Effects of Static Axial Magnetic Fields on Directional Solidification of HgCdTe

by

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B.S.M.E. West Virginia University (1987)
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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

at the

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Abstract

In order to achieve homogeneous semiconductor crystals through melt stabilization during the crystal growth process, $Hg_{1-x}Cd_xTe$ crystals were grown by the Bridgman-Stockbarger method in space and on the ground in the presence and absence of magnetic fields up to 5 Tesla. A crystal growth system was designed with a thermal environment similar to that of the NASA microgravity crystal growth furnace to permit a direct comparison with results observed in a microgravity environment. The influence of convection, by magneto hydrodynamic damping, on mass transfer in the melt was investigated by measuring axial and radial composition variations in the grown samples.

For conventional growth, the axial composition profile experienced an initial transient, a steady state region of relatively constant composition and a final transient which could be explained by a diffusive transport model, with the caveat that some convection is present. Radial segregation was found not to be in agreement with the diffusion limited theory as proposed by Coriell and Sekerka. Thus, it is concluded that convection, although not a primary contributing factor to axial segregation, controls radial segregation.

Application of a magnetic field was found to primarily affect the mass transfer process through a reduction of convective interference with radial segregation. While the axial compositional distribution during the initial transient and steady state growth portions of the solidification process remained virtually unaffected, an abrupt rise in the CdTe content occurred near the end of the solidification process. This effect could be attributed to constitutional supercooling brought about by the magnetic suppression of a convective cell near the growth interface as mentioned previously by Kim and Brown. It was also found that in the presence of magnetic fields in excess of 0.5 Tesla the curvature of the growth interface was reduced by a factor of three and that radial segregation approached the diffusion limited regime.

Segregation during growth in a microgravity environment, showed dependence on the relative magnitude and orientation of residual acceleration due to drag. Experimental data to date, indicate that whenever the drag vector is not aligned with the
growth direction (liquid to solid) three-dimensional fluid flow results which destroys the symmetry of the system and leads to non-uniform radial segregation. Crystals grown on the ground in a similar thermal environment with an applied axial magnetic field exhibited composition homogeneity which exceeded that of material grown, thus far, in a microgravity environment.

Thesis Supervisor: August F. Witt
Title: Professor of Materials Science
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Nomenclature

LATIN
Bi  Biot number
C   composition
$C_p$ specific heat
$CdTe$ cadmium telluride
D   solutal diffusivity
g   gravity
G   thermal gradient
Gr  Grashof number
h   heat transfer coefficient
Ha  Hartman number
$\Delta H$ Latent heat of solidification
k   segregation coefficient
K   thermal conductivity
L   characteristic length
n   direction normal to a surface
N   magnetic interaction parameter
Pe  Peclet number
Pr  Prandlt number
q   heat flux
r   radial coordinate direction
R   crucible translation rate
Ra  Rayleigh number
Re  Reynolds number
St  Stefan number
$T_m$ melting point temperature
$W_o$ non-dimensional velocity
z   axial coordinate direction
Au  Gold
Cd  Cadmium
Ga  Gallium
Ge  Germanium
Hg  Mercury
In  Indium
Sb  Antimony
Se  Selenium
Si  Silicon
Sn  Tin
Te  Tellurium
Zn  Zinc

AADSF  Advanced Automated Directional Solidification Furnace
EDS  Energy Dispersive x-ray Spectroscopy
NASA  National Aeronautics and Space Administration
USML  United States Microgravity Laboratory

GREEK
\( \alpha \)  thermal diffusivity
\( \beta \)  expansion coefficient
\( \delta \)  boundary layer thickness
\( \Delta \)  difference
\( \mu \)  viscosity
\( \mu_0 \)  permeability
\( \nu \)  kinematic viscosity
\( \rho \)  density
\( \sigma \)  electrical conductivity
\( \xi \)  centerline interface deflection
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<td>furnace</td>
</tr>
<tr>
<td>$i$</td>
<td>interface, or variable</td>
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<tr>
<td>$l$</td>
<td>liquid</td>
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<tr>
<td>$m$</td>
<td>melt, or melting point</td>
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<td>momentum</td>
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<tr>
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<td>reference, start value</td>
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<td>solid</td>
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## VECTORS

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<td>$\vec{E}$</td>
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<tr>
<td>$\vec{F}$</td>
<td>force</td>
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<tr>
<td>$\vec{V}$</td>
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Chapter 1

Introduction

Growth of large semiconductor homogeneous single crystals with low defect densities is of interest to the electronic industry. Semiconductors are used for a multitude of devices such as logic circuits, memory chips, optoelectronic circuits, lasers and detectors. The performance of these devices is strongly influenced by defects generated during the growth process brought about by incorporation of contaminants such as carbon and oxygen. Also, advances towards miniaturization of integrated circuits are hampered by non-uniform incorporation of dopants.

The spatial distribution of dopants, known as segregation, is highly dependent on the nature of fluid flow in the melt. The flow patterns are a result of buoyancy induced natural convection and are inherent to all non-capillary crystal growth systems [56]. Thus, control of fluid flow in these systems is one of the primary objectives in crystal growth.

One way to reduce or eliminate the interference of buoyancy-induced convection with segregation at the solidification front is to conduct crystal growth experiments in the reduced gravity environment of space. Early experiments on the Apollo-Soyuz Test Project showed that axial diffusion controlled growth could thus be achieved [1, 2]. However, radial segregation in the crystal was found to be larger, by as much as a factor of three, as compared to earth grown crystals. Subsequent analysis revealed that during diffusion-controlled growth the shape of the growth interface has an overriding influence on the radial compositional uniformity of the crystal [57]. Ex-
periments performed aboard the Skylab Mission [3] have shown that systems with either liquid or solid immiscibility such as AuGe, PbZnSb, and PbSnIn, could be produced in space with unique metallurgical features and improved electronic properties. Another area where the microgravity environment of space is beneficial is in crystal growth by vapor transport. Since mass transport rates are controlled by gravity-driven convection, space processing has resulted in crystals with notably improved properties [4]. More recent microgravity experiments with CdZnTe [5] have resulted in a reduction of etch pit densities from $5 \times 10^4 \, \text{cm}^{-2}$ to $5 \times 10^2 \, \text{cm}^{-2}$. These results suggest that space can provide an excellent environment for production of high quality semiconductor crystals. Commercial exploitation of space is costly and, thus, prohibits production on a commercial scale.

An alternate, less expensive, method to suppress convection during melt growth of semiconductors is through the use of magnetic fields. For nearly four decades, the usefulness of applied magnetic fields in crystal growth from the melt has been recognized. The fundamental basis for the interaction between magnetic fields and convection was first discussed in references [6]-[10]. The basic mechanism for the interaction of a magnetic field and a molten semiconductor involves the 'electrical currents' generated by the convective movement of charge carriers in the presence of a magnetic field. This flow (current) creates an opposing Lorentz force, thereby, damping the velocity of the melt flow. The application of magnetic fields during crystal growth was tested in 1966 by Utech and Flemings [11, 12]. They investigated the effects of a transverse, vertically oriented magnetic field on tellurium-doped antimonide grown in a horizontal furnace by directional solidification. Their experiments revealed that in the presence of a vertical magnetic field (1300 and 1750 gauss), turbulent natural convection and related temperature fluctuations in the melt are suppressed as is the associated fluctuation in the dopant concentration in the grown crystal. Independently, Chedzey and Hurle [13, 14] performed similar horizontal Bridgman growth experiments on indium antimonide with a transverse field, but applied it along a horizontal axis. This configuration, as well, was effective in eliminating the formation of dopant striations. Since these early experiments, the use of a magnetic field has been
applied to several crystal growth systems with various results.

1.1 Magnetic Czochralski Growth

Czochralski [15] in 1917 pioneered a technique of pulling single crystals from the melt in effort to determine the maximum speeds at which metals could be solidified. The technique includes a crucible which contains the material to be solidified. It is surrounded by a heater used to melt the material. Once the material is molten, a seed crystal attached to a pull rod is lowered into the melt. The thermal profile is then adjusted until a meniscus is supported by the end of the seed. The system is allowed to come to thermal equilibrium and the seed is slowly lifted and rotated with crystallization occurring on the end of the seed. For some materials the crucible containing the charge may be rotated in the opposite direction in order to modify the melt flow and temperature distribution in the melt. The Czochralski technique has been modified over the years and one variation, the liquid encapsulated Czochralski (LEC) method [16], is particularly useful for the growth of III-V single crystals. In this process, boric oxide, $B_2O_3$, is used to cover the melt, and thus prevents the preferential evaporation of the group V elements. At present, LEC is the most productive industrial method for GaAs and GaP growth. A typical LEC crystal growth system with a vertical magnetic field is shown in figure 1-1.

In most cases, the buoyancy induced natural convection in the Czochralski system is turbulent due to unavoidable destabilizing temperature gradients present in the system. This turbulent flow produces temperature fluctuations which cause melting and resolidification at the growth interface and associated fluctuations in the dopant concentration in the grown crystal (i.e., striations). These turbulent flows, in most instances, are strong enough to effect the boundary layer at the crystal-melt interface, resulting in a non-uniform radial solute distribution. Segregation inhomogeneities constitute significant property degradation and adversely affect the yield and performance of a multitude of devices.

Another problem with the Czochralski method is the incorporation of impurities
such as oxygen and carbon. For example, during the Czochralski growth of silicon crystals oxygen enters the melt as the SiO$_2$ crucible is slowly dissolved by the molten semiconductor. As the diffusion coefficient for oxygen in molten silicon is very small, the transport of this oxygen from the ampoule wall to the crystal is highly dependent on the fluid flow patterns and melt velocity.

Extremely demanding requirements on oxygen level and dopant distribution have led to the use of a magnetic field to control the fluid flow in Czochralski systems. To this end, magnetic Czochralski crystal growth experiments have been conducted with transverse, axial and cusped field orientations. An excellent review paper by Series and Hurle [18], gives a detailed explanation of both the experimental theoretical aspects magnetic Czochralski crystal growth.
1.1.1 Czochralski Growth with a Transverse Field

The first reported experimental results of Czochralski crystal growth in a transverse magnetic field were given by Witt, Herman and Gatos [19]. They grew a $Te-InSb$ crystal in a 4 $kG$ magnetic field and found that the magnetic field decreased convection significantly, so that inherent irregularities in horizontal thermal gradients were preserved during rotation. This lead to more pronounced rotational striations in the crystal. A schematic diagram of the Czochralski crystal growth system used by Witt et al is shown in figure 1-2. Similar results have been observed by Ravishankar et al [20] for the case of silicon.

As mentioned previously, the incorporation of impurities is highly dependent on the pattern of fluid flow in the melt. Therefore, the application of a transverse magnetic field which removes the axial symmetry of the natural convective flow in Czochralski growth should significantly affect impurity incorporation. Results reported by Suzuki et al [22] suggest that the transverse field was effective in reducing the oxygen concentration in Czochralski grown silicon. Terashima et al [21] showed that the residual impurities, silicon and boron, from a PBN or $SiO_2$ crucible were reduced by orders of magnitude in LEC GaAs crystals grown in a transverse mag-
netic field. These observations of reduced impurity incorporation stimulated a broad interest in the application of magnetic fields to Czochralski crystal growth.

