left[ \ln \left( \frac{2R_c}{a} \right) - 1 \right].
\]

(1.32)

Using the values for iron the critical radius \( R_c \sim 0.7 \times 10^{-6} = 7\text{nm} \) [Kittel, 1949].

1.4.3 Advantages of Nanocomposites for This Study

Several studies have been performed to investigate nanoparticles of iron [Suslick et al., 1991, Gangopadhyay et al., 1992] or iron oxide [Cabot et al., 2009] and as magnetic components in a non-magnetic matrix [Fnidiki et al., 2003]. The interest in magnetic nanocomposites comes from the use of these materials both in medicine and in technological advances. In medicine, magnetic nanocomposites can be used as “dying” agents to enhance MRI images as well as for other medical equipment using some form of magnetic detection [Uchida et al., 2008]. Outside of medicinal applications, the interest in magnetic nanocomposites arises from applications seeking to exploit the unique properties of nanocomposites, such as giant magnetoresistance (GMR) devices and to exploit the GMR effect of tunneling magnetoresistance (TMR) [Fnidiki et al., 2003]. The interest in nanocomposites was further bolstered by the 2007 Nobel Prize being awarded to Albert Fert and Peter Grünberg for the discovery of GMR. Other uses of nanocomposites include colloids [Herring and Hempelman, 1996], ferrofluids [Prozorov et al., 1999], and alloys [Shafi et al., 1998]. Within the last decade, advances in research techniques and technology have resulted in an increase interest in nanocomposites as they become easier and cheaper to produce. Nanoparticles, and nanocomposites, often have unique properties over their bulk counterparts. This phenomena, despite long research, is not fully understood and only adds to the interest of producing and studying these systems.

For superconductors like MgB\(_2\), the benefits of nanocomposites provides increased pinning, and the addition of magnetic nanoparticles provides an additional energy to the pinning force, but also acts to reduce the \( T_c \). However, in creating superparamagnetic nanocomposites, the primary concern is preventing agglomeration and consequently forming a multi-domain particle which creates dissipative losses. Nanopowders can be formed in a number of ways, but in order
for them to be used in devices like rotors, transformers, or as any part of a machine, the powder needs to be in a solid machinable form. Also, pure nanopowders tend to agglomerate causing multi-domain regions. In order to prevent this multi-domain, a nanocomposite is necessary where nanosized paramagnetic particles are distributed through some inert matrix. The inert matrix acts to separate these particles and allows the nanoparticles to be sufficiently spaced so as to prevent agglomeration and preserve the single domain nature. To make a machinable sample, one needs to apply a significant amount of pressure. For this study, hot isostatic pressure (HIP) is used to make a dense form of the nanocomposite which is then stable enough to withstand polishing and machining. Higher ratios of nanoparticles to matrix will also compromise the stability of the bulk sample and tend to make the sample fall apart. In this way, the effects of nanoparticle concentration becomes the key interest to optimize a sample with high saturation magnetization and low field switching between $M_s$ and -$M_s$ while still offering a dense, machinable sample that shows no dissipative losses.
CHAPTER 2. EXPERIMENTAL SETUP

This chapter explains the experimental setup and equipment used during this study. This chapter also contains information on equipment and parts that were used to produce the samples that were measured. Specific mention is made with models and parts information where available. The next chapter discusses the application of this equipment to sample processing and to sample modifications made before measurement.

2.1 Sonochemical Setup

This section contains information on the sonicator equipment used during this experiment. The sonicator is defined as the apparatus that produces the acoustic waves as well as the vessel and attachments that are designed to optimize and isolate the sonochemical process. Some elements discussed here are: the power supply, the sonication cell, the sonication horn, the cooling bath, and all the relevant connections made between these parts. These elements can be seen in the diagram included in figure 2.1.

2.1.1 Sonication Cell and Direct Immersion Horn

All sonications were carried out using a Sonics and Materials VC 750 - 750 watt ultrasonic processor with an operation frequency of 20kHz. This is connected to a model CV33, Piezoelectric lead zirconate titanate crystal (PZT), which is then connected to the standard probe with a threaded end and a replaceable tip made of titanium alloy Ti-6Al-4V. PZT will be used to refer to the transducer as the attachments such as the direct immersion horn. The replaceable tip was selected because over the course of several sonications the tip will receive considerable wear due to cavitation collapse on the tip surface. An adapter is attached to
Figure 2.1: Diagram showing the sonication equipment used in this study. The glass cell is submerged into the cooling bath to cover the entire liquid contents of the sonication cell. The cooling bath was kept at -10°C and Ar gas was introduced through a small diameter tube inserted into the gas inlet.

the probe at the nodal point and contains an internal o-ring that holds the sonication cell, a Suslick Cell, in place during the operation. The cells used in this project had three side ports with threaded ends to allow for controlled sealing off of each port.

Multiple ports were used to deliver Argon gas and remove reaction gases from the sonication cell. Nylon tubing was connected to a high purity Argon tank and attached with a rubber fitting to the second threaded end of the sonication cell. A smaller tube, 0.031” inner diameter, was pushed inside the Argon line to allow Argon flow directly into the liquid being sonicated. The secondary tubing was used to prevent back-flow and contamination of the main line if the Argon gas was turned off before being removed from the sonicated liquid. Argon flow causes the cavitation collapse and resulting shock wave to be more efficient [Suslick, 1998, p. 530]. The third port was closed with a cap containing a 0.5 mm diameter hole drilled at the top to allow for the Argon gas to escape, when rubber stoppers were used needles were placed into
the rubber to allow the gas to escape. This will prevent over pressurization of the sonication cell.

The PZT was then mounted on a ring stand and the sonication cell was lowered directly into a circulating cooling bath set at -10 degrees C. The cooling bath was filled with a mixture of equal parts ethanol and ethylene glycol, assuring adequate cooling power. This mixture can provide cooling down to the lower temperature limits of the cooling bath if necessary, -100-150 °C. The cooling bath ensures effective cooling of the sonochemically irradiated liquid, which otherwise can become overheated by the heat generated by the PZT and the probe. Decane was used for the sonication liquid. Decane was chosen for it’s low vapor pressure making cavitation more favorable as a lower vapor pressure would prevent the liquid from entering into the bubble. However, liquids with higher vapor pressures, like organometallics, could enter the cavitation bubble making the collapse of those bubbles more efficient [Suslick, 1998, p. 531]. Other equipment used during the sonication process and post sonication process includes: a standard centrifuge, a sonication bath used for cleaning glassware, and 10 ton press, mostly used to flatten Mg metals and sometimes to press cold pellets. The 10 ton press was also used to punch the Ta pouches.

2.2 Tantalum Press and Copper Blocks

Samples were sealed in tantalum pouches, see section 3.2.5, that were created using thin tantalum sheets pressed with a aluminum form press (Figure 2.2a), and were then sealed using a copper heat sink (Figure 2.2b) and an arc melter (Figure 2.2c). The form of the press consisted of three parts, the base or die, the cover, and the ram. The form was fashioned out of aluminum since it was softer and easier to machine, but steel could be used to preserve the forms shape over a longer period of use. The base consisted of a 1.660” square block about 0.5” thick with a 1.560” square milled to a depth of 0.024” to hold the Ta sheet for centering. The center was milled to a depth of 0.130” with a circular bit of radius 0.54”. The edges of the well were smoothed slightly to prevent it from shearing the Ta sheet when it was pressed. The cover was a 1.800” square with a center bore drilled through with 0.50” radius on center
with the base hole. The bottom edge was milled to accept the outer rim of the base section, thus connecting the two pieces and prevent them from sliding off center. The ram was 2” in length with a radius of 0.50” and was reduced in size by lathing at the ”pressing” end to again prevent cutting the Ta sheet while pressing.

![Tantalum Press](image1)

![Copper blocks with steel "clamps"](image2)

![Arc welder](image3)

Figure 2.2: Tantalum press, copper block heat sinks, and arc welding apparatus

The heat sink consisted of two halves of a copper blocks. The one side contained a 0.55” radius bore hole to a depth of 0.15” to allow the blocks to be placed on either side of the two Ta sheets during arc welding. A separate copper block was made with two such holes to allow two pouches to be seal simultaneously. This was to accept the indentation placed in the one Ta sheet, so that the maximum surface area of Ta was in contact with the copper block. The two copper blocks were held together by two simple steel rectangles that extended outside the block width and had screws with nuts and washers to press the two sides together. The Ta pouches had to be welded vertically and the steel rectangles, the clamps, assured that no powder was
able to fall out during the sealing process. The arc melter is a vertically mounted welding tool inside of a sealed Argon chamber. Sealing under Argon helps to remove air trapped in the pouches and prevents contamination of the samples during the HIP process.