1.1.2 Czochralski Growth with an Axial Field

The effects of axial magnetic fields on Czochralski growth of silicon were investigated by Hoshikawa [23]. He was able to obtain crystals that were striation free and stated that the primary advantages of an axial field were: a strong homogeneous magnetic field could be obtained with a relative small solenoid; no modifications were necessary in the conventional Czochralski heater to withstand the large forces associated with strong magnetic fields; the axial symmetry characteristic of Czochralski growth was maintained. The primary disadvantage noted was that of poor radial dopant distribution.

Osaka et al [24] studied the effect of a vertical magnetic field on both LEC GaAs melt temperature distribution and homogeneity. They found that the melt flow fluctuations that caused irregular striations could be easily eliminated. However, residual laminar thermal convection was still present in the melt which degraded the radial homogeneity of the crystals. Similar effects were observed in the vertical magnetic growth of Te-doped LEC GaAs by Carlson and Witt [25]. Osaka and colleagues [24] continued their study and discovered that striation-free crystals having a doped Se concentration variation of less than 2.5 percent across the wafer could be obtained by optimizing the seed rotation rate in the presence of the vertical magnetic field.

In their review paper, Series and Hurle [18] and Cartwright et al [26] investigated the effect of crystal rotation on radial homogeneity during the vertical magnetic Czochralski growth of semiconductors. They showed that the magnetic damping of convection allowed for the diffusion boundary layer to approach the 'magnetic' momentum boundary layer. This resulted in significant radial compositional variations in the crystals. Increasing crystal rotation rate enhanced convection near the crystal interface and resulted in improved radial segregation. A plot of crystal rotation required for uniform silicon growth for a given vertical magnetic field is shown in figure 1-3. It is of interest to note that the crystal rotation rates required for radial unifor-
Figure 1-3: Plot of crystal rotation rate versus magnetic field strength illustrating the region of parameter space for which radial uniformity of dopant concentration in silicon is obtained [18].

Morty quickly become impractical. For example, to achieve acceptable uniformity in silicon with a 2 kG field would require rotation rates in excess of 700 rpm.

1.1.3 Czochralski Growth with a Cusped Field

The application of both axial and transverse fields both effective in damping turbulent convection in the melt. However, an axial field degrades the radial homogeneity which is a feature of conventional Czochralski growth and the transverse field causes thermal asymmetry and introduces significant rotational striations. Clearly, the best option would be to capitalize on the effects of both fields simultaneously. Namely, create a purely transverse field near the crystal-melt interface and in the bulk melt create a field that is purely axial. This way the rotational symmetry of the system would remain and near the melt interface there would be no axial field to destroy the radial uniformity.

It was shown independently by Series [27] and Hirata et al [28] that this type of field could be configured by the use of a pair of axially mounted Helmholtz coils. A schematic of the system is shown in figure 1-4. Series [27] and Hirata [28] indicate
that low oxygen concentration and uniform radial segregation can be obtained with this method in silicon.

Summary

The above experiments have shown that the primary result of the magnetic field is the damping of the convective melt flows from the turbulent to the laminar regime. If the field orientation and crystal rotation rates are judiciously chosen, this can lead to improved homogeneity and reduced impurity incorporation in the grown crystals. Consistent with this result, it has been reported that on the application of magnetic fields [24, 26], the effective segregation coefficients of the dopants approach the value of one. Theoretical investigations, see for example [29], on the interactions of the fluid flow present during Czochralski growth, for the most part, are phenomenological in nature. This is due to the non-availability of important thermophysical properties and the lack of quantifiable boundary conditions associated with Czochralski growth. Without quantifiable conditions it is impossible to predict \textit{a priori} whether field strength, crystal and crucible rotation, boundary layer thickness or other parameters
are the primary influence on segregation.

With advancements in analytical techniques with adequate sensitivity and resolution we may, one day, be able to accurately model the magnetic Czochralski process. In the mean time, it would be advantageous to have a crystal growth system with quantifiable boundary conditions that could be used in a combined experimental and theoretical study to quantify the effect of a magnetic field on segregation. One such system is the Bridgman-Stockbarger directional solidification system.

1.2 Magnetic Bridgman-Stockbarger Growth

The work by Bridgman dealt with the growth of single crystals of pure metals which were critical for his studies of thermophysical properties of materials. In a paper published in 1925, Bridgman [30] described his method of growing large single crystals. The basic method is that of slow solidification from the melt. A vertically mounted tubular furnace was used to melt the charge contained in a pyrex ampoule. The charge was directionally solidified by slowly lowering the ampoule through the bottom of the furnace into the laboratory environment or a cooling bath of oil. Bridgman also described in detail a method of cleaning the starting material and of necking the ampoule in order to ensure formation of only one grain. Figure 1-5 is a schematic of a vertical Bridgman furnace.

A similar method of directional solidification was undertaken by Stockbarger for crystallization of lithium fluoride [31]. Stockbarger realized that control of the thermal gradient significantly beyond that commonly employed was necessary in order to improve the crystalline material. The gradient was obtained by modifying the Bridgman technique. The changes consisted of using two vertical furnaces separated by a platinum baffle having a hole just large enough for the crucible to pass through. Melting of the lithium fluoride was accomplished in the upper furnace. The lower furnace was continuously controlled to enable solidification to occur in the high gradient region between the furnaces as the crucible was lowered. This two furnace arrangement is commonly referred to as the vertical Bridgman-Stockbarger directional solidification
Figure 1-5: Schematic representation of a vertical Bridgman furnace.

The Bridgman-Stockbarger technique has been modified over the years to permit directional solidification of a wide range of metal and semiconductor materials. There are two primary modifications worth noting. First is the modification by Chalmers and colleagues. They used a horizontal Bridgman system to study the crystallization of low melting point metals. This work led to a quantitative understanding of how solute buildup near a solidifying planar interface could lead to instability of the plane front. Chalmers and colleagues termed this phenomena constitutional supercooling [37]. Second, is the modification suggested by Chang and Wilcox [32]. They indicated the replacement of the platinum baffle with a layer of insulation as one way of decreasing the dependence of the growth interface morphology on thermal conditions and perturbations in the system. Subsequent modeling by Fu and Wilcox [33, 34] showed that the effect of the insulation zone was to force the heat transfer to be nearly axial over a much larger distance. This reduced the radial thermal gradient in the vicinity of the crystal-melt interface with a corresponding reduction in natural convection. This configuration is known as a modified Bridgman-Stockbarger furnace.
depicted schematically in figure 1-6.

As Bridgman-Stockbarger furnaces are relatively easy to construct and integrate with magnetic fields as compared to Czochralski systems, they are the preferred system to use in a combined experimental and theoretical study to quantify the effect of a magnetic fields on segregation.

1.2.1 Horizontal Bridgman

As previously mentioned, the original horizontal magnetic Bridgman crystal growth experiments were independently performed by Utech and Flemmings [11, 12] and Chedzey and Hurle [13, 14]. They studied transverse magnetic field effects on
indium antimonide. Results indicated that in the presence of a magnetic field, the turbulent convection was suppressed. This eliminated temperature fluctuations in the system and the associated dopant striations.

Hurle and Hunt [35] studied the rod eutectic system of indium antimonide-nickel antimonide. In conventional horizontal growth of this eutectic, turbulence in the melt produces a banded form where the rods are terminated by temperature fluctuations. Upon the application of a transverse magnetic field, banding was eliminated and long rods in a uniform eutectic microstructure were obtained.

A systematic comprehensive study of the effects of magnetic fields on horizontal Bridgman crystal growth was conducted by Alboussiere [36]. He extended the asymptotic magneto hydrodynamic theory to cover thermogravitational forces and solutions are derived for velocity fields in crystal growth configurations. A coupled experimental and numerical investigation was conducted on the axial magnetic effects on segregation. Results indicated that the magnetic damping of the flow was dependent on the growth rate and thermal gradients.

### 1.2.2 Vertical Bridgman

Su, Lehoczky and Szofran [85] were the first to apply transverse magnetic fields to the mercury based II-VI semiconductors $HgCdTe$ and $HgZnTe$. Magnetic field effects were shown to be significant over the field range of 2-5 $kG$. Axial compositional profiles showed an abrupt decrease in the mole fraction of $CdTe$ upon application of the field. Radial compositional mapping revealed that the crystal-melt interface evolves through three stages, i.e., from a radially symmetric to an off-center concave shape when the field was initially applied, then to a tilted plane, and, finally, to an off-center concave interface. This suggests the main influence of the transverse magnetic field was to destroy the axisymmetric fluid flow in system.

Becla et al [39] grew $HgMnTe$ crystals by the vertical Bridgman method with a vertical magnetic field of 30 $kG$. Reduction of convective intensity was found to decrease radial segregation and eliminate small-scale compositional variations in the grown material. These results were consistent with a model by Han et al [40] for the
residual convection present during growth of $HgMnTe$.

Matthiesen [41] investigated the effects of a 1.8 and 30 $kG$ axial and a 3 $kG$ transverse magnetic field on $Ga$-doped Germanium. He used current pulsing to mark the crystal-melt interface shape and to measure the growth rate. The current pulsing for interface demarcation in the presence of an applied magnetic field was determined to have a pronounced effect on the segregation behavior during growth and was not used in most crystals. Also, there were inherent thermal asymmetries in his growth system which caused slightly asymmetric concave (into the solid) interfaces. Nevertheless, he was able to determine that the 1.8 $kG$ axial field did not have an effect on interface shape. The 3 $kG$ transverse field did, however, change the interface shape. The asymmetry parameter tripled with the application of the magnetic field. For both field strengths, the axial concentration profile indicated that growth was essentially the same as growth with no magnetic field (i.e., complete mixing occurred). Application of the 30 $kG$ axial magnetic field resulted in an axial solute distribution, for 2.5 cm out of 9.0 cm of growth, that was characteristic of that in diffusion-controlled growth, showing that the field effectively suppressed convective interference with segregation during the initial portion of growth.

1.3 Magnetic Float Zone Growth

For growth of single crystals, it is not always necessary to melt the entire charge. In some cases it is advantageous to melt only a portion of the charge and move this molten zone through the charge. This technique was first introduced by Pfann [42] who used the technique to refine or purify materials. Zone melting can occur with or without a crucible. Zone melting without a crucible is known as float zone crystal growth.

The effect of transverse and axial fields on the float zone processing of $Ga$-doped silicon single crystals has been investigated [43]. Transverse fields of 5.5 $kG$ had a large effect on the shape of the crystal-melt interface and pronounced periodic dopant striations were found in the as grown crystal. The axial field made control of
the crystal shape difficult and improved uniformity was only observed in the center of the crystal.

1.4 Summary of Magnetic Crystal Growth Results

A large amount of magnetic crystal growth work has been carried out over the years. However, the majority of the experimental work has been focused on the growth of GaAs, Si and Ge by the Czochralski growth process. In these experiments small (2-5 kG) fields were applied both transverse and axially to the melt. Both orientations were effective in suppressing turbulent convection. However, both orientations have undesirable effects on segregation: the transverse field destroyed the thermal symmetry of the system and led to increased rotational striations while the axial field degraded the radial segregation. A cusped field was developed which capitalized on the positive effects of both fields simultaneously. Growth of silicon with this field orientation indicated that low oxygen concentration and uniform radial segregation could be obtained.