2.3 Hot Isostatic Press, HIP

The usual process for forming pellets or bulk samples out of powders includes the application of linear pressure followed by some form of sintering, heating process. In some instances, this two step process is reduced to a single process through the application of hot isostatic pressure. A hot isostatic press (HIP) is a machine that provides isostatic pressure, meaning equal pressure on all sides, through the heating and compacting of a medium, usually an inert gas like Ar. Typically, a powder sample is sealed in a die or container made from a non-reactive material and placed in the hot zone. The space is evacuated and back filled with Ar gas and then the space is heated and/or pressurized to the desired specifications of the user. This study used a IPS Eagle HIP machine with operating pressures up to 44.5 ksi (∼310 MPa) and heating up to 1800°C. In order to provide such high pressures and temperatures, the hot zone is relatively limited in size, being only 5.5” tall × 2-3” diameter. HIP machines with hot zones of larger dimensions are commercially available, however the maximum pressure is significantly reduced.
CHAPTER 3. EXPERIMENTAL DESIGN AND SAMPLE PREPARATIONS

This work is focused on the use of ultrasound to create nanocomposites of both superconducting MgB$_2$ and superparamagnetic iron oxides in an alumina, Al$_2$O$_3$, matrix. Superconducting MgB$_2$ was created from in situ sonication of precursors with different magnetic and non-magnetic particles, some being nano powders. Superparamagnetic nanocomposites were formed through co-sonication of Fe(CO)$_5$ and Al$_2$O$_3$. A study of the properties of these materials was investigated using SEM microscopy, SQUID MPMS, and X-ray diffractometry.

As discussed in section 1.3, MgB$_2$ can be produced from exposure of B to Mg vapor. The resulting MgB$_2$ has similar grain size, shape, and connectivity as the original B powder. This process was used in the development of MgB$_2$ thin films and MgB$_2$ wires. Also, sonication has been shown to reduce grain size and improve grain connectivity even in superconducting powders that resulted in improved superconducting properties [Prozorov et al., 2003]. This suggests that sonication of B powder prior to reaction with Mg vapor could also result in improved properties as well as offering an opportunity to introduce magnetic and non-magnetic materials as pinning centers to help prevent flux motion. This flux motion causes resistive losses in high temperature superconductors. Also, increased pinning can improve critical current values and improve performance for higher applied fields, resulting in higher field or current applications.

Prior to introducing magnetic and non-magnetic inclusions, one must first understand how sonication affects B and how to optimize the sonication process. It should be noted that sonication has many adjustable parameters, such as: exposure time, cooling bath temperature, sonication amplitude, slurry loading, “doping” ratio, sonication medium (in our case decane),
type of gas reaction, rate of gas flow, sonication cell design, PZT horn location, and many more. Instead of trying to study each of these, this thesis focused on studying only the effects of sonication on different slurry loading of B and different material inclusions. Each system of powders potentially has its own optimizeable parameters that could be studied in more detail in future studies, but here only one set of parameters is presented.

The study of sonication effects on Fe(CO)$_5$ and Al$_2$O$_3$ powders produced superparamagnetic materials. Prior research has shown that sonication on Fe(CO)$_5$ can result in amorphous iron when isolated from oxidation effects. The magnetic response of the powder is that of a soft ferromagnet with indications of superparamagnetism [Grinstaff et al., 1993]. Fe(CO)$_5$ co-sonicated with carbon powders resulted in hollow spheres of hematite ($\alpha$-Fe$_2$O$_3$) [Bang and Suslick, 2007]. The amorphous iron was deposited on the carbon grains during sonication, but after drying, the carbon was burned away by the heat of the iron oxidation process leaving only hollow hematite spheres. This study attempts, by sonicating Fe(CO)$_5$ in the presence of Al$_2$O$_3$, to form superparamagnetic ceramics with interesting and tuneable magnetic properties based on the adjustment of sonication parameters. As superparamagnetism relies on particle size (being small enough that domains cannot form but large enough to avoid thermal randomization), particular attention is paid to adjust loading of Fe(CO)$_5$ as increased loading may result in agglomeration of Fe inside the Al$_2$O$_3$ matrix. Al$_2$O$_3$ was chosen as it is inexpensive, commercially available, and is non-magnetic. Other ceramic matrices were expected to work in a similar manner, however they remained beyond the scope of this particular study.

3.1 Sample Preparations

The high intensity ultrasound irradiation, or sonication also abbreviated as ), of the liquid-solid systems in this study have the same basic operational technique regardless of whether the solid is MgB$_2$ or Al$_2$O$_3$ and Fe(CO)$_5$. This process was broken into three major portions. The first was the actually powder preparation and sonication. The second was the washing process that removes any remaining organic by products created during sonication. The third
and final process was the drying and sample storage method, or the sealing and HIPing process in the case of MgB$_2$.

The measured mass of each powder and volume of decane was placed into the sonication cell, rinsing any powder to the bottom of the sonication cell. The sonication cell was then secured to the ultrasonic horn and lowered until the tip of the horn was submerged approximately 0.5” into the liquid solution, but being careful the decane did not cover the neck of any of the three side ports resulting in decane traveling up the neck and spilling into the cooling bath during sonication. The power supply was then set to the appropriate amplitude and duration. The argon line was placed into the slurry and argon flowed for several minutes to replace the less dense air that exits from the outlet of the sonication cell. Argon was chosen as it is inert and makes the implosive collapse of the cavitation bubble more efficient. The cell was then lowered into the cooling bath so that all of the slurry inside the sonication cell was submerged in the cooling liquid. The timer and amplitude were set on the power supply and the sonication was started. The sample was watched for several minutes to make sure that the sonication was running properly. In some cases, the amplitude of the power supply was adjusted slightly to prevent overflows, but never more than 2%.

Upon completion, the cell must be quickly removed from the cooling bath and the ultrasonic horn. If the cell remains in the cooling bath for more than 5-10 minutes, the liquid becomes cold and powder adheres to the sonication horn, and this powder was very difficult to rinse off and recover. This loss of powder was avoided by removing the cell and rinsing the horn immediately with pentane allowing the wash to drain into the sonication cell. The cell was then placed on the rack and the solution transferred by pipetting from the bottom of the cell into two 15ml centrifuge tubes. The remaining liquid was used in a preliminary wash of the sides of the cell to recover any powder that adhered to the sides. Every attempt was made to recover all of the sonicated powder since the masses and volumes were small. The tubes were then centrifuged for 30 minutes in a Block Scientific Octafuge 12 Volt Centrifuge. The liquids were easily poured off into a waste container and pentane was added until the 15ml mark was reached and the tubes were resealed and shaken vigorously for several minutes.
Pentane was used to rinse away the residual decane and other organics that were used during the sonication process. This washing process (pentane, shake, centrifuge, pour-off, pentane, etc.) was repeated up to 5 times or until an odor test revealed mostly pentane.

After the last washing, ending at the pouring off step, the tubes were set into holders and Parafilm® M wax was placed over the top. A needle, or small diameter wire, was then used to poke several tiny holes in the top to allow the pentane to evaporate out, while preventing dust from getting inside. Samples were generally left to dry overnight approximately 10-15 hours. The powders were then removed from the centrifuge tubes and gently broken up to separate the clumps in the powder. This powder was then transferred into small vials until being measured, pressed, or sealed in Ta to go to HIP. In most cases, powders were measured as quickly as possible after being processed to avoid any degradation effect from affecting the data and subsequent analysis. However, repeat measurements of a single sample two weeks after processing show no recordable degradation.

### 3.2 MgB$_2$

A preliminary study of the effects of ultrasonic irradiation on the superconducting properties of MgB$_2$ has already been reported [Prozorov et al., 2003]. The initial studies were performed to study the modification of the superconducting properties of BSCCO-2212, but the sonication process only served to degrade the fragile BSCCO structure. This was the reason for the choice of using MgB$_2$ as the structure is more robust and survives the extreme environment created during sonication. Our group began studying the effects of sonication on commercial MgB$_2$ powders, but no new information was learned over previous studies [Prozorov et al., 2003].

This thesis and work attempted to take MgB$_2$ precursors, namely B powder and Mg powder, and make superconducting composites through a process which would allow one to tune the superconducting properties. This thesis discusses three separate but related studies evaluating the conditions and parameters for the sonication process with the end goal being a method of sonication with magnetic and non-magnetic compounds to achieve tunable superconducting
properties for MgB₂. The three studies are as follows: a study of the effects of ultrasound on B powder of different purities and a study of co-sonication effects on B + Mg powder before HIP; a study of B slurry loading; and a study of specific additions during the sonication process as described by B + X below.

3.2.1 Study of the Effects of Ultrasound on B Powders of Differing Purities and the Formation of MgB₂

The first study involved looking at different purities of B powder being 86%, 90%, 95%, 99%, and commercially available Eagle Pitcher B₁₁ (EPB). During this study, B powder was sonicated alone, sonicated with Mg powder, unsonicated or as is, and unsonicated with Mg powder. At this stage in the research, the B powders not involving Mg powder were then added to Mg chunks before being sealed in the tantalum sheets. This was achieved by pressing Mg chunks under cold pressure to flatten the Mg and placing it on top of the B powder in the tantalum sheet, as seen in Figure 3.1. This flattening was done to fit the necessary Mg into the indented portion of the Ta sheet. The added advantage of using Mg chunks over Mg powder is that the chunks have a smaller Mg surface area and therefore are hoped to have less oxidation so as to avoid the formation of MgO in the HIP process. After the HIP process, samples were cut and polished to approximately 2 mm x 1 mm x 0.5 mm.