The first magnetic field studies with horizontal Bridgman crystal growth [11]-[14]. indicated that a small (~ 1-2 kG) transverse field suppressed turbulent convection and associated temperature fluctuations which reduced the striations in the material. Transverse magnetic field effects in vertical Bridgman growth caused asymmetric crystal-melt interfaces in GaGe [41] and in HgCdTe [85]. However, the application of an axial magnetic field of 30 kG during growth of GaGe resulted in an axial solute distribution that was characteristic for diffusion controlled growth [41]. This result, coupled with the development of detailed scaling laws by Motakef [44] for elimination of convective interference with segregation by magnetic fields, has led to a wide spread interest in theoretical and experimental work in magnetic stabilized crystal growth.
1.5 Present Work

1.5.1 Objectives of this Research

This thesis focuses on the influence of an applied axial magnetic field on melt growth of the semiconductor $Hg_{1-x}Cd_xTe$. The primary goal is to assess the effectiveness of magnetic fields in reducing thermo-solutal convective flows that occurs in these pseudo-binary systems during melt growth. This thermo-solutal convection, also referred to as double diffusive convection, interferes with the mass boundary layer near the crystal-melt interface resulting in non-uniform radial segregation.

Experimental data on magnetic effects during growth of this compound is limited. No conclusive evidence exists on the magnitude of magnetic fields required to suppress convective interference with segregation. This research is intended to provide a substantial data base on the effects of magnetic fields in pseudo-binary systems which is relevant for previous terrestrial and microgravity studies. The results are expected to be used for testing the validity of magneto hydrodynamic modeling predictions on the effectiveness of the magnetic field for suppressing convective flows.

1.5.2 Approach of this Research

The crystal growth system utilized in these experiments was a modified vertical Bridgman-Stockbarger furnace coaxially aligned with a superconducting magnet capable of producing axial magnetic fields up to 50 kG. The furnace was designed to provide a thermal environment similar to that used in previous experiments for growth of $Hg_{0.8}Cd_{0.2}Te$. The ampoule and cartridge assembly design, as well, was based on furnace geometry of past experiments. The facility is capable of growing crystals in ampoules up to 2 cm in diameter by 20 cm long.

Four series of experiments were performed in this study. The first series of experiments was conducted with crystal growth parameters similar to those used by Lehoczky et al [64] during microgravity growth of $Hg_{0.8}Cd_{0.2}Te$. They were con-
ducted without the application of magnetic fields. The experiments were used primarily to characterize the growth system and to verify that it was producing similar results as those presented in the literature, see for example [64], [66], [70] and [91]. The second series of experiments was conducted with varying applied magnetic fields but maintaining all other parameters constant. The third set of experiments was performed at various growth rates and with the same applied magnetic fields as used in the second series of experiments. Again, all other parameters were held constant. The final set of experiments involved marking the crystal-melt interface at various field strengths. In all growth experiments with applied magnetic fields, the field was turned on prior to growth and held constant throughout the experiment.

Radial and axial segregation variations were determined from samples cut perpendicular to the growth direction and interface morphology studies were conducted on slabs cut from the center of the crystal parallel with the growth direction as shown in figure 4-1. All samples were mechanically lapped and chemically polished prior to analysis. Average axial macrodistribution of cadmium telluride was determined from density measurements. Radial microdistribution of cadmium telluride was quantitatively determined from the transmission edge of the IR transmission spectrum and by energy dispersive X-ray spectroscopy (EDS) using pseudo-binary solid solutions as standards. Details of sample preparation and characterization techniques are described in Chapter 4. The axial and radial segregation measurements were used to determine the relative effectiveness of an axial magnetic field in suppressing the convective interference with segregation.

### 1.5.3 Structure of this Thesis

The basic effect of the magnetic field is damping of convection in the melt which is known to interfere with segregation. This topic is discussed in detail in Chapter 2 with emphasis given on the pseudo-binary semiconductor systems. The experimental setup, such as the crystal growth system, ampoule design, cartridge design and superconducting magnet are addressed in Chapter 3. Chapter 4 describes the characterization techniques used to determine segregation in the resolidified crystals.
Segregation results in the absence of magnetic melt stabilization are discussed in Chapter 5. Segregation results in the presence of magnetic melt stabilization and related discussions are given in Chapter 6. Conclusions of the present work and recommendations for further study are given in Chapter 7.
Chapter 2

Convection and Segregation
During Crystal Growth

This chapter is divided into three sections. The first section is an introduction to the transport equations for crystal growth from the melt to be used in a scaling analysis to familiarize the reader with the important parameters which govern convection, heat and mass transfer in crystal growth systems. The second section will discuss segregation theory including the influence of convection on segregation. Special attention will be paid to growth system parameters that can be manipulated in order to decrease convective effects on segregation. The last section discusses convection and segregation as related to the alloy $Hg_{1-x}Cd_xTe$.

2.1 Transport Equations for Crystal Growth

In all non-capillary solidification processes, the melted region undergoes buoyancy induced convection during solidification. The equation which determines the intensity of convection is the Navier-Stokes (N-S) or momentum equation,

$$\rho \frac{D\vec{V}}{Dt} = -\nabla P + \mu \nabla^2 \vec{V} + \rho \vec{G}. \quad (2.1)$$
<table>
<thead>
<tr>
<th>Term</th>
<th>Meaning</th>
<th>Order of Magnitude Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho \frac{\partial V_x}{\partial t}$</td>
<td>Temporal Force</td>
<td>$F_{\text{temporal}} \approx \frac{\partial V^2}{t}$</td>
</tr>
<tr>
<td>$\rho V_x \frac{\partial V_x}{\partial x}$</td>
<td>Inertial Force</td>
<td>$F_{\text{inertial}} \approx \frac{\partial V^2}{t}$</td>
</tr>
<tr>
<td>$\frac{\partial P}{\partial x}$</td>
<td>Pressure Force</td>
<td>$F_{\text{pressure}} \approx \frac{\partial V^2}{t}$</td>
</tr>
<tr>
<td>$\mu \frac{\partial^2 V_x}{\partial x^2}$</td>
<td>Viscous Force</td>
<td>$F_{\text{viscous}} \approx \frac{\partial V^2}{t}$</td>
</tr>
<tr>
<td>$\rho g \beta_t (T - T_{\text{inf}})$</td>
<td>Thermal Buoyancy Force</td>
<td>$F_{\text{buoyancy}_t} \approx \rho g \beta_t \Delta T$</td>
</tr>
<tr>
<td>$\rho g \beta_s (C - C_{\text{inf}})$</td>
<td>Solutal Buoyancy Force</td>
<td>$F_{\text{buoyancy}_s} \approx \rho g \beta_s \Delta C$</td>
</tr>
</tbody>
</table>

Table 2.1: The meanings and relative magnitude of the terms in the Navier-Stokes equation.

Expanding equation 2.1 in the $x$ direction with the Boussinesq approximation for the density dependence on temperature and solute concentration yields,

$$
\rho \left[ \frac{\partial V_x}{\partial t} + V_x \frac{\partial V_x}{\partial x} + V_y \frac{\partial V_x}{\partial y} \right] = -\frac{\partial P}{\partial x} + \mu \left[ \frac{\partial^2 V_x}{\partial x^2} + \frac{\partial^2 V_x}{\partial y^2} \right] \rho g \beta_t (\Delta T) + \rho g \beta_s (\Delta C) \tag{2.2}
$$

where $\rho$ is the fluid density, $\mu$ is the fluid viscosity, $g$ is the acceleration due to gravity, $\beta_t$ is the thermal expansion coefficient, $\beta_s$ is the solutal expansion coefficient, $\Delta T$ is the driving temperature difference and $\Delta C$ is the driving solutal difference. This equation is nothing more than Newton's first law:

$$
M \frac{D \vec{V}}{Dt} = \sum \vec{F} \tag{2.3}
$$

i.e., the summation of forces is equal to the product of an object's mass, $M$, and acceleration, $\frac{D \vec{V}}{Dt}$, derived for an elemental fluid volume. Therefore, every term in the N-S equation is merely a force. The meanings, as well as the relative magnitude of these terms, are important for the basic understanding of fluid flow phenomena and are listed in Table 2.1.

The driving temperature difference, $\Delta T$, in the thermal buoyant force is deter-
mined by the energy equation:

\[ \rho C_p \frac{D T}{D t} = K \nabla^2 T \]  

(2.4)

where \( \rho \) is the density, \( C_p \) is the specific heat at constant pressure and \( K \) is the thermal conductivity. Similarly, the driving solutal difference, \( \Delta C \), in the solutal force is determined by the species equation:

\[ \frac{D C}{D t} = D_t \nabla^2 C \]  

(2.5)

where \( D_t \) is the solutal diffusivity.

Equations 2.1, 2.4 and 2.5 are coupled to each other and must be solved simultaneously to determine the level of convection in a given system. However, we will see later that there are limiting cases where the equations may be decoupled.

During crystal growth, the severity of convection is governed by the ratio of the thermal and solutal buoyant forces to the viscous forces. The ratio of these forces is given by a dimensionless parameter known as the Grashof number, \( Gr \),

\[ Gr_t = \frac{g \beta_t \Delta T L^3}{\nu^2} \quad \text{and} \quad Gr_s = \frac{g \beta_s \Delta C L^3}{\nu^2} \]  

(2.6)

where \( L^3 \) is the characteristic length scale of the system and \( \nu \) is the kinematic viscosity. The subscripts, \( t \) and \( s \), denote thermal and solutal respectively.

The thermal force is due to density differences arising from unavoidable radial temperature gradients in the melt which promote convection. Solutal forces are due to density differences due to the rejection of solute during solidification. In dilute alloys the solute rejection has little influence on density and the \( Gr_s \) is small compared to the \( Gr_t \). However, in non-dilute alloys such as \( Hg_{1-x}Cd_xTe \) this solutal force is significant and can not be neglected. This phenomena will be discussed in the next section. However, it is of importance to note that the solutal force may enhance or suppress convection depending on the sign of the solutal expansion coefficient, \( \beta_s \).

For small values of the Grashof number, the viscous forces are large enough to
suppress convection and the fluid is stable. At some critical value of the Grashof number, the buoyant forces exceed the viscous forces and laminar convection occurs. As the Grashof number increases there are other critical transitions from laminar to oscillatory and finally to turbulent flow.

Other Important Non-dimensional Parameters

In laminar convective flow the relative magnitude of the thermal ($\delta_t$), momentum ($\delta_{mom}$) and mass ($\delta_s$) boundary layers are important. The Prandtl number, $Pr$, is the ratio of the kinematic viscosity to the thermal diffusivity and a comparison of the momentum and thermal boundary layer thickness,

\[
Pr = \frac{\nu}{\alpha} = \frac{\delta_{mom}}{\delta_t}.
\]  

(2.7)

Similarly, the Schmidt number, $Sc$, the ratio of the kinematic viscosity to the solutal diffusivity, is an indication of the magnitude of the momentum boundary layer and the mass boundary layer

\[
Sc = \frac{\nu}{D} = \frac{\delta_{mom}}{\delta_s}.
\]  

(2.8)

For most semiconductors, $Pr << 1$ and $Sc >> 1$, which means that $\delta_s < \delta_{mom} < \delta_t$. This indicates convective effects on segregation but little or no convective effect on heat transfer.