3.2.2 Adjustment of Slurry Loading of B Powder During Irradiation

Variations in slurry loading can affect the distance between particles and make collisions during cavitation collapse more or less energetic based on the slurry loading. This suggests that there is an optimal loading where particles are far enough apart to allow energetic collisions, but not so far apart that collisions are less likely to occur. Previous studies have found that the optimal range for MgB₂ is around the 1% – 2% volume region. Therefore, this study focused on the region between 0.5% loading and 2% loading increasing in .25% steps.

The slurry loading was measured as a volume percent of B powder to the liquid, in this case decane, used during the sonication process. Volume percentages were calculated using the
formula: \( V\% = \frac{V_{\text{powder}}}{V_{\text{total}}} \), where \( V_{\text{total}} \) is the total volume of liquid and powder. The powder volume was determined using the mass of the powder and the density listed on the material data sheet for the material. All samples were made and sent to be HIPed in the same HIP cycle. This reduced any variation associated in changes in HIP procedure.

3.2.3 Irradiation of B + X in the Formation of Superconducting Composites

Samples were fabricated to obtain dense MgB\(_2\) pellets with the material X uniformly distributed inside the sample to study the effect on the superconducting properties. This was achieved by sonication of B powder as well as co-sonication of B + X, where X is one of the materials or compounds described in table 3.1. These powders were mechanically mixed and then placed in decane using a 2% slurry loading and sonicated in the process describe in section 3.1 with the added procedures of section 3.2.4. After sonication and drying the powders were added in a stoichiometric mass ratio of B to Mg of 2:1. This resulted in a slight Mg excess as
some of the sonicated powders contained B plus X, but as the ratio of B to X was kept small, this excess should be fairly negligible. The exact masses of X and B are presented in table 3.1 as well as the mass of Mg added before HIPing. In some cases, B powder was sonicated and then X was manually mixed before adding Mg and sealing for the HIP process, but these sample are identified. This step was performed to determine if sonication adversely affected X. After this first run seen in table 3.1, a second run was made with a new set of samples represented in Table 3.2.

Table 3.1: Mass of powders used for sonication of B + X, and Mg added to mass of post-))) powder before HIP procedure.

<table>
<thead>
<tr>
<th>Additive (X)</th>
<th>))) masses of B + X</th>
<th>Mass used to make MgB(_2) in HIP process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B mass (mg)</td>
<td>X mass (mg)</td>
</tr>
<tr>
<td>In</td>
<td>372.5</td>
<td>4.6</td>
</tr>
<tr>
<td>EuS</td>
<td>375.5</td>
<td>4.2</td>
</tr>
<tr>
<td>Pb</td>
<td>372.1</td>
<td>3.7</td>
</tr>
<tr>
<td>BSCCO-2212</td>
<td>373.8</td>
<td>3.9</td>
</tr>
<tr>
<td>YBCO</td>
<td>373.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Al(_2)B</td>
<td>373.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Sn nano</td>
<td>372.9</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 3.2: Second run of B + X and mass of powders. Values listed with “( )” are the masses of B post-))) mixed with the additive “X” before measuring the mass for HIP. M\(_{())))\) powder is the mass of post sonicated B + X powder mixed with Mg before the HIP process, but for B non-))), the value is the mass of non-))) B added to Mg prior to HIP.

<table>
<thead>
<tr>
<th>Samples</th>
<th>))) masses of B + X</th>
<th>Mass used to make MgB(_2) in HIP process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B mass (mg)</td>
<td>X mass (mg)</td>
</tr>
<tr>
<td>B</td>
<td>360.6</td>
<td>N/A</td>
</tr>
<tr>
<td>B non-)))</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>[B + EuS] )))</td>
<td>372.4</td>
<td>4.0</td>
</tr>
<tr>
<td>[B ] ))) + EuS</td>
<td>(193.0)</td>
<td>(1.7)</td>
</tr>
<tr>
<td>[B + BSCCO] )))</td>
<td>373.7</td>
<td>3.5</td>
</tr>
<tr>
<td>[B ] ))) + BSCCO</td>
<td>(260.4)</td>
<td>(2.7)</td>
</tr>
<tr>
<td>[B + Fe nano] )))</td>
<td>373.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>
3.2.4 Irradiation Process

The sonication process for the MgB$_2$ precursors was similar to the process described in section 3.1. All three studies used the same sonication procedure. Each slurry, powder and liquid system, was sonicated at 60% maximum amplitude for 2 hours resulting in an average amount of Joules added of $\sim 250000$. The second run, table 3.2, was performed with 15ml of decane at 40% with an average of $\sim 190000$ Joules added. This change was made after the larger sonication cell was broken forcing us to use a slightly smaller cell. 60% amplitude, and 40% for 15ml decane, was determined as the point of optimal sonication based on the sound produced. When cavitation begins during sonication, an audible change occurs in the screeching made by the sonicated fluid. Too low an amplitude results in a low gurgling sound where as cavitation is a fairly even “hiss” sound. Higher amplitudes increase the heat of the PZT and also cause the fluid surface to oscillate rapidly pushing it closer to the sonication cells ports. Therefore, 60% amplitude was determined to produce effective cavitation while not producing a large amount of surface disturbance causing sample loss through ejection from the sonication cell ports. After the sonication process, the samples were washed in the standard washing and drying procedure. Samples were then sealed in vials and placed in a vacuum chamber to prevent any degradation before being sent to HIP.

3.2.5 Pouches and HIP

This section describes the process of pressing, sealing, and HIPing the Ta sheets that form the environment for the reaction of B and Mg into MgB$_2$ during the HIP process. Figure 2.2a shows the press form that acts to punch an indentation into one of the Ta sheets. The Ta sheet ($1.5" \times 1.5" \times 0.24"$) was placed on the base of the die and the cover was placed on the top thus positioning the ram hole in the center of the sheet. The ram was inserted into the top of the die and the entire apparatus was placed on the cold press. Pressure was applied to the ram until the pressure needle began to indicate a building of pressure. If the piston of the press was allowed to build pressure, the ram, being made out of aluminum, will begin to flex and bend as well as punch a hole through the Ta sheet. Releasing the pressure, just as it
builds, prevented damage to the rod and Ta sheet and provided a suitably shaped indentation
to receive the precursor powders. After pressing, the Ta sheet became deformed. A steel plate
with a 0.56” bore hole was placed over the Ta sheet to preserve the indentation while the sides
are pressed flat.

The flattened Mg chunks and the B or B + X powder were placed in this indentation before
being sealed, seen in figure 3.1. The space was filled by layering Mg on bottom, powder in the
middle, and Mg on top. In the case of samples using Mg powder, the mixed powder was simply
filled into the indentation. The layering was intended to help the Mg vapor to penetrate the B
powders to react more completely in a shorter amount of time. A second Ta sheet was placed
on top and the two sheets were squeezed together being held at the edge with a small clamp.
The clamped Ta was then positioned on the copper block with the indentation matching the
Ta sheets. This matching allowed the copper block to be in full contact with the Ta sheet
without touching the sample space, the indentation. The matching was very important to
prevent premature heating of the sample space during the arc welding of the Ta edges. The
small clamp was removed from the Ta edge once the second copper block was positioned on
top and the steel rectangle clamps were secured and tightened, seen in figure 2.2b. The two
Ta sheets were completely held together by the clamp pressure and, even while inverted, the
powder was not able to escape the sample space. The edge of the Ta sheet to be welded
extended from the copper block approximately by .25”.

The copper blocks were then placed on the arc welding stage, figure 2.2c, making flush
contact with the stage, as the stage is water cooled from the bottom, with the Ta sheet being
oriented vertically. The cover and arc welding tip were then placed over the vacuum chamber
and the space was pumped and purged with argon several times. The power supply was then
turned on and the tip was positioned above the Ta edge. The beam was quickly run across
the top edge of the Ta sheet, and the weld was inspected to be sure that a complete weld was
made. The vacuum chamber was then opened and the copper block was carefully removed
with gloves as the block was uncomfortably hot. The blocks were cooled by removing the Ta
sheets and running the copper block under cold water, then drying, and finally remounting
Table 3.3: Hip procedures for the three separate studies performed

<table>
<thead>
<tr>
<th>Study</th>
<th>HIP Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>B Purity</td>
<td>RTP → 600 °C, 35kpsi → 950 °C, 35kpsi, hold 8 hours → 600 °C, 35kpsi → RTP</td>
</tr>
<tr>
<td>B Slurry Loading</td>
<td>RTP → 600 °C, 35kpsi → 1000 °C, 35kpsi, hold 8 hours → 600 °C, 35kpsi → RTP</td>
</tr>
<tr>
<td>B + X First Run</td>
<td>RTP → 600 °C, 35kpsi → 950 °C, 35kpsi, hold 8 hours → 600 °C, 35kpsi → RTP</td>
</tr>
<tr>
<td>B + X Second Run</td>
<td>RTP → 600 °C, 35kpsi → 950 °C, 35kpsi, hold 8 hours → RT, 35kpsi → RTP</td>
</tr>
</tbody>
</table>

the Ta sheets horizontally to prevent powder spilling from the sample space. The pumping and welding process continued until all sides were welded and a designating mark was made with a punch in order to identify the sample after HIPing. This was done with a set of dot indentations arranged in patterns, such as . . . : :: et cetera.