Two other important parameters are the thermal and solutal Peclet number, $Pe_t$ and $Pe_s$, respectively. The $Pe_t$ is obtained by comparing the convective heat transfer term with the conduction heat transfer term in the energy equation and is given by:

\[
Pe_t = \frac{UL}{\nu}
\]  

(2.9)

where $U$ is the characteristic velocity. For $Pe_t << 1$, convective heat transfer is small compared to conductive heat transfer and the system is known as diffusion limited.

By analogy, the solutal Peclet number, $Pe_s$, is the ratio of the convective mass
transfer to the conductive or diffusive mass transfer and is given by:

\[ Pe_s = \frac{UL}{D_l} \]  

(2.10)

where \( D_l \) is the solutal diffusivity. The system is mass diffusion limited when \( Pe_s \ll 1 \).

The above mentioned parameters are only a few of the dimensionless groups appearing as a result of the scaling of the transport equations. A more complete listing is given in appendix C.

### 2.2 Segregation Theory

The term segregation refers to the redistribution of constituents in the melt during solidification. Therefore, segregation is one of the primary factors controlling the yield of crystals obtained by growth from the melt. This section reviews the basic physics of segregation and highlights some of the theoretical techniques useful in predicting segregation behavior. Most notable texts covering this topic are the works of Flemings [46], Muller [47] and Garandet et al [48].

#### 2.2.1 Conservation of Species

Segregation during solidification is controlled by the alloy's equilibrium phase diagram, see figure 2-1. The condition of equilibrium at the crystal-melt interface requires that the liquid composition, \( C_l \), and the solid composition, \( C_s \), at the interface be fixed by the phase diagram. The ratio of \( C_s \) to \( C_l \) is assumed to be identical with the equilibrium partition coefficient, \( k \):

\[ k = \frac{C_s}{C_l} \]  

(2.11)

The uniformity of incorporation of the solute into the solid and its distribution in the melt is controlled by the Navier-Stokes, energy and species continuity equations
Figure 2-1: (a) Schematic phase diagram for a binary or pseudo-binary alloy, $C_0$, $k < 1$; (b) corresponding compositional profile across the crystal-melt growth interface; (c) axial profile of solidified ingot; (d), (e) and (f) corresponding cases for $k > 1$ (after Flemings [46]).
discussed in section 2.1. In this section, it was stated that these transport equations are highly coupled. However, in the limiting case with idealized assumptions these equations may be decoupled and analytical solutions may be derived. The assumptions unless otherwise stated are as follows:

Dilute Alloy Approximation: An alloy is considered dilute if the mixture is formed with traces of species in a melt consisting of a nearly pure constituent. It is further assumed that the total mass density of the solution is independent of composition. In cases where this assumption is valid, the momentum and species continuity equations may be decoupled which greatly simplifies the problem. The other assumptions are: the crystal-melt interface is planar (i.e., the following analysis is good only for axial segregation); solid state diffusion is neglected and the equilibrium segregation coefficient, \( k \), and growth rate, \( R \), are constant. It should be noted that these approximations are not strictly valid for the pseudo-binary alloy, \( HgCdTe \). Nevertheless, this section is necessary to familiarize the reader with the current limitations of solidification theory.

Complete Mixing

The equations describing the solute distribution during the limiting case of complete mixing can be derived by performing a mass balance on a 'pill box' across the crystal-melt interface. By equating the solute rejected when a small amount of solid forms with the resulting solute increase in the liquid one obtains:

\[
C_s = kC_0(1 - f_s)(k-1)
\]  

(2.12)

where the solid concentration, segregation coefficient, initial solute concentration and fraction solidified are given by \( C_s, k, C_0, f_s \) respectively. Many investigators have derived this equation. The most notable of whom are Scheil [52] and Pfann [53]. Equation 2.12 is commonly known as Pfann’s equation for complete mixing.
Diffusion Limited, No Convection

Using the above assumptions along with the limiting case of no convective mixing in the melt equation 2.5, at steady state, reduces to:

$$D_l \frac{\partial^2 C_l}{\partial z'^2} + R \frac{\partial C_l}{\partial z'} = 0 \quad (2.13)$$

where $D_l$ is the solutal diffusion coefficient, $R$ is the solidification velocity and $z'$ is the location in the liquid as measured from the crystal-melt interface. This equation was solved by Tiller et al [49] using the boundary conditions of solute conservation at the interface:

$$\left( \frac{\partial C_l}{\partial z'} \right)_{z' = 0} = -\frac{R}{D_l} C_l(1 - k) \quad (2.14)$$

and the conditions that $C_l = \frac{C_0}{k}$ at $z' = 0$, and $C_l = C_0$ at $z' = \infty$. The solution is

$$C_l(z') = C_0 \left[ 1 + \frac{1 - k}{k} \exp \left( \frac{-kC_0}{D_l} \right) \right]. \quad (2.15)$$

From equation 2.15, Tiller and colleagues calculated the form of the transient solid distribution up to the equilibrium level by assuming that the curve of the solute concentration in the solid at the beginning of the ingot must satisfy the following conditions: it must change from $kC_0$ at the beginning of the crystal; it must tend asymptotically to $C_0$ with distance along the crystal and it must change continuously from $kC_0$ to $C_0$. Using these conditions with the further assumption of conservation of the solute, the equation for the composition of the transient solid distribution was determined to be:

$$C_s(z) = C_0 \left[ 1 - (1 - k) \exp \left( \frac{-kC_0}{D_l} \right) \right] \quad (2.16)$$

where $z$ is the distance of the solidified ingot as measured from the first to freeze end. A similar derivation yielded the liquid composition as measured away from the interface during the initial transient as:

$$C_l(z', t) = C_0 \left\{ \left( \frac{1 - k}{k} \right) \left[ 1 - \exp \left( \frac{-kC_0}{D_l} \right) \right] \exp \left( \frac{-kC_0}{D_l} (z' - R_t) \right) + 1 \right\} \quad (2.17)$$
where \( t \) represents time. Due to the imposed constraints employed by Tiller et al equations 2.16 and 2.17 are only valid for the limit \( k \to 0 \) (i.e., \( k \ll 1 \)).

To relax the constraint on the segregation coefficient Pohl [50] solved the transient form of equation 2.5 for the composition of the solid and corresponding distribution of solute in the liquid. In the limit that

\[
\frac{1 - 2k}{1 - k} \sim 1
\]

the transient composition in the solid is

\[
C_s(z) = C_0 \left[ 1 - (1 - k) \exp^{-(1-k)\frac{kR_s}{D_t}} \right]
\]

and the corresponding time dependent spatial distribution of solute in the liquid is

\[
C_l(z', t) = C_0 \left\{ 1 + \frac{(1 - k)}{k} \left[ \exp^{-\frac{R_s'}{D_t}} - \exp^{-(1-k)\frac{R_s'}{D_t}} \exp^{-(1-k)\frac{kR_s^2}{D_t}} \right] \right\}
\]

In the limit \( k \to 0 \) equation 2.19 reduces to equation 2.16.

Later, Smith et al [51] derived the rigorous solution (valid for all \( k \)) for the initial and final transient cases. The solutions are rather cumbersome, however. In the limit \( k \to 0 \) their equation reduces to equation 2.16. These results showed that the characteristic distance of the initial transient was dependent on \( \frac{D_l}{rk} \) for \( k < 1 \). The final transient length was shown to be the result of the impingement of the solute diffusion layer on the end of the crucible given by \( \frac{D_l}{R} \).

Convective Effects

So far we have considered the two limiting cases of limited liquid diffusion with no convection and complete mixing. No discussion on segregation theory would be complete without considering the case of partial mixing. This topic was first investigated by Burton, Prim and Slichter [54], hereafter referred to as BPS. They performed a theoretical investigation on the incorporation of the solute in single crystals of germanium grown by the Czochralski process. The effects of diffusion and convection
were included in their model by defining a diffusion boundary layer of thickness, $\delta$. Inside this boundary layer mass transport was by diffusion only and outside the liquid composition was assumed to be kept uniform by convection. This 'stagnant film model' was used in conjunction with equation 2.13 to derive an effective segregation coefficient, $k_{\text{eff}}$

$$k_{\text{eff}} = \frac{k}{k + (1 - k) \exp\left(-\frac{\delta}{L}\right)}$$  \hspace{1cm} (2.21)

Recently, it has been stated by Garandet [48] and Wilson [55] that the somewhat arbitrary quantity, $\delta$, is not based on adequate physical reasoning. They suggest alternate definitions for the diffusion boundary layer thickness that are more intuitive. Nevertheless, the BPS theory has been shown to be applicable to many crystal growth systems as long as the thickness of the boundary layer, $\delta$, is small compared with the length of the crucible.

**Radial Segregation, No Convection**

When the assumption of a planar crystal-melt interface is relaxed and the dilute alloy approximation is not valid (i.e., for $\text{HgCdTe}$), the problem becomes quite complicated and must be solved using numerical techniques, see for example [56]. There is, however, one exception that is of interest to note: the case where there is no convection in the melt. Coriell and Sekerka [57, 58] developed analytical and numerical methods to relate the interface curvature and radial segregation in the melt by solving the steady state species continuity equation. Their work revealed, that in the limiting case, the radial segregation in the solid was proportional to the deviation of the interface from planarity, the proportionally factor being just the product of the unperturbed concentration gradient and the distribution coefficient. This analysis shows, that in the limit of no convection in the melt, the interface morphology has primary influence on segregation.
2.2.2 Methods to Reduce Segregation

It has been shown that convective interference with segregation can lead to non-uniform distribution of constituents into the grown crystal. This directly effects the yield and, thus, cost of the grown material. In order to control convection and segregation in the material, the growth system parameters such as charge size, temperature gradients and acceleration due to gravity must be modified, through, for example, growing small diameter crystals, processing in space or under the influence of applied magnetic fields.

Reduction of Charge Diameter

Recall, the severity of convection in crystal growth from the melt is controlled by the Grashof number shown in equation 2.6 which has a cubic dependence on the crystal radius, $r_{rc}$. Therefore, the radius is one parameter to change in order to reduce convection. To this end, experiments were performed with various charge diameters during vertical Bridgman growth of Ga-doped Ge [59]. Results showed that the crystal diameter had to be reduced to capillary size to avoid convection in the melt. Obviously, capillary sized crystals are of no value to the electronic industry. They have, however, been found useful for important studies of the semiconductor's thermophysical properties.

Reduction of Gravity

Another parameter which can be used to control convection is the acceleration due to gravity, $g$. Experiments [1]-[5] performed in the reduced gravity environment of space have shown that diffusion limited growth can be obtained. The real advantage of processing in microgravity is that it provides the opportunity to grow larger diameter crystals in the diffusion limited regime than is possible on earth. This can be readily shown through scaling analysis by considering the magnitude of fluid velocity to the thermal driving force. This relationship is shown in figure 2-2 as the Reynolds number,
Figure 2-2: Plot of (a) \( \text{Re} \) vs. \( Gr_t \); (b) \( Pe_t \) vs. \( Gr_t \); (c) \( Pe_s \) vs. \( Gr_t \) for a typical semiconductor material.

\[
\text{Re},
\]

\[
\text{Re} = \frac{V_{\text{rc}}}{\nu} \quad (2.22)
\]

versus the Grashof number, \( Gr_t \). Multiplying \( \text{Re} \) with the Prandtl number, \( Pr \), for the first case, and the Schmidt number, \( Sc \), for the second case, yields plots similar to figure 2-2 where \( (\text{RePr}) = Pe_t \) and \( (\text{ReSc}) = Pe_s \). Noting that

\[
\frac{Pe_t}{Pe_s} = \frac{D}{\alpha} = 10^{-3} \quad (2.23)
\]

for typical semiconductors, \( Re \) of 10 in figure 2-2 leads to a \( Pe_t \) of 0.1 and a \( Pe_s \) of 100 in figures 2-2b and 2-2c respectively.

These figures schematically show that diffusion limited heat transfer \((Pe_t < 1)\) can be obtained at high values of \( g \) (say on earth) and at the same \( g \)-level have convection dominated mass transfer \((Pe_s > 1)\). Therefore, to get diffusion limited mass transfer, the \( Gr_t \) (\( g \)-level) has to be reduced to very low levels such that \( Pe_s < 1 \), at which point \( Pe_t \) is very small (recall: the ratio of the two was \( 10^{-3} \)). It can be shown that
the functional dependence of $Pe_s$ on $Gr_t$ is

$$Pe_s = \frac{V_T \nu}{\nu D} \sim fcn\left(\frac{g\beta \Delta T r^3}{\alpha v^2}, Pr, Sc\right). \quad (2.24)$$

The quantities $\beta$, $\Delta T$, $\nu$, $\alpha$ are fixed for a given crystal growth system and $g$ is fixed on earth which leaves the crystal radius as the only adjustable parameter. However, in space one can lower $g$ easily by four to six orders of magnitude. Thus, from equation 2.24, with all other parameters constant

$$\frac{r_{space}}{r_{earth}} \sim \left(\frac{g_{space}}{g_{earth}}\right)^{-\frac{1}{3}} \sim (10)^{\frac{3}{4}} \sim 30 \quad (2.25)$$

i.e., space provides an excellent opportunity to increase the size of grown crystals.

**Application of Static Magnetic Fields**

The basic mechanism for the interaction of an applied magnetic field and a molten semiconductor involves the electrical currents induced by the movement of a 'conductor' in the presence of a magnetic field. When convection is present, flow of the electrically conductive fluid perpendicular to the field results in a Lorentz force which opposes that motion. To determine the effectiveness of the magnetic field on the suppression of convection it is necessary to solve Maxwell's equations and the fluid flow equations for the velocity and electromagnetic fields. A complete derivation of the MHD equations, given in [60, 61], basically results in the incorporation of the Lorentz force

$$\vec{F}_{Lorentz} = \sigma(\vec{E} + \vec{V} \times \vec{B}) \times \vec{B} \quad (2.26)$$

into the Navier-Stokes equation (equation. 2.1), neglecting the induced EMF, $\vec{E}$, has been shown to be acceptable in the limit of two-dimensional flow [62]. With this approximation equation 2.26 reduces to

$$\vec{F}_{Lorentz} = \sigma(\vec{V} \times \vec{B}) \times \vec{B} \quad (2.27)$$
where $\sigma$ is the electrical conductivity of the fluid, $\mathbf{V}$ is the fluid velocity vector and $\mathbf{B}$ determines the magnitude and orientation of the magnetic field. In many respects, damping of convection by magnetic fields is similar to an increase in the viscosity of the liquid. This has given rise to the term 'magnetic viscosity' which is analogous to the kinematic viscosity and is commonly denoted as

$$\nu_{magn} = \sigma \mu_0$$

(2.28)

where $\mu_0$ is the fluid permeability.

The non-dimensional parameter which determines the effectiveness of a magnetic field on suppression of convection is the Hartman number, $Ha$,

$$Ha = BL \left( \frac{\sigma}{\mu} \right)^{\frac{1}{2}}$$

(2.29)

which is the ratio of the Lorentz force to the viscous force. For typical semiconductors and medium to large field strengths, $Ha \sim 10^3$, indicating that the electrical currents are better at transporting energy over larger distances in the melt than the viscous forces. Using a similar scaling argument as that presented above and noting for most semiconductors,

$$\frac{\nu_{magn}}{\nu} \sim 10^6,$$

(2.30)

it can be shown that

$$\frac{r_{magn}}{r} \sim \left( \frac{\nu_{magn}}{\nu} \right)^{\frac{1}{3}} \sim 100.$$  

(2.31)

Thus, both processing in microgravity and with the application of a magnetic field provide the potential to increase the size of semiconductor materials.

### 2.3 Convection and Segregation in $Hg_{1-x}Cd_xTe$

The $Hg$ based II-VI semiconductor, $Hg_{1-x}Cd_xTe$, is important for application in infrared detection and imaging applications. Its band gap, $E_g$, varies linearly with
For HgCdTe: $K_m/K_s > 1$

Figure 2-3: "Crucible effects" which lead to radial temperature gradients during the solidification of a pseudo-binary alloy.

composition, $x$,

$$E_g = 1.9x - 0.3 \quad (2.32)$$

which allows it to be compositionally tuned for a broad range of wavelengths from 0.8 $\mu m$ to the far-infrared spectrum beyond 30 $\mu m$. Due to the high $Hg$ vapor pressure present during the processing of this material it must either be sealed in a thick silica ampoule or grown in a high pressure furnace. Growth in thick ampoules, as in this study, causes a large destabilizing horizontal temperature gradient to be generated due to a difference in the thermal conductivities of the melt and crystal and the release of latent heat at the growth interface in the presence of the silica ampoules as predicted by Jasinski and Witt [63], see figure 2-3. Additionally, a stabilizing vertical solutal gradient is produced by the rejection of the denser solute, $HgTe$, in to the melt. These phenomena, coupled with a large solutal-to-thermal expansion coefficient
(for $x = 0.2$)

$$\frac{\beta_2 C_0}{\beta_1 \Delta T} \sim 100$$

(2.33)

and a large thermal-to-solutal diffusion coefficient ratio

$$\frac{\alpha}{D_l} \sim 200,$$

(2.34)

give rise to double diffusive convection during melt growth. This buoyancy induced convection, when sufficient to cause $Pe > 1$, interferes with segregation near the crystal-melt interface resulting in a non-homogeneous crystal.

As $Hg_{1-x}Cd_xTe$ is a non-dilute alloy and the curvature of the crystal-melt interface is not planar, most of the segregation analysis developed in section 2.2 does not apply. Therefore, detailed Computational Fluid Dynamic modeling is required to determine the convective effects on segregation in this material.
Chapter 3

Magnetic Crystal Growth System

3.1 Preparation of Materials

3.1.1 Ampoule Fabrication

The ampoule geometry used in this study was identical to that used in the microgravity growth experiment of Lehoczky et al [64]. The ampoules were made from commercial grade, T08, fused silica. Thick walled, 8 mm I.D. × 12 mm O.D., ampoules were necessary for containment of the charge due to the high vapor pressure of Hg over the melt (~ 30 atm). All growth experiments were unseeded, however, a tapered section was formed on the ampoule to enhance the probability of single crystal growth. The ampoules were cut to the proper length as shown in figure 3-1 using a diamond saw and were washed with PEX laboratory glass cleaning soap followed by a triple rinse in de-ionized water. The ampoules were then cleaned with electronic grade methanol and etched for a minimum of one hour in an aqua regia solution. After rinsing with de-ionized water, the ampoules were re-etched in concentrated HF acid for 45 seconds. The final cleaning was a triple rinse in de-ionized water.

In order to remove volatile impurities in the fused silica like H₂, H₂O, CO, CO₂, N₂ and O₂, the quartz ampoules were outgassed and annealed at 900 °C under a 10⁻⁶ torr vacuum for 24 hours as described in [65]. To avoid ”wetting” of the ampoules by \( Hg_{1-x}Cd_xTe \), the ampoule I.D. was coated with graphite by flooding the ampoule
with a methane-argon mixture (9.51% CH\textsubscript{4} balance Ar). This was accomplished at the end of the annealing/outgassing process by purging the heated (900 °C) ampoule with the gas mixture at a flow rate of 20 sccs for 15 minutes. A positive pressure was kept on the ampoule at all times. Once graphitization was complete the ampoule was re-evacuated to 10\textsuperscript{-6} torr and removed from the annealing furnace where it was allowed to cool to room temperature. Once cooled, the ampoule was removed from the vacuum system and placed in a clean room where it was loaded with the charge material.

\section{3.1.2 Bulk Material Preparation}

The starting materials were triple-distilled instrument grade Hg from Bethlehem Apparatus and six nines grade Cd and Te from Johnson Matthey. The elements weighed for Hg\textsubscript{0.8}Cd\textsubscript{0.2}Te (Hg = 24.54 g, Cd = 3.43 g, Te = 19.47 g) with some extra Hg (∼ 1g) added to compensate for the high Hg pressure over the melts. Next, the constituents were loaded into the ampoule and sealed off under a 10\textsuperscript{-6} torr vacuum. Ingots were then formed utilizing a homogenization process described below.
3.1.3 Homogenization

The $Hg_{0.8}Cd_{0.2}Te$ ingots were compounded by a homogenization process that was developed by Su et al [66] in order to eliminate wetting and silicon contamination that occurs even in graphitized ampoules. Su and colleagues determined that wetting was due to reaction of $Cd$ with the silica ampoule. Their approach was to decrease $Cd$ activity in the sample in order to reduce the rate of reaction of $Cd$ and the silica wall. This was accomplished by first heating the sample to an intermediate temperature, low enough, so that the activity of pure $Cd$ was too low for reaction with silica. However, the temperature had to be high enough for the reaction between the elements $Hg$, $Cd$ and $Te$ to take place. It was shown that, once the $Cd$ was well reacted, subsequent heating to a temperature above the liquidus temperature would not cause any significant reaction of $Cd$ and silica. The intermediate temperature determined by Su et al [66] was 450-500 °C, which is higher than the melting points of all three elements and just above the temperature of the pseudo-binary reactions, which are 413 °C and 450 °C for $Hg$-$Te$ and $Cd$-$Te$, respectively.