Finally, the samples were sent to be HIPed. Several samples were run in the same HIP run. A profile was determined that includes both temperature and pressure over time. The usual HIP process was from room temperature and pressure (RTP) ramping temperature to 600 °C while reaching full pressure in the same interval, followed by increasing temperature to full temperature and pressure (FTP) and holding for a desired length of time. After the holding period, usually between 8-24 hours, the temperature was reduced to RT under full pressure to help avoid stress fractures from cooling and releasing pressure. Once RT was reached, the pressure was gradually released until reaching RTP, thereby completing the HIP process. The maximum temperature and pressure is set by the user and can be any value within the range of the particular HIP machine. The Hip procedures used in this work changed over the course of the three studies performed, but the specific HIP process during each study is listed in table 3.3.

3.3 Al₂O₃ and Fe(CO)₅

Al₂O₃ was mixed with Fe(CO)₅ and then sonicated to break the bonds of the Fe(CO)₅ to obtain finely dispersed Fe and Fe(CO)₅ in the Al₂O₃ matrix. Samples were studied based on
two primary parameters: the slurry loading, or the ratio of solid material to the liquid media, and the volume percentage of Fe to the Al₂O₃. Using Equation 3.1 and Equation 3.2, mixtures for the appropriate amounts of both Al₂O₃ and Fe(CO)₅ could be formed by combining the equations and solving for Al₂O₃ in terms of the mass percent, densities, volume percent, and volume of Decane.

\[
M\% = \left( \frac{M_{Fe}}{M_{Al} + M_{Fe}} \right) \quad (3.1)
\]

\[
V\% = \left( \frac{V_{Al} + V_{Fe(CO)5}}{V_{Al} + V_{Fe(CO)5} + V_{Decane}} \right) \quad (3.2)
\]

The densities for Fe(CO)₅ and Al₂O₃ were used to convert between mass and volume in the these two equations. The density of the combined powders was determined through

\[
\rho_{total} = \frac{M_{total}}{V_{total}}, \text{ where } V_{total} \text{ was determined as } V_{total} = \frac{M_{Al} + M_{Fe(CO)5}}{\rho_{Al} + \rho_{Fe(CO)5}}.
\]

These equations were used to calculate the mass of each to provide the set mass and volume percents from the equations above, as given by Equations 3.3 and 3.4.

\[
M_{Fe(CO)5} = \frac{V_{Decane} (\rho_{Al2O3})(\rho_{Fe(CO)5})}{\left( \rho_{Fe(CO)} \left( \frac{M_{Al}(1-M\%)}{M\%} \right) + \rho_{Al2O3} \right)} (1-V\%)
\]

\[
M_{Al2O3} = \frac{V_{Decane} (\rho_{Al2O3})(\rho_{Fe(CO)5})}{\left( \rho_{Al2O3} \left( \frac{M\%}{M_{R}(1-M\%)} \right) + \rho_{Fe(CO)5} \right)} (1-V\%)
\]

where \( \rho_{Fe(CO)5} = 1.457 \text{ g/cm}^3 \) and \( \rho_{Al2O3} = 3.97 \text{ g/cm}^3 \) and the molar ratio between Fe and Fe(CO)₅, \( M_{R} = m_{Fe}/m_{Fe(CO)5} = (55.847 \text{ g/mol}) / (195.9 \text{ g/mol}) = 0.28508. \)

Fe(CO)₅ is a liquid that is highly sensitive to photo-effects, and reacts quickly and violently with air. It is important that the Fe(CO)₅ be weighed out quickly and mixed with decane to limit the time for the Fe(CO)₅ to react with air or light. Once the Fe(CO)₅ is removed from the bottle, the bottle was sealed with argon gas by flowing argon into the bottle. Any pipettes or vials used for transferring Fe(CO)₅ were left to sit on the counter under the fume hood until all the Fe(CO)₅ was reacted before disposal. The vials used to weigh out the Fe(CO)₅ were rinsed several times with decane and poured into the sonication cell. The decane solution was used to rinse any Fe(CO)₅ from the vial, but also to rinse any Al₂O₃ that may have adhered to the sides of the cell while adding to the mixture. Decane was then added until the mixture was
approximately 15 ml of decane plus the Al$_2$O$_3$ and Fe(CO)$_5$ amounts taken from equations 3.3 and 3.4.

The sonication cell was then mounted on the sonication horn and lowered into the cooling bath. The solution was sonicated for 30 minutes at 40% maximum amplitude. The samples were then removed and washed five times with pentane as described in the usual sonication process. The samples were left overnight to dry in their centrifuge tubes covered with vented Parafilm® M wax. 6 mg of each powder was then placed into a capsule and measured. Approximately 40 mg was then placed into a die cast used to press a cold-pressed sample which was then measured.
CHAPTER 4. RESULTS

This chapter presents and discusses the results of this project in light of the current state of knowledge, but specific data comparisons to other studies will be presented in the next chapter. The MgB$_2$ samples showed favorable improvements in superconducting properties, but the results show that further optimization is needed. The data of the Fe(CO)$_5$ and Al$_2$O$_3$ study shows superparamagnetic particles in a non-magnetic matrix. However, the properties of the resulting superparamagnetic samples have not been optimized or fully understood. This means that further study is needed to determine the tunability of the superparamagnetic properties. The results presented in this chapter only offer the beginnings of a much larger study that needs to be completed to fully understand and realize the potential of sonication to produce tunable superparamagnetic ceramics.

4.1 MgB$_2$

As discussed in Chapter 1, sonication has a marked effect on the morphology of powders. This is important to the process of forming MgB$_2$ as sonication can change the grain size and shape of B powder. Section 1.3 describes how MgB$_2$ can be formed through exposing B to a Mg vapor reaction thus producing MgB$_2$ taking on the form of the B in the reaction. Alternatively, mixing magnetic and non-magnetic materials using high intensity ultrasound into the B powder before the Mg vapor reaction can increase the pinning properties of the MgB$_2$. The results of sonication of both pure B powder and B powder plus magnetic and non-magnetic particles as a precursor to forming MgB$_2$ in a Mg vapor process performed in Ta pouches in a HIP machine will be presented in the following sections. Here the measurements are presented and interpreted while reserving the comparison of the results to previous studies.
and discussions of criticism and further research for the following chapter.

4.1.1 B Powder of Different Purity and B + Mg

The study starts with sonication of several purities of B powder mixing with Mg powder and Mg chunks before reacting in the HIP process. These were compared to unmodified B powders of the same purity to see the effects of sonication on B precursors. For comparison, the data needs to be normalized to account for small variations in shape and volume.

Below $H_{c1}$, the magnetic induction penetrating the core of the superconductor is reduced to zero. In this region, $B = H_a + H_d + 4\pi M$ (in cgs units), where $H_a$ is the applied field (Oe); $H_d$ is the demagnetization field (G); and $M$ is the volume magnetization (emu/cm$^3$). Since $B=0$ below $H_{c1}$ and $H_d = -N_d M$, one can determine this demagnetizing factor $N_d$ from the slope of the $4\pi M$ versus $H$ plots in the shielding state. This formula was used in the field-cooled warming (FCW) curves to find the factor necessary to normalize the magnetization to $-H_a = 50$ Oe. Alternatively, the raw moment (emu) measured from the SQUID MPMS versus $H$ (Oe) was plotted and the normalization factor becomes,

$$N_f = \left(\frac{V}{4\pi(1 - N_d)}\right)$$

where $V$ is the volume of the sample. An estimate of $N_d$ was calculated from the estimated volume and the normalization factor, $N_f$, was used to convert the raw moments to the desired $4\pi M$ taking slight sample shape differences into account. The FCW curves also provided a way to identify the transition temperature. Figure 4.1 shows both the normalized $4\pi M$ and the transition temperature for the 86% purity boron, referenced on graphs as 86B. This shows also that the transition temperature for the sonicated sample has a sharper transition to the normal state, but both seem to retain the same $T_c = 38K$, where $T_c$ is defined as the temperature indicated by the knee of the curve on the $4\pi M$ versus $T$ graph. Figure 4.2 shows SEM images taken from the freshly exposed edge of the MgB$_2$ samples. The grains in the MgB$_2$ produced from the unsonicated 86% purity B, figure 4.2a, can clearly be seen, and figure 4.2b shows the smoother and more connected grains after sonication. Table 4.1 shows the $N_f$, $T_c$, and $\Delta T_c$ for all the B purities. It should be noted at this point that the sonicated 99% B
purity sample was damaged, or not sealed completely, and powder was lost during the HIP process. The table shows each of the sonicated samples has a larger transition width, with the exception of 86% and 95%+Mg. This is possibly caused by the introduction of additional impurities during the sonication process, particularly in the case of EPB ))) [ ))) being an abbreviation meaning sonicated. 

Figure 4.1: Warming after field-cooling in a 50 Oe field. Tc can clearly be seen from the point where the warming curve increases to ∼0 showing the return to the normal state where the shielding currents are destroyed.

Table 4.1: Normalization factor, Nf, critical temperature, Tc, and transition width, Δ Tc for the measured samples. Δ Tc was defined as the temperature difference from onset of shielding until the temperature at which 4πM ≤ -0.98Ha (or -49 G).

<table>
<thead>
<tr>
<th>Boron Purity</th>
<th>Nf (10^{-3})</th>
<th>Tc</th>
<th>Δ Tc</th>
</tr>
</thead>
<tbody>
<tr>
<td>86B, 86B )))</td>
<td>1.06218, 3.13683</td>
<td>38K</td>
<td>10K, 4.5K</td>
</tr>
<tr>
<td>90B, 90B )))</td>
<td>2.50475, 1.67899</td>
<td>38.5K</td>
<td>2.5K, 7K</td>
</tr>
<tr>
<td>95B, 95B )))</td>
<td>3.20349, 1.16941</td>
<td>38K, 37.5K</td>
<td>2K, 5K</td>
</tr>
<tr>
<td>95B+Mg, 95B+Mg )))</td>
<td>2.21065, 3.14873</td>
<td>37K</td>
<td>3K, 2.5K</td>
</tr>
<tr>
<td>EPB, EPB )))</td>
<td>2.01542, 4.89516</td>
<td>39K</td>
<td>2.5K, 9K</td>
</tr>
</tbody>
</table>

The normalization factor was used to scale the hysteresis curves, and a second normalization
Figure 4.2: SEM images at 20,000 magnification showing MgB$_2$ produced from 86% purity B (a) and sonicated 86% purity B (b). The morphological change can easily be seen in the sonicated sample. The sonicated image shows more connectivity as well as a smoothing of the grains over its un-sonicated counterpart.
was tested for 95B+Mg and 95B+Mg)). This normalization comes from using the same relationship as before, but instead applying a linear fit parameter to the low field as the field is ramped to 2 T. This method gave similar normalization factors of $2.27461 \times 10^{-4}$ and $3.08755 \times 10^{-4}$ which results in a 2.85% difference and 1.96% difference, respectively. This shows that the normalization is consistent between the two normalization methods.

Figure 4.3 shows hysteresis data for 86% B, 95% B, 95% B + Mg, and EPB versus their sonicated counterparts. This shows that sonication does have an effect on the hysteresis loops of the resulting MgB$_2$. These hysteresis loops are normalized using the scaling factor from 50 Oe zero-field-cooled warmed and field cooled warmed data. The area of the hysteresis loop is proportional to the critical current and the strength of the pinning force in the superconductor. Using the Bean model, one can estimate the critical current density and also estimate the strength of the pinning force in the superconductor.
These hysteresis loops can be decomposed into reversible and irreversible parts by taking $M_{up}$ and $M_{dn}$ values from the increasing field, -2T to 2T, and decreasing field, 2T to -2T. $M_{rev} = \frac{(M_{dn} + M_{up})}{2}$ can be used to estimate the thermodynamic critical field, $H_c$, for $T$ near $T_c$ by integrating $M_{rev}$ vs $H$ [Finnemore et al., 2001], but as the loops are at 30K nearly 10K below $T_c$, this method could not be employed for these samples. $M_{irr} = \frac{(M_{dn} - M_{up})}{2}$ can be used to calculate the critical current using a Bean model approach with the conversion factor related to the samples geometry. In the case of a rectangular cross-section, as in this studies samples, of sides $2w$ and $2b$ where $w \leq b$, the formula is:

$$M = \frac{J_c w}{20} \left( 1 - \frac{w}{3b} \right) V$$  \hspace{1cm} (4.2)

where $M$ is the total magnetic moment (emu), $V$ is volume given as $8wbd$ (cm$^3$), and $J_c$ is the critical current density (A/cm$^2$) [Charles P. Poole et al., 2007, 396]. Figure 4.4 shows the resulting critical current densities as well as the pinning strengths of several purities. As we would expect, the lower purity B, un-)), has a much lower Jc than the higher 90% and 95% purities, almost 3-4 times higher, but the large increase in 86B ))) suggests that ))) may have a much more profound effect on lower purity B over high purity B. The drastic improvement of $J_c$ in the case of 86B is most likely attributed to the washing away of some of the impurities as well as the increase in connectivity shown by figure 4.2. Comparison of the Mg powder samples, (95B+Mg and 95B+Mg)),, with the Mg metal chunks, (95B and 95B))),, shows a 14.3% difference for the unsonicated and 17.6% difference for the sonicated samples. This increase in $J_c$ is attributed to higher levels of MgO formation in the Mg powder samples. The use of Mg powders does however result in a minor increase in the field where $P_{f\max}$ occurs by $\simeq 500$ Oe. This is consistent with the extra formation of MgO which acts as pinning sites thus reducing vortex flux flow at slightly higher fields. X-ray diffraction verifies that the Mg powder resulted in a noticeable MgO peak while the MgB$_2$ from the Mg chunks shows no visible MgO peaks. The decrease in $J_c$ seen for the sonicated 90% B is harder to understand, and could be a result of higher levels of impurities which were unidentified, or in possible inaccuracy of volume measurements, which is understandable for such small volumes of samples. Further study would be necessary to understand this $\sim 8\%$ decrease in $J_c$. 
J_c can also be estimated using the remnant field data and a sense for the J_c(T) can be attained. By applying a field of 5T at 5K then reducing the field to 0T, flux becomes trapped inside the superconductor. As the temperature is increased, flux becomes thermally activated and without sufficient pinning will result in a flux decrease as flux leaves the superconductor. One can convert the magnetic moment response using equation 4.2. In sufficiently pinned samples, the magnetic moment and consequently the J_c will remain fairly unaffected until near T_c where the superconducting state is destroyed.

With the information from the first part of the study, it was determined that the sonication of B in its precursor powder form does enhance MgB_2 properties and the actual sonication process was worth investigating. The sonication process was adjusted to attempt to find the
optimal slurry loading for the sonication of B powders. Although B powder was sonicated at each of the slurry loading described in Chapter 3, due to time and high cost of HIP per cycle, it was decided to not finish this study and instead use the 2% slurry loading used in the previous study of MgB$_2$ and sonication [Prozorov et al., 2003].

4.1.2 Ultrasonic Irradiation of B + X to Form Superconducting Composites

Of the available samples from Tables 3.1 and 3.2, only a few were actually measured as there were complications with the sealing process. Primarily the samples from table 3.1 were unmeasurable as most did not react properly due to excessive heating during the sealing procedure. This is a result of sealing the pouches using a copper cylinder which allowed heat to reach the sample space as their was no copper contact between the pouch edge and the sample space. This was the prime motivation behind using the copper blocks seen in figure 2.2b, as these contained a contact point between the edge and the sample space allowing heat to be absorbed by the copper block and preventing excessive heating and reaction of powders before the HIP process.

This second attempt at this study focused on the effects of sonication of B powder before the mixing of additives, and the cosonication of additives with B. Focus again will be on magnetic measurement with the SQUID MPMS, particularly $J_c$ enhancement. These $J_c$ values were obtained through the same use of equation 4.2 as above from hysteresis loops at 25K. Figure 4.5 shows the $J_c$ measurements (all given in A/cm$^2$) for a few of the samples that were made. This figure shows that sonicated B has a higher critical current than purchased B, $1.14\times10^5$ versus $1.09\times10^5$, which is a $\sim4.7\%$ increase over the as purchased B at 25K and 0T. For comparison, figure 4.6 shows data from MgB$_2$ wires showing similar $J_c$ values when measured at 25K.