This homogenization procedure was adapted for this work and involved heating the ampoule in a rocking furnace from room temperature to 450 °C in three hours. The ampoule was held at this temperature for 16 hours to allow for the elemental reactions to occur. Then the temperature was slowly raised over 8 hours to 850 °C which is about 55 °C above the liquidus temperature for $x = 0.2$ [91]. The ampoule was held at this temperature for 24 hours while the furnace was allowed to 'rock' through a 270° angle to ensure homogenization of the material and to proof test the ampoule. Casting of the sample was accomplished by lowering the ampoule out of the rocking furnace into the ambient environment. After casting the ampoule was shortened, filled with quartz wool and resealed under vacuum. This limited the amount of free volume during processing. The formed ingots were 14 cm long and weighed approximately 47 g.
3.2 Crystal Growth Apparatus

The ingots were regrown by directional solidification in a vertical Bridgman-Stockbarger furnace. The furnace consisted of: a hot zone where the sample was melted; a booster heater located between the hot zone and gradient zone and a 0.3 cm heat extraction plate placed between the gradient and cold zone. The booster heater and heat extraction plate were necessary to produce the high axial gradients (∼ 80°C/cm) necessary for this research. A guard heater was utilized on the end of the hot and cold zones to minimize any thermal losses out the end of the furnace. The furnace surface was maintained at 20 °C with a water coolant loop. A detailed drawing of the furnace is shown in figure 3-2. This furnace was designed to provide a similar thermal environment as that produced by NASA’s microgravity furnace, the Advanced Automated Directional Solidification Furnace (AADSF). The ampoule was contained in a cartridge assembly which is described in detail in section 3.3. The cartridge was held in a fixed position using a pedestal bolted to the laboratory floor and crystal growth was accomplished by translating the furnace upward. Translating the furnace instead of the cartridge minimized any movement and vibrations of the sample and allowed the crystallization to take place in the homogenous region of the magnetic field.

The furnace assembly was co-axially aligned with a superconducting magnet system designed specifically for this research [68]. The design parameters are listed in table 3.1. The magnet was manufactured using NbTi wire and is contained in a dual dewar system shown in figure 3-3. This dual dewar design minimizes LHe loss while allowing the inner bore of the magnet to operate at room temperature. The crystal growth system fits inside the magnet and is translated during growth.

As the furnace elements are basically electromagnets, precautions had to be taken in order to reduce the forces induced by the external magnetic field on these heaters. The residual force on the heaters was minimized by using bi-filar wound heater elements. Furthermore, the AC power source had to be full wave rectified and filtered to provide a low ripple DC voltage to power the heaters during operation in the mag-
Figure 3-2: Cross section of the crystal growth system used for magnetic growth of HgCdTe.
Figure 3-3: Schematic of superconducting magnet and crystal growth system.
Related Central Magnetic Field $50 \, kG$
Related Current $519.25 \, G/A$
Maximum Test Field $52.1 \, kG$
Homogeneity $5\%$ over a $6 \, cm \times 30 \, cm$ cylinder
Inductance $125 \, H$
Clear Cold Bore Dia. $12 \, in$
Clear Rm. Temperature Bore Dia. $10 \, in$
Overall Cold Magnet Dia. $16 \, in$
Overall Cold Magnet Length $20.3 \, in$
LHe Loss Rate Less than $20 \, ml/hr$
Magnetic Center $24.25 \, in$ from top flange

Table 3.1: Superconducting magnet design parameters.

netic field. The furnace thermal profile was controlled using 3-mode PID controllers for each heated zone.

### 3.3 Ampoule/Cartridge Assembly

The ampoule was supported by a cartridge assembly shown in figure 3-4. This configuration was used during microgravity growth of $H_{90.8}Cd_{0.2}Te$ and was adapted for this research in order to have a direct comparison. The assembly consists of a multilayer structure: first the charge is sealed inside a quartz ampoule, the ampoule is, then, placed inside an inconel 625 cartridge. Alumina ampoule supports are used to co-axially align the ampoule and cartridge centers. A quartz rod holds the entire ampoule assembly in place and thermocouples are used to measure the processing temperatures. The cartridge may be hermetically sealed depending on the operating environment. Processing in the manned environment of space mandated that cartridges be sealed. This extra procedure was not implemented in the laboratory experiments. Since the cartridge was not sealed all internal components could be reused guaranteeing that these processing variables remained constant from experiment to experiment.

An instrumented cartridge was used to fine tune the PID constants and the control
Table 3.2: Optimized PID constants for the LFE Model 2005 zone controllers and the magnetic crystal growth furnace.

<table>
<thead>
<tr>
<th>Heater Location</th>
<th>Proportional Band (%)</th>
<th>Reset (Repeats/minute)</th>
<th>Rate (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot Guard Heater</td>
<td>14</td>
<td>0.38</td>
<td>0.37</td>
</tr>
<tr>
<td>Hot Zone</td>
<td>4</td>
<td>0.42</td>
<td>0.39</td>
</tr>
<tr>
<td>Booster Heater</td>
<td>12</td>
<td>0.57</td>
<td>0.28</td>
</tr>
<tr>
<td>Cold Zone Heater</td>
<td>9</td>
<td>0.40</td>
<td>0.30</td>
</tr>
<tr>
<td>Cold Guard Heater</td>
<td>25</td>
<td>0.50</td>
<td>0.35</td>
</tr>
</tbody>
</table>

algorithm for the furnace. The $H_{g0.8}Cd_{0.2}Te$ charge was replaced with an alumina rod with four thermocouples placed axially along its centerline. The PID constants shown in table 3.2 for each zone were optimized utilizing the in situ thermocouple measurements. This procedure allowed one to account for the effects of multilayer containment and the semitransparency of the silica ampoule and resulted in temperature control of within 0.03% of the solidus temperature, 703 °C [91], at steady state growth.
Figure 3-4: Containment cartridge utilized for magnetically stabilized growth of HgCdTe.
Chapter 4

Material Characterization Techniques

4.1 Sectioning

The solidified ingots of $Hg_0.8Cd_{0.2}Te$ were removed from their ampoules by dissolution of the silica glass in concentrated $HF$ acid over a period of two days. The ingots were then triple rinsed in de-ionized water.

The effect of convection on segregation was determined by measuring radial and axial compositional variations. For segregation measurements 2 mm thick wafers were cut perpendicular to the growth direction using a diamond wire saw with 0.008 inch diameter wire. Crystal-melt interface morphology was determined from centerline samples cut parallel with the growth direction as shown in figure 4-1.

Average axial macrosegregation of $CdTe$ was determined by Precision Density Measurements (PDM) while radial segregation was determined from the transmission edge of the IR transmission spectrum and Energy Dispersive X-ray Spectroscopy analysis (EDS). These methods, as well as, sample surface preparation techniques are described in detail in the following sections.
Figure 4-1: Sectioning of crystal for compositional analysis.
4.2 Surface Preparation

To prepare the surface for compositional analysis the cut samples were mechanically lapped and chemically polished in two separate steps. Mechanical lapping was accomplished using a LOGITECH PM2A lapping & polishing machine with a 9 \( \mu m \) Al\(_2\)O\(_3\)-H\(_2\)O slurry. After triple rinsing in de-ionized water, the samples were chemically polished on a Struers polishing machine using a 20% Br\(_2\)-ethylene glycol solution. Approximately 300 \( \mu m \) of material was, thus, removed to ensure that no surface damage due to mechanical lapping was present.

4.2.1 Precision Density Measurements (PDM)

The determination of alloy composition by mass density measurements is a combination of Archimedes’ principle and the density measurement method described by Bowman and Schoonover [69]. Lehoczky et al [70] were among the first to apply this technique to determine the axial macrosegregation in \( H_{90.8}Cd_{0.2}Te \). In their technique the average composition, \( x \), of wafers cut perpendicular to the growth direction was calculated from the measured densities and values of the crystal lattice constant published by Woolley and Ray [71].

The density of the wafer was determined by measuring its mass in air and water at room temperature. The resulting force balance yields

\[
\rho_{\text{wafer}} = \frac{M_a \rho_w - M_w \rho_a}{M_a - M_w},
\]

where \( M \) is the specimen’s mass and \( \rho \) is the density. The subscripts \( a \) and \( w \) are for air and water, respectively. An accurate measurement of the wafer’s mass, air and water density were critical for the precise determination of the wafer’s composition. To this end, a microbalance was used to measure the wafer’s mass and the influence of barometric pressure, relative humidity, air temperature, water temperature, depth of immersion and diffusion of oxygen into the water were incorporated in the calculation of the air and water densities. The related equations are given in reference [69]. The
Table 4.1: Effects of relative measurement error on the accuracy of the calculated composition, \( x \). Listed in order of importance.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Error ( \Delta )</th>
<th>Composition Error, ( \Delta x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrostatic mass</td>
<td>0.0001 g</td>
<td>( 4 \times 10^{-3} )</td>
</tr>
<tr>
<td>Air mass</td>
<td>0.0001 g</td>
<td>( 3 \times 10^{-3} )</td>
</tr>
<tr>
<td>Water temperature</td>
<td>1 (^\circ)C</td>
<td>( 7 \times 10^{-4} )</td>
</tr>
<tr>
<td>Air temperature</td>
<td>1 (^\circ)C</td>
<td>( 6 \times 10^{-6} )</td>
</tr>
<tr>
<td>Barometric pressure</td>
<td>0.5 mm Hg</td>
<td>( 2.5 \times 10^{-7} )</td>
</tr>
<tr>
<td>Immersion depth</td>
<td>1 cm</td>
<td>( 2 \times 10^{-7} )</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>1%</td>
<td>( 4 \times 10^{-8} )</td>
</tr>
</tbody>
</table>

measured density can now be used to calculate the composition of the wafer by noting that

\[
\rho_{\text{wafer}} = \frac{\sum M}{a_0^3},
\]  

where \( \sum M \) is the mass of the number of atoms of each element present in a cubic unit cell and \( a_0 \) is the lattice constant of \( \text{Hg}_{1-x}\text{Cd}_x\text{Te} \) (units of Å) given by

\[
a_0 = 6.4614 + 0.0084x + 0.0168x^2 - 0.0057x^3,
\]  

where \( x \) is the mole fraction of \( \text{CdTe} \). If we note that on the average there are: \( 4(1 - x) \) \( \text{Hg} \) atoms; \( 4x \) \( \text{Cd} \) atoms and \( 4 \) \( \text{Te} \) atoms in each cubic unit cell. Equation 4.2, with the rearrangement of terms, becomes

\[
a_0 = \left( \frac{(4(1 - x)M_{\text{Hg}}^\text{Hg} + 4xM_{\text{Cd}}^\text{Cd} + 4M_{\text{Te}}^\text{Te}) (1.660531)}{\rho_{\text{wafer}}} \right)^{\frac{1}{3}},
\]  

where \( M_{\text{Hg}}^\text{Hg}, M_{\text{Cd}}^\text{Cd}, M_{\text{Te}}^\text{Te} \) are the molecular weights of mercury, cadmium and tellurium, respectively and \( a_0 \) is the crystal lattice constant (in units of Å) and \( \rho_{\text{wafer}} \) is given by equation 4.1. Now equation 4.3 and equation 4.4 can be equated and solved using numerical techniques for the average composition, \( x \), of the wafer.

The accuracy of the calculation is obviously dependent on the accuracy of the measured parameters used in the calculations and on the microstructure of the solidified crystal. To investigate relative measurement errors on the accuracy of the calculated composition, a study was undertaken by Alexander [72]. The findings of
the study are shown in table 4.1 and indicate that the measurement error can be contained to ±0.008 in x.

The error measurements associated with crystal microstructure such as grain boundaries, point defects, voids and precipitates cannot be quantified for this measurement technique. However, composition obtained by this method has been shown to agree well with average compositional measurements obtained by EDS and FTIR [85] techniques. The data in table 4.1 suggests the primary error associated with crystal microstructure will be due to voids as they directly affect accuracy of the measured mass.