From an unpublished previous study by this lab group, BSCCO was determined to be too fragile for sonication as the violent nature of the cavitation collapse seemed to degrade the BSCCO structure. This was seen as an overall decrease in performance of sonicated BSCCO in terms of hysteresis and $J_c$. As such, [B+BSCCO] was expected to have lower values than
its unsonicated BSCCO counterpart. However, the resulting cosonization had an increased effect on the $J_c$ giving $\sim 10\%$ increase from $1.77 \times 10^5$ to $1.95 \times 10^5$ in the cosonicated sample at zero field. However at higher fields, the samples share a similar shape and magnitude. EuS resulted in a lower $J_c$ for the cosonicated samples with a $\sim 1\%$ decrease from $1.04 \times 10^5$ to $1.02 \times 10^5$ for the cosonicated sample. These values were all smaller then the almost 6 times larger value given by commercial Alfa Aesar MgB$_2$, $6.35 \times 10^5$. This is believed to be a result of a high MgB$_2$ purity in the HIPed commercial sample over the often contaminated MgB$_2$ samples produced from the HIP where Mg and MgO are present. Figure 4.7 features the SEM images for four of the above samples showing the changes achieved by sonication. While the unsonicated sample has larger grains that are stacked inefficiently, all of the sonicated samples show smaller grains with much more connectivity between grains.
Figure 4.6: The top image shows $J_c$ values for MgB$_2$ wires of varying thickness taken at 25K [Finnemore et al., 2003]. The bottom image shows $J_c$ values for MgB$_2$ pellets and wires from 5K to 35K and Nb$_3$Sn at 4.2K is provided for reference [Canfield et al., 2003]. In direct comparison, the $J_c$ values in figure 4.5 show similar values, but with a slight field range improvement for MgB$_2$ with BSCCO.
Figure 4.7: MgB$_2$ created from different sonicated and unsonicated powders. The unsonicated B (a) produced large grains with void space between, which may explain the increased $J_c$ seen in the sonicated B (b) sample that shows a much closer packing and better connectivity. The samples producing the highest $J_c$ were the [B + BSCCO] (c) and B )]] + BSCCO (d). These images (c and d) show similar connectivity which is consistent with the very similar $J_c$ behavior.
4.2 $\text{Al}_2\text{O}_3$ and $\text{Fe(CO)}_5$

This section focuses on the study performed on sonication effects on $\text{Al}_2\text{O}_3$ and $\text{Fe(CO)}_5$ cosonicated to obtain superparamagnetic nanocomposites. The goal of this study was to disperse superparamagnetic particles within the $\text{Al}_2\text{O}_3$ matrix and will study the ability to use sonication to tune the magnetic properties of these samples.

4.2.1 Nanocomposite Results

The study of $\text{Al}_2\text{O}_3$ and $\text{Fe(CO)}_5$ began by determining two parameters that should have the largest affect on the magnetic properties. These were identified as the mass percentage of Fe in the $\text{Al}_2\text{O}_3$ matrix and the volume percentage of the additives of $\text{Al}_2\text{O}_3$ and $\text{Fe(CO)}_5$ to the decane sonication medium. Hysteresis loops were measured at four temperatures above the blocking temperatures. The blocking temperature was determined from the zero field cooled, ZFC, and field cooled, FC, data. This is seen in figure 4.8 that shows the separation of the ZFC and FC measurements and is identified as the blocking temperature. The same process was used to determine the blocking temperature, $T_b$, of each of the samples. The blocking temperature can also be defined as where the ZFC data has a local peak, instead of where ZFC deviates from the FC data. Above $T_b$, the samples should have negligible magnetic hysteresis, and therefore a definition resulting in an increased $T_b$ is acceptable. Figure 4.8 shows an inset where one sees $T_b$ as defined formerly is about 55K, but $T_b$ defined by the local peak in ZFC is at about 40K. Hysteresis loops at 50K showed small hysteresis but did not collapse when plotted on M vs H/T with the other 100K, 150K, 200K, and 250K.

Superparamagnetism was identified in these samples by a collapse of M vs H/T for hysteresis loops at several temperatures above $T_b$. Superparamagnetic (SPM) samples show a collapse of these loops to a single curve, as well as very little to no hysteresis during increasing and decreasing field sweeping. The defining parameters of the superparamagnetic samples is the average magnetic moment, $<\mu>$ and the saturation magnetization, $M_s$, where $M_s = N <\mu>$ and N is the volume density given by the number of magnetic particles per sample volume. All samples collapsed when plotting M vs H/T so only one sample will be presented, and the
primary focus will be on the fitting parameters. Figure 4.9 shows the collapse of $M$ vs $H/T$ for sample 24 M% 1V% at temperatures of 100K, 150K, 200K, and 250K. Another indication of SPM behavior is that SPM samples typically have $<\mu>$ around 1000 $\mu_b$, where $\mu_b$ is the bohr magneton.

Sonication of Fe(CO)$_5$ has shown to result in amorphous iron when isolated from oxidation processes [Suslick et al., 1991]. During the drying procedure, the samples were allowed to oxidize under air at room temperature. This led to either partially oxidized iron cores with surface oxidation, or complete oxidation where either iron oxide hollow spheres or iron oxide particles are formed. Figure 4.10 contains SEM images showing the effects of sonication on Al$_2$O$_3$ when cosonicated with Fe(CO)$_5$. The SEM images show that the Al$_2$O$_3$ grains are being coated with the iron and iron oxide particles. These images also verify that the particles created during sonication are in fact nanosized particles, as was expected. Further oxidation
can be seen in a sample that was heat treated to 150°C in air for 2 hrs. This further oxidation could suggest formation of non-fully oxidized iron oxide species, such as magnetite, in these sonicated slurries. Alternatively, this oxidation suggests that oxidation may be controlled to give the desired iron oxide species when the sonication process is isolated from oxidizing elements until the post sonication and drying phase is completed. While unable to determine the exact proportion of iron oxide or the oxide species, the small bumps on the SEM images for the sonicated samples are shown to be some combination of iron and iron oxide by EDAX, and X-ray Diffraction verifies the presence of iron and iron oxide.

The samples were then fit to two functions, a Langevin function plus linear term and a dual Langevin function with two sets of independent variables. The linear term was added to the fitting function after plotting and noticing a paramagnetic contribution in the data. The dual Langevin function was suggested to account for the possibility of two separate paramagnetic species with different sizes and average magnetic moments. The Langevin function, \( L(x) = \)
Figure 4.10: SEM images of as received Al$_2$O$_3$ powder, sonicated Al$_2$O$_3$ powder with Fe(CO)$_5$, and heat treated (150$^\circ$ C for 2 hrs in air) post-) Al$_2$O$_3$ powder with Fe(CO)$_5$. 
\( \coth(x) - 1/x \), is typical of paramagnetic response to a magnetic field. The magnetic moment \( \mu \) follows the formula \( \mu(H,T) = <\mu>L(x) \) where \( x = (\mu H/k_B T) \). When writing the Langevin fitting function, two free parameters are allowed, A and B. A is equal to \( \mu_t \) and B is related to \( <\mu> \) by the thermal dynamic energy, \( k_B T \). The total magnetic moment of the sample, \( \mu_t \), is given by \( \mu_t = n <\mu> \) and \( n \) is the number of magnetic particles in the sample. The paramagnetic term was accounted for by adding a \( \chi H \) term to the first fitting function. This gives the two fitting functions as:

\[
\mu = A \left( \coth(BH) - \frac{1}{BH} \right) + \chi H, \quad \text{where} \quad A = \mu_t \quad \text{and} \quad B = \frac{<\mu>}{k_B T} \quad (4.3)
\]

\[
\mu = A_1 \left( \coth(B_1 H) - \frac{1}{B_1 H} \right) + A_2 \left( \coth(B_2 H) - \frac{1}{B_2 H} \right) \quad (4.4)
\]

From these fitting functions one can estimate the average moment, \( <\mu> \) from B and the number of moments, from \( n = A/<\mu> \).

Attempts to fit a Langevin function to the data resulted in Figure 4.11a, and Figure 4.11b shows the fitting to a Langevin and paramagnetic term. This paramagnetic term does seem to fit the experimental data quite well. The linear term has been explained for hollow maghemite nanoparticles obtained from \( \text{Fe(CO)}_5 \) as arising from the spins at the shell surface and crystalline interfaces being strongly pinned along the local axis due to surface anisotropy [Cabot et al., 2009]. Figure 4.11c shows the resulting data after the linear term is subtracted out. This figure demonstrates that as the field increases the slope decreases as the downturn in the figure suggests. This could be a result of approaching the saturation of the paramagnetic contribution. Additionally, the slight downturn at high applied \( H \) can be attributed to left over organic material.

Another possible explanation would be a superparamagnetic species and a second paramagnetic species. Superparamagnetic samples should align under a small applied field and saturate very quickly, while a paramagnetic sample would exhibit a longer field range of linear-like behavior before approaching saturation. Figure 4.11d features the two Langevin functions used to fit the data and shows a better fit to the decreasing slope at higher fields. Comparing these fit parameters one can understand the affects of volume percentage and mass percentage.
Figure 4.11: 40M% 1V% sample demonstrating different fitting functions at 100K. A) Demonstration of the very poor fitting to a single Langevin fitting. B) The addition of the linear terms seems to conform to the shape of the data. C) When the linear term is subtracted the decreasing slope over increasing field can be seen. D) Two Langevin functions shows a linear-like Fit #1 and a quickly saturated Fit #2.

on forming superparamagnetic powders from this Fe(CO)$_5$ and Al$_2$O$_3$ composite.