4.2.2 Energy Dispersive X-ray Spectroscopy (EDS)

The energy dispersive X-ray spectroscopy is an electron microprobe analysis technique which uses energy dispersive spectrometry for quantitative elemental analysis. This technique was adapted by Gillies [73] for the rapid analysis of Hg based II-IV semiconductors with high spatial resolution. Quantitative analysis uses reference peak shapes stored in standards to determine the composition of a sample. This routine first determines k-ratios for specified element X-ray lines by filtered least squares fitting of the unknown spectrum to the stored standards. The sample composition is determined using Love-Scott ZAF (atomic number, absorption and fluorescence) matrix corrections for the k-ratio data. The spectra for the standards and a measurement on a HgCdTe wafer are shown in figures 4-2, 4-3 and 4-4.

The Cd l, Te l and Hg m lines are used in the analysis which allows the data to be taken at a beam current of 10 keV. Data collection at this current avoids preferential Hg loss during analysis as discussed by Moore [106]. It has been reported [73] that a compositional variation of \( \Delta x = 0.002 \) can be determined between locations as close as 5 \( \mu m \), using a beam size of 1\( \mu m \).
Figure 4-2: Spectrum of Cd standard used for EDS compositional analysis.
Figure 4-3: Spectrum of HgTe standard used for EDS compositional analysis.
Figure 4-4: (a) Spectrum of HgCdTe wafer, (b) quantitative analysis results.
4.2.3 IR Measurements

Infrared transmission maps of the samples were used to determine the area uniformity of the composition as calculated from the cut-on wavelengths. The instrumentation and software used for these measurements was developed by Szofran and colleagues and is described in detail in ref. [74]. Briefly, the hardware consists of a Mattson Instruments, Inc. Sirius 100 Fourier Transform IR Spectrometer equipped with a software controllable xy stage driven by stepper motors. The stage can position the sample throughout a 2.54 cm square in 50 μm steps. The optical beam was split using a KBr beam splitter. The beam is focused to 250 μm at the aperture to maximize the power to the sample. A 100 μm aperture in conjunction with 256 resolution elements gave the optimum compromise between spatial resolution and time required to obtain spectra with satisfactory signal-to-noise ratios (i.e., Felgett’s advantage).

Spectra are taken at each point of the sample on a square grid with the grid spacing equal to an integral number of stepper motor increments. For rectangular samples, the analysis begins in one corner and proceeds back and forth along horizontal lines of increasing vertical position until the sample is covered. Circular samples are covered with a similar pattern beginning at the center sample and covering one semicircle, returning to the center and then doing the remaining semicircle. The spectra are then analyzed to obtain the cut-on wavelength and the mole fractions of CdTe are calculated from the compositional dependence of the energy band gap. An arbitrary spectrum from a Hg$_1$–xCd$_x$Te sample, obtained with this system, is shown in figure 4-5.

The above techniques have been proven successful for the analysis of both axial and radial compositional distributions in the Hg based II-VI semiconductors [66, 75].
Figure 4-5: HgCdTe transmittance spectrum.
Chapter 5

Segregation Results in the Absence of Magnetic Melt Stabilization

In this chapter, results of $Hg$ based II-IV crystal growth experiments will be reviewed with particular emphasis on axial and radial segregation. This review discusses the progress made in the growth of these semiconductors during the past 20 years and is meant to familiarize the reader with the limitations of these growth techniques. Segregation results in the absence of magnetic melt stabilization are then discussed and direct comparisons with the ground based portion of a $HgCdTe$ microgravity experiment [64] are made.

5.1 Previous Bulk Growth Experimental Results

A review by Reynolds [107] indicates that the II-IV compounds comprise a group of semiconductor materials having a greater variety of properties for exploitation than any other semiconductor materials family. The direct energy band gaps vary from a negative 0.3 $eV$ for the Hg-base compounds to 4.0 $eV$ for ZnS. As a result, they luminesce efficiently throughout the visible spectrum. Despite the large range of technologically significant properties, the premier use of II-VI semiconductors remains
as an infrared sensor.

The choice material for IR applications has long been $Hg_{1-x}Cd_xTe$, thus a large amount of research has been devoted to improving impurity control, defects and crystalline quality of this material. The most complete and systematic study of the $HgCdTe$ system during the past 20 years has been the work of Lehoczky and colleagues [70]. Their work has lead to the determination of many thermophysical properties such as: the effective mass diffusion coefficient [70]; liquid thermal diffusivity [76]; kinematic viscosity [77]; liquid density [79]; heat capacity, enthalpy of mixing and thermal conductivity [80] and the establishment of the phase diagram [78]. Their work also determined the effects of furnace translation rates on the compositional distributions in $HgCdTe$ by the vertical Bridgman-Stockbarger directional solidification technique. The two experimental curves [70], shown in figure 5-1, illustrate the effects of varying translation rates on compositional uniformity. The translation rates for ingots MCT-L6 and MCT-L7 were 0.310 and 0.068 $\mu m/s$, respectively. Solidification at the slower rates results in the build up of a much wider solute boundary layer (approximately 8 cm from $\frac{D_l}{R}$ calculations). Hence, the stabilizing solutal forces are expected to be less during the growth. This reduced stabilizing force and wider boundary layer effects the fluid flow pattern in the melt and the crystal-melt interface morphology resulting in a very uniform radial segregation (radial segregation is better than 0.4%). However, the axial compositional profile never reaches a steady state value due to the impingement of the wider boundary layer on the end of the ampoule. Therefore improved radial segregation is gained at the expense of less uniform axial composition. If the translation rate is increased, as in MCT-L6, shorter transients result in steady state axial compositional distribution, but radial segregation increases to 40%. For both growth rates the axial compositional profile were closer to the diffusion limited profile as predicted by a one-dimensional model [70] than to the complete mixing equation of Pfann [42] obtained using a starting composition, $C_o = 0.2$, and a constant segregation coefficient, $k = 4.2$. This suggests that either uniform radial segregation or uniform axial segregation can be obtained by conventional growth of $HgCdTe$ but not both due to the length of the solute boundary and its effects on
Figure 5-1: Effects of furnace translation rates on composition distributions in HgCdTe grown by the vertical Bridgman-Stockbarger directional solidification technique [70].
convection at different translation rates. Another problem with the $HgCdTe$ system is that the presence of cadmium tends to weaken the $Hg-Te$ bond and, thus, effects lattice stability. Due to lattice stability problems, several alternate $Hg$-based II-VI materials have been investigated to determine their usefulness for IR applications.

For example, the influence of growth conditions on the radial and axial compositional variations in directionally solidified $Hg_{0.8}Cd_{0.2}Se$ was undertaken by Andrews et al [97]. They grew crystals at different translation rates and under different thermal conditions in order to determine the effective $(CdSe)$ diffusion coefficient in the melt. Their results indicate a diffusion coefficient of $3.0 \pm 0.5 \times 10^{-5}$ $cm^2/s$ which did not appear to be significantly affected by the crystal growth rate. However, the axial and radial crystal uniformity was shown to be highly growth rate dependent, with the faster growth rates producing more axially uniform crystals and the slower growth rates producing more radially uniform crystals. The growth rate effects on axial and radial segregation are illustrated in figures 5-2 and 5-3, respectively.

Diffusion limited crystal growth of $HgCdSe$ was investigated by Summers and Nelson [83]. They used the vertical Bridgman method to directionally solidify ingots of $HgCdSe$ with a $G/R$ ratio (temperature gradient, $G$, to growth rate, $R$, ratio) that exceeded the constitutional supercooling criteria [49]. Figure 5-4 compares the axial compositional distribution of $CdSe$ to the theoretical profile. The slow increase in composition along the axis of the ingot was associated with end effects that were hard to include in the theoretical calculations. It will be shown in the chapter 6 that this increase in composition is more likely due to constitutional supercooling effects.

$HgZnSe$ alloys with compositional ranges between $x = 0.08$ and 0.115 were grown using a vertical Bridgman-Stockbarger growth technique by Cobb et al [84]. Both axial and radial compositional variations in the directionally solidified ingots were determined to be growth rate dependent, see figure 5-5. The effective diffusion coefficient values, as determined using the diffusion coefficient as a fitting parameter in a one-dimensional diffusion limited model, ranged from $1.5 \times 10^{-5}$ to $2.9 \times 10^{-5}$ $cm^2/s$. The authors attributed the variation in the diffusion coefficient to localized convective mixing effects.
Figure 5-2: Composition versus axial position for: (a) ingot A-2; (b) ingot A-4; (c) ingot A-5; (d) ingot A-9. Diamonds are the experimental results (from [97]).
Figure 5-3: Radial compositional maps of: (a) a sample taken 2.00 cm from the tip of ingot A-2; (b) a sample taken 1.28 cm from the tip of ingot A-4; (c) a sample taken 2.10 cm for the tip of ingot A-5; (d) a sample taken from the tip of ingot A-9 (from [97]).
Figure 5-4: Theoretical and experimental compositional profiles of HgCdSe grown by the vertical Bridgman method (from [83]). Dashed lines are experimental results while solid lines are theoretical.
Figure 5-5: Compositional variations in directionally solidified $Hg_{1-x}Zn_xTe$ for: (a) Ingot SC-5: solid line represents the best fit of the experimental data with the numerical solution to the one-dimensional diffusion equation; (b) cut-on wavenumber map for a radial slice taken 6.26 cm from the first to freeze end of crystal SC-5; (c) composition versus axial position for ingot SC-6; (d) cut-on wavenumber map for a radial slice taken 7.70 cm from the first to freeze end of crystal SC-6 (from [84]).
Figure 5-6: Axial compositional variation in $\text{HgZnTe}$ for: (a) ingot B16-A grown at a rate of 0.173 $\mu m/s$; (b) ingot B16-B grown at a rate of 0.090 $\mu m/s$. The solid curve is the theoretical result based on the one-dimensional diffusion equation (from [85]).

$\text{HgZnTe}$ is another $\text{Hg}$-based II-VI compound that has been shown to have improved lattice stability in comparison to $\text{HgCdTe}$ and, therefore, is regarded as a potentially superior material for IR applications. A series of $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ crystals were grown by directional solidification by Su et al [85], with $x$ ranging from 0.15 to 0.22. Their studies revealed that the length of the initial transient region decreases as the translation rate decreases from 0.173 $\mu m/s$ to 0.090 $\mu m/s$ which was contrary to diffusion limited theory, see figure 5-6. This implies that even at a rather slow translation rate, convective mixing was present. This convective mixing was sufficient to interfere with radial segregation as illustrated in figure 5-7.