Here the parameters of 40 M% over 0.5, 1.0, 1.5 and 2.0 V% are compared, and the parameters of 1 V% over a range of M%’s from 6% to 100% are compared. Figure 4.12 shows the effect that volume percentage has on a single mass percentage. The indices indicate the two Langevin fit parameters ($\mu_i/k_B$ is the average moment per Boltzman constant and $M_s$ is the total moment $\mu_t$) for each of the Langevin fits. The 1 index is responsible for the linear-like Langevin function shown in Figure 4.11d, which is the portion of the Langevin well below saturation where the Langevin function is near linear. The 2 index is then responsible for
Figure 4.12: The top, A and B, are the parameters responsible for the linear-like Langevin function. C and D clearly shows a peak at 1.5% and suggests that with adjusting the volume percentage samples can be made with the maximum average moment.

the quickly saturated superparamagnetic portion of the data curves in Figure 4.11d. Over the studied volume percentage, $\mu_1$ varies slightly, but shows a general increasing tendency. Converting from moment to Bohr magnetons and from Ms and $\mu_1$ to the number of magnetic particles results in a maximum of 92 $\mu_b$ and minimum of $1.15 \times 10^{16}$ number of particles. When this data is compared to the superparamagnetic particles parameters, a maximum occurs at 1.5%V of 3186 $\mu_b$ and $6.77 \times 10^{13}$ number of particles. This indicates that at 1.5%V the superparamagnetic particles are maximized both in number and average moment while minimizing the number of paramagnetic particles. The Langevin plus linear parameters shows the same maximization at the 1.5%V with more particles, $1.08 \times 10^{14}$, but with a reduced average moment of 2341 $\mu_b$ over the Langevin parameters associated with the superparamagnetic values.
from the two Langevin fits. The linear terms from both the V% study and the M% study will
be discussed together later (see Figure 4.14).

![Figure 4.13: Fit parameters from two Langevin functions showing the effect of changing mass percentage at 1% volume.](image)

Figure 4.13: Fit parameters from two Langevin functions showing the effect of changing mass percentage at 1% volume.

The effects of changing the mass percentage at a set volume percent of 1% are now com-
pared. Figure 4.13 shows the results of fitting two Langevin fits to the sample data. These fit
parameters are obtained in the same way as in the previous study of the volume percentage
study. The upper data again corresponds to the linear-like Langevin function and shows a
gradual increase in the saturation magnetization. Linearity can not be verified without pro-
ducing and measuring more samples in the intermediate ranges, but the data seems fairly
linear with the low values deviating slightly from linearity. This is either due to the data
following a non-linear function, or due to unavoidable small inaccuracies in the measurement
of mass percent in the lower region. However, the magnetic moment per particle in the upper graph at 200K varies minimally with an average of 79 $\mu_b$ with the highest number, 85 $\mu_b$ at 67 M% and the minimum of 71 $\mu_b$ at 100 M%. This trend demonstrates that the increase in saturation magnetization is due to an increase in the number of magnetic particles, but not an optimization of the average moment as $\mu_1$ seems to remain fairly consistent over the mass range.

This is not seen in the lower graphs of $\mu_2$ where the minimum occurs at 67 M% and a maximum at 100 M%. Further samples in the 40% to 100% range are needed to determine the meaning of the minimum and maximums, but the variation clearly suggests the possibility of adjusting the mass percent to achieve a desired saturation and average moment within the ranges of these maximums and minimums. The saturation $M_{s2}$ does show a increase though values are less linear looking than the upper graphs. This would suggest that the saturation does not follow a linear function, but more points would be needed to verify a reliable trend. Despite the uncertainty in a fit function, clearly increasing the mass percentage in these samples results in an increase of the saturation magnetization, which can be explained in part by the increase in the number of magnetic particles in the sample. The average magnetic moment, $\mu$, is assumed to vary based on variations in the average particle size.

Previously, only the two Langevin fit parameters were presented. This is because the trend in the Langevin function for the Langevin plus linear, paramagnetic term, fitting exhibits the same trends seen in the second indexed values, $\mu_2$ and $M_{s2}$, in both the above mass and volume percentage studies. Figure 4.14 shows the paramagnetic term found in each case of 40% mass and 1% volume. Over the volume percentages studied, the value of $\chi$ decreases slightly, but remains fairly unchanged particularly in the higher temperatures of 200 K and 250 K. However, adjusting the mass percentage has a marked effect on the resulting $\chi$ value. The value of $\chi$ increase by $\sim$4 times between 40% and 100% over the presented temperature. This suggests that the mass percentage is more effective to optimize or minimize $\chi$, however, higher values of volume percentage may yield a greater effect providing further optimization or minimization.
Figure 4.14: The top panel shows the fairly unchanged $\chi$ across the volume percentages studied. The bottom presents a near linear increase in $\chi$ over mass percents. This is explained by the increase in the number of paramagnetic particles.

### 4.2.1.1 Coercivity

Coercivity is defined as the field required to reduce the magnetization to zero after saturation is reached in the sample. The coercivity, or coercive field, of these samples is hard to estimate based on the measurements performed. However, the order of magnitude from the hysteresis loops at 100 K to 250 K can be estimated. The reason for the need to estimate, rather than reading the number from the data, comes from the sampling step size on the hysteresis loops which was 2000 Oe. As the region near zero is fairly linear, one can estimate the coercivity more accurately by fitting the 2000 Oe, 0 Oe, and -2000 Oe points to a linear curve on either side of the hysteresis loop. By this method, the coercivity can be estimated by the fit of a linear function and look for the range over which the magnetization switches sign. Using this method, the samples show a less than 100 Oe coercive field. Unfortunately, the coercive field can not be measure to a higher accuracy with these hysteresis loops.
CHAPTER 5. SUMMARY AND DISCUSSION

The objective of this project and thesis was to demonstrate the ability of high intensity ultrasound to achieve a tunable procedure to create desirable superconducting and superparamagnetic nanocomposites. After completing this study, it was determined that further research is needed to truly understand the effects of the extreme environments created during acoustic cavitation. However, the data presented in the previous chapter demonstrates that sonication can have a positive effect on superconducting samples, albeit a slight improvement. Also, superparamagnetic samples can be easily obtained using sonication, and further study is needed to optimize the formation of superparamagnetic particles. The results of this study should not be seen as a failure of sonication as a method for tuning sample properties. Further research should be designed to optimize specific systems, e.g., study all aspects of sonication to find the optimized conditions for each sample composite.

While sonication is a powerful tool for chemical and physical reactions, the use of a chaotic process such as sonication and cavitation to gain accurate tuneability of various physical properties seems to be more complex than originally accessed. This complexity does not suggest that it is difficult, but simply that the complex nature of the study requires more time and resources than previously thought. This chapter addresses specific issues and compares this studies results to other methods as well as to help direct future research on this subject should one want to continue the study.

5.1 Use of Ultrasound to Increase Pinning in MgB$_2$

MgB$_2$ has been shown to be a phonon-mediated double gapped superconductor. Since 2001, research has been focused on producing quality MgB$_2$ samples and currently there are
reliable ways of producing quality MgB$_2$ samples in both bulk forms as well as thin films. The focus of much of the current research is on optimizing pinning through doping with various elements or compounds and on improving grain connectivity. Sonication can be used for both purposes as cavitation can decrease and homogenize particle sizes, thereby improving grain connectivity, and can be used to homogeneously distribute dopants into MgB$_2$.

The results show modest $J_c$ values at low field and do not exhibit high field $J_c$'s at 30 K or 25 K. The measurements at lower temperatures such as at 5K showed the same flux jumps that other groups have experienced with bulk MgB$_2$ samples. Flux jumps remain problematic at low fields up to around the 20-25 K region as can be seen in figure 5.1. The choice of 30 K and 25 K in these two studies was to avoid flux jumps in all of the samples. $J_c$ values can still be obtained from sample exhibiting flux jump but only for the higher field regions before any flux jumps. The data shows this flux jump free region to be fields of $\sim$2T and higher at 5K.

Figure 5.2 shows the values obtained from four of the measured samples in the B + X study. These values are smaller than results obtained from ball-milling studies where samples were produced with higher $J_c$ at the same fields, but also remained above $10^4$ A/cm$^2$ at 5 K even at fields of 7.5-8 T [Lee et al., 2009, Xu et al., 2008], and fields as high as 13.5 T for C doped samples at 4.2 K [Senkowicz et al., 2008]. However at the lower fields of 1.5-2 T, the results show comparable values around $2 \times 10^5$ at 5K, and even at 30K in the B purity study at 0T. All of the MgB$_2$ samples show this similarly rapid drop off with higher applied fields (see Figures 4.4, 4.5, and 5.2). As many samples show a lack of homogeneity, this decrease is believed to be caused by the MgB$_2$ formation process and not a consequence of the sonication process.

The advantage of the Ta pouches over cylindrical tubes is that the pouches allow direct pressure to the powders, but the samples produced were irregularly shaped and were never nice pellets of near uniform thickness as was hoped. The high pressures experienced during HIP were applied uniformly, but due to the inability to distribute the powders and/or Mg chunks homogeneously, the samples did not show an even surface and extracting a measurable sample from these pouches was difficult to acquire. Two solutions to this problem are suggested. The
Figure 5.1: 95B + Mg Powder at 20K and 25K, respectively. A flux jump is clearly seen at about 1T in the 20K data.

first requires increasing the depth of the indentation in the pouch so that more material may be placed inside. With a larger sample depth, an acceptable sample may be attainable through cutting and polishing. The second solution is to press a pellet from the powders similar in size to the indentation. The sample would then have an even distribution of “powder” and hopefully result in a nice disk-like sample with few cracks. Of course, there are many more solutions that would avoid this problem and result in more homogeneous results.

5.1.1 Self Criticism of the Studies on MgB$_2$

The results presented here should not be dismissed as offering meager results when other methods have shown more impressive gains, but should be seen as the beginning works to a much larger and more in depth study. It is important to keep in mind that the “phase
Figure 5.2: $J_c$ values at 5 K for fields of 1.5 T to 4 T.

The "phase space" of this study is very large. As was mentioned in Chapter 3, the study of sonication effects has a large number of parameters that can be optimized. Unfortunately, studying each parameter separately would take 10's of years by a single person or group. To exhaustively study the effects of sonication, a multitude of scientists or groups would need to communicate and cooperate each focused on a different aspect of sonication. Also, each element or compound will have its own set of optimized parameters thus making the "phase space" of this experiment enormous and impossible to study as a single individual. That is why this study focused on two parameters which were anticipated as having the largest effect: slurry loading and inclusions. Therefore, there were many things that could have been done differently and also many paths not explored in this study that need to be performed to claim a complete study of this process.
and its benefits for superconductors. This section explains some of the avenues that were unexplored. Two such avenues were of the greatest importance.

The first was producing samples and measuring them across measurement devices such as using 4-probe techniques, the MPMS, and the PPMS to verify physical properties and cross check for anomalies. For example, direct measurement of the critical current through a 4 probe process would have enabled one to verify the critical current as well as help identify $H_c^2$. Further measurements beyond MPMS data were not obtained as the decision was made to save the limited resources available for this project for the second part of the study, namely the superparamagnetic study. This decision was also based on the mediocrity of the results, the length of time already spent on this portion of the project, and the additional resources necessary to fully study this system.

The second avenue was the repeatability of individual samples. This was of a two fold nature. Initially, samples should be compared where several measurable samples were gathered from a single sonication and HIP pouch. The results of which will verify the homogeneity of the sample across the HIP pouch. Also, separate sonications with identical conditions should be performed to test for the reliability of the sonication process. As sonication is a violent and chaotic process, more study is needed to determine if these results are typical of the sonication parameters or are simply one point of a random distribution.

Another area that was not explored was the variation of doping levels and the selection of X on the B + X study. The percentage of dopants can have a dramatic effect on the results of any sample. This is clearly evident in the field of alloying of metals. Similarly, one would expect to see an optimization of different properties with different dopant levels. Also, the materials chosen to be used in this B + X study were not chosen systematically. Some were chosen specifically based on current research at the time, e.g. BSCCO and Fe nano powder, but the effect of various additions needed to be shown and readily available additives were chosen, thus neglecting some important dopants like C powder.

Finally, the study was rushed and the slurry loading study was not finished for the B precursors, and instead the value from a previous study done with sonication on MgB$_2$ pow-
ders was used. This choice was made to expedite the additive/dopant part of the research. Optimization of the slurry loading could potentially have dramatic effects on the results of sonication on a specific sample system. Slurry loading effects the distance between collisions as well as the statistical chance for a collision to occur. As discussed previously, when the slurry loading is too high particles bunch up and effective collisions can not be achieved and too low particle collisions are reduced due to low particle densities in the medium.

5.2 Use of Ultrasound to Produce Superparamagnetic Nanocomposites

Sonication is highly effective in creating nanocomposites from organometallic systems such as Fe(CO)$_5$. The samples from this study and the previous studies performed by Suslick, et. al. demonstrates that nano-sized particles can be produced in various forms. The initial studies of volume and mass percents demonstrated peaks in the Langevin parameters associated with an increase in the overall average magnetic moment and an increase in the number of these magnetic particles. However, it is difficult to make conclusive statements on the volume percentage study as there are only four points.

The fitting of Langevin plus linear functions seem to match with the experimental measurements and are consistent with other Fe oxide studies, but it does not account for the decrease in slope at the high field values. The dual Langevin fitting seemed to account for this down turn, but unfortunately higher fields and more data in the 0 T field range would be needed to determine the proper fitting function. Increasing the number of points in the 0 T field will help to define the Langevin function and the saturation point for the superparamagnetic fitting. Higher field data would help determine which of these fitting functions is appropriate. The dual Langevin function may simply result in better fitting based on the increased number of parameters, and the second Langevin function does resemble a nearly straight line within the field range. From Fit #1 in figure 4.11d, one can estimate the field at which the data approaches saturation as around 10 T. Extending the measured range to around 10 T would result in an increased understanding of the necessary fitting function. The mass percentage study shows an increase in $M_s$ with increasing mass percentage. This is not surprising as
there is more Fe available from the added Fe(CO)\textsubscript{5}. However, the average moment per particle demonstrates small variations and even though there are local peaks, more points are needed to separate these from statistical variations.

Clearly, there is a superparamagnetic component and further work is needed to optimize the superparamagnetic properties. My group is currently involved in research to study the effect of sonication length and the effect of increased Fe(CO)\textsubscript{5} additions to the Al\textsubscript{2}O\textsubscript{3} matrix on these properties. Another aspect that needs to be studied is the repeatability of these sample values to verify that subsequent sonications with the same parameters will result in the same fit values. The next section will address some of the problems with this study, and also, attempt to highlight how the project can be improved.

5.2.1 Self Criticism of Superparamagnetic Study

One major critique of this superparamagnetic project was the lack of powder analysis to help accurately assess what species of iron oxide and the mass percentage of the magnetic species. Unfortunately, most of the comparable data lists the moment and saturations in either emu/(g of sample) or emu/(g of Fe\textsubscript{2}O\textsubscript{3}). In the first instance, the samples are usually pure iron oxide or pure Fe nanoparticles or at least samples with a high percentage of either of these. In the case of the moments listed in emu/g of Fe (or Fe\textsubscript{2}O\textsubscript{3}), the mass percents are well known for their chemical reactions.

In my experiment the mass percents are listed as Fe mass percent before reaction, and one can not reliably tell what the resulting mass percentage is. As the goal was to set the initial parameters and optimize the sample performance, this representation of the mass percent is acceptable. However, the data was difficult to compare to other studies as a reliable estimate of the mass percent after the sonication process was unobtainable. This also complicates the ability to interpret the results and presents a challenge for a meaningful conclusion. Powder analysis was not performed due to time and expense issues, but mostly expense issues.

Another drawback to this study is that the samples were allowed to oxidize “naturally.” During the drying procedure after sonication, samples were allowed to be exposed to air without
attempts to control the oxidation process. Control of the oxidation is important as sonication of Fe(CO)$_5$ can result in amorphous iron, and with the appropriate oxidation conditions, it is possible to control which Fe-oxide species would be present in the samples. Additionally, attempts could be made to perform the sonication under a closed inert atmosphere such as a glovebox. It is unclear if oxidation is occurring during the sonication process and the Argon flow should help to reduce the exposure to ambient air during the cycle, but this can only be verified through performing the work in a glovebox for comparison.

Finally, the samples were measured in a powder form and not as pressed pellets. Cold pressed pellets were not expected to behave differently, but HIPing or heating during the pellet process may result in further oxidation and effect the result presented here. Overall, the results of this study were very positive, and demonstrated that superparamagnetic species are produced. However, there are many avenues left to be studied that may result in further optimization and offer further tunability of the magnetic particles.

5.3 Conclusions

As was mentioned previously, the study of the use of sonication to enhance the physical properties of superconductors presented a great challenge as there were many free parameters that needed to be investigated. This study attempted to influence these properties through sonication with different additives and different purities of Boron. While the maximum $J_c$'s were in the “normal” range for MgB$_2$ in the O T field range, the samples did not show good high field $J_c$ values and were far below samples made from ball-milling and other MgB$_2$ studies. However, the samples from unmodified B also showed similar $J_c$ values and sonicated B does show a slight improvement. The decrease in the high field region could be produced by poor grain connectivity due to unreacted B, high amounts of excess Mg, or other contamination. Optimistically, sonication of B precursors used in a different reaction method, or procedure, will result in improved $J_c$ even at high fields. Also, additives like SiC and C should be investigated as these have resulted in increases properties in other studies. Further research of sonications affect on precursors and research of different nanocomposites should be studied in the future.
to determine the full extent of sonication benefits.

The use of sonication to motivate chemical changes has been studied extensively. Sonication was used on Fe(CO)$_5$ to fabricate nano-scaled composites of Fe and Fe$_2$O$_3$ in an Al$_2$O$_3$ matrix. The small grain size produced a sample with superparamagnetic properties with an underlying paramagnetic response. By controlling the sonication parameters, it was shown that within the range of values studied, one can tune certain properties like the average moment per particle through controlling particle size and saturation magnetization by increasing the percent mass of Fe. Further study is needed to explore higher % volumes as well as more mass % values to flush-out the nature of the fitting parameters. This group continues to study the effects of sonication length and increased Fe(CO)$_5$ loading. The results of that study will be presented in future papers by this group.