$\text{HgMnTe}$ is yet another alloy that is a viable alternative to $\text{HgCdTe}$ as a material for infrared detectors. Results of the growth of $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ crystals by both vertical Bridgman and vertical gradient freeze techniques [86] indicate that the axial composition is highly dependent on the crystal growth rate, but only slightly related to the growth technique used. As shown in figure 5-8, the initial manganese concentration is more than twice the stoichiometric amount and the gradient covers nearly
Figure 5-7: Radial compositional distributions for: (a) radial compositional map for a slice taken 2.00 cm from the first to freeze end of ingot B16-B as determined by IR transmission-edge measurements; (b) radial compositional variations along two perpendicular diameters on a wafer 4.84 cm from the first to freeze end of crystal B16-B as determined by EDS analysis (from [85]).
Hot Zone Temperature, $T_H$ & 860 °C \\
Cold Zone Temperature, $T_C$ & 350 °C \\
Axial Thermal Gradient, $G$ & 75 °C/cm \\
Furnace Translation Rate & 0.2 μm/s \\
Ampoule Diameter & 8 mm \\
Ampoule Length & 140 mm \\
Starting Composition & $x = 0.2$

Table 5.1: Growth system parameters used in this study.

a third of the ingot for the slowly-grown ingot. However, in the most rapidly grown sample, the initial transient is much smaller. Similar results have been observed in the $HgMnTe$ system studied by Piotrowski and colleagues [87], see figure 5-9.

The above experimental results suggest that improved material compositional uniformity in the $Hg$-based II-VI semiconductors requires sufficiently fast growth rates to produce short initial transients in the axial compositional profile and a simultaneous reduction of radial segregation caused by convective effects.

In the next section, the zero magnetic field results of this study are presented. General comparisons will be made to the experiments listed above and direct comparisons will be made to the microgravity flight experiment of Lehoczky and colleagues [64].

5.2 Zero Magnetic Field Results

5.2.1 Growth Conditions and Experimental Procedure

The thermal growth conditions and ampoule geometry used in this study are listed in table 5.1. An instrumented variation of the ampoule/cartridge assembly was used to tune the furnace temperature control algorithm to ensure that the growth parameters listed in table 5.1 were met. Figure 5-10 is a comparison of the growth and thermal probe cartridges. In (b) the charge has been replaced by an alumina rod instrumented with four thermocouples (exposed tip, type-K) along its centerline otherwise the two cartridges are identical. This configuration allows one to account
Figure 5-8: Manganese concentration as a function of position along the ingot for the Bridgman crystals, measured from the first to freeze end. The nominal concentration was 0.11 for all ingots shown. Furnace lift rates were (a) 0.4 mm/h; (b) 1.0 mm/h and (c) 2.6 mm/h (from [86]).
Figure 5-9: Distribution of composition along the growth direction measured by PL, PV and X-ray microprobe. Pulling rate: (a) 0.4; (b) 0.8; and (c) 1 mm/h (from [87]).
Figure 5-10: Comparison of: (a) growth cartridge and (b) instrumented thermal probe.
for the effects of multilayer containment and the semitransparency of the quartz ampoule. The thermal profile, as measured by the probe, is shown in figure 5-11. The thermocouple data have been shifted to correspond to their relative positions in the furnace bore. TC4 was the first thermocouple to be translated through the gradient section followed by TC2 and TC1. Thermocouple TC3 experienced an open circuit during furnace heat up, thus, no data was obtained. The physical locations of the thermocouples in the alumina rod were 25 mm, 144 mm and 180 mm as measured from the 'first to freeze' end for TC4, TC2 and TC1, respectively (see figure 5-10 (b)). Thermal data from TC4 and TC2 suggest that, during the first 144 mm of translation, the axial gradient is nearly constant at 75 °C/cm. However, its position relative to the furnace is changing. The largest shift in the gradient location was registered by TC1 and is attributed end effects (it is located at the very end of the alumina rod). It should be noted that the gradient 'shift' is due to the changing thermal coupling between the furnace and charge and is unavoidable in all conventional vertical Bridgman-Stockbarger crystal growth systems. As a result, the location of the crystal-melt interface with respect to the furnace, and its shape, change during growth. This, in turn, affects the radial segregation, stresses, crystal perfection and causes the growth rate to diverge from the translation rate. As a rule-of-thumb, the thermal coupling has primary influence within 2 diameters from the end of the crystal. Since the aspect ratio (length/diameter) for this work is 22.5, end effects are felt to have little effect on the crystal growth results. Moreover, thermal profiles obtained with the alumina probe tend to support this rule-of-thumb i.e., there was little change in the thermal gradient obtained with TC4 and TC2 (3 and 18 diameters from the 'first-to-freeze' end, respectively) whereas, a significant change in the TC1 profile was observed (located at the end of the alumina rod). Nevertheless, these inherent relocation transients were realized in this work and, in order to draw meaningful conclusions, comparisons of radial segregation are only made at the same axial positions on the resolidified crystals.

The precast alloys were regrown by directional solidification in the growth system illustrated in figures 3-2 and 3-3. The ampoule/cartridge assembly, previously
Figure 5-11: Axial temperature gradient as measured with thermal probe.
described in section 3.3, was mounted atop a leveling pedestal located beneath the furnace. Alignment of the cartridge parallel with the furnace bore and the gravity vector was accomplished with a plumb-bob and a bubble level which was mounted on top of the cartridge. Once aligned the cartridge remained stationary during the growth process. Next, the furnace was translated downward until the ampoule was located in the hot zone of the furnace. The temperature profile shown in figure 5-11 was established by increasing the zone set point temperatures at a rate of 150 °C/hr until the setpoints shown in table 5.1 were reached. A 24 hour thermal soak was used to achieve thermal equilibrium and to assure melt homogenization. Growth was then initiated by translating the furnace upward at a rate of 0.072 cm/hr (0.2 μm/s).

5.2.2 Axial Compositional Distribution

Baseline results with zero field were obtained by utilizing the above crystal growth system and growth procedure. During growth the thermal profile was measured with a thermocouple located at the ingot’s tip. Figure 5-12 illustrates that there is good agreement between the thermal profile obtained with the thermal probe cartridge (for TC4 and TC2) and the profile during growth.

For determination of the axial compositional distribution, 2 mm wafers transverse to the growth axis were prepared from the grown crystal as shown in figure 4-1. The average compositions, \( x \), of these wafers, listed in table 5.2 and shown graphically in figure 5-13, were calculated from the measured mass densities and published values of the crystal lattice constant as described in section 4.2.1.

Comparison of Axial Composition with Theory

As discussed in section 2.2.1, under diffusion limited conditions, the compositional variation along the growth axis is dependent on the relative values of the interface translation rate, \( R \), and the solutal diffusivity rate, \( D_t \), in the melt. For values of the equilibrium constant, \( k > 1 \), the axial compositional profile is expected to undergo an initial transient of decreasing solute composition, a region of constant composition
Figure 5-12: Comparison of the thermal profile obtained with a thermal probe and the thermal profile measured during the growth of ingot MCT-D2 (zero field).
Figure 5-13: Axial compositional distribution for ingot MCT-D2 (zero field).
equal to the starting composition (commonly referred to as the steady state region), and finally a transient region of rapidly decreasing solute concentration. Figure 2-1 illustrates the transient build up of the solute boundary during various stages of growth as well as the phase diagram for a material with \( k > 1 \). Smith, Tiller and Rutter [51] have obtained analytical solutions for this case in terms of the growth system and material parameters. The solution for the initial solute transient in the solid for constant \( k \) and \( R \) is given by

\[
C_s(z) = \frac{C_0}{2} \left\{ 1 + erf\left(\frac{\sqrt{RD_i}}{2}\right) + 2(k - 1) \exp\frac{-(1-k)Rz}{D_i} \right\},
\]

(5.1)

For the final solute transient, they obtained the expression

\[
C_s(z) = C_0 \left\{ 1 + \sum_{n=1}^{n=\infty} (2n+1)\frac{(1-k)(2-k)\ldots(n-k)}{(1+k)(2+k)\ldots(n+k)} \exp\frac{-n(n+1)Rz}{D_i} \right\}
\]

(5.2)

where \( L \) is the overall length of the grown ingot. A useful plot of equation 5.1 for the limit \( k \to 0 \) was obtained by Pohl [50]. He showed that by plotting the quantity

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Distance From Tip (cm)</th>
<th>Density (g/cm³)</th>
<th>Average Composition (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.0</td>
<td>7.178</td>
<td>0.4067</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>7.486</td>
<td>0.2684</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>7.563</td>
<td>0.2338</td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>7.571</td>
<td>0.2304</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td>7.592</td>
<td>0.2207</td>
</tr>
<tr>
<td>7</td>
<td>7.0</td>
<td>7.591</td>
<td>0.2210</td>
</tr>
<tr>
<td>8</td>
<td>8.0</td>
<td>7.650</td>
<td>0.1946</td>
</tr>
<tr>
<td>9</td>
<td>9.0</td>
<td>7.658</td>
<td>0.1910</td>
</tr>
<tr>
<td>10</td>
<td>10.0</td>
<td>7.698</td>
<td>0.1727</td>
</tr>
<tr>
<td>11</td>
<td>11.0</td>
<td>7.775</td>
<td>0.1382</td>
</tr>
<tr>
<td>12</td>
<td>12.0</td>
<td>7.881</td>
<td>0.0902</td>
</tr>
<tr>
<td>13</td>
<td>13.0</td>
<td>8.049</td>
<td>0.0140</td>
</tr>
</tbody>
</table>

Table 5.2: Average alloy densities and compositions for various positions along the axis of ingot MCT-D2.
1 \text{-} C_s(z)/C_0$ verses distance solidified, $z$, on semilog paper the slope of the straight line would yield $k$ directly. Moreover, if $k$ and $R$ were known, the value of the diffusion coefficient, $D_i$, could be determined. Thus, equations 5.1 and 5.2 are not only useful to determine if the crystal growth is diffusion limited, but also can be used to determine an effective diffusion coefficient (by using the diffusion coefficient as a fitting parameter) for the near diffusion limited case.

Equations 5.1 and 5.2 are only valid when the crystal growth rate and segregation coefficient are constant. As shown in figures A-1, A-2 and A-3, these conditions are violated during directional solidification of $\text{HgCdTe}$. Lehoczky and colleagues [70] were able to approximate the effects of the changes in $R$ and $k$ by defining an instantaneous interface translation rate and segregation coefficient. The instantaneous values were then averaged along the length of the ingot and used in equations 5.1 and 5.2. Comparisons between the measured and theoretical compositional profiles using the diffusion coefficient as a fitting parameter were good, indicating that the axial solute distribution in directionally solidified $\text{HgCdTe}$ crystals was dominated by diffusion. Using this method they were able to show that the best fit to the measured data over a wide range of growth conditions yielded an effective diffusion coefficient of $5.5 \times 10^{-5}$ $\text{cm}^2/\text{s}$ for $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$.

Based on the above work of Lehoczky et al [70] and other more classical approaches [49], [51], Clayton et al [88] developed an exact numerical solution to the one-dimensional diffusion equation for directional solidification of $\text{HgCdTe}$ which accounts for the non-constant interface solidification velocity and segregation coefficient’s dependence on temperature and composition. The inputs to the model are the phase diagram (pseudo-binary), ampoule translation rate and length, initial solute composition and axial temperature gradient. An additional input was the effective diffusion coefficient (taken to be independent of temperature and concentration) which was used as a fitting parameter. The model gives axial solute concentration in the solid, and interface velocity at each chosen time interval. This transient analysis model has been successfully applied to several solid solution crystal growth experiments which cover a wide range of growth parameters. Additionally, the model can
Figure 5-14: Comparison of the axial compositional distribution for ingot MCT-D2 (zero field) to a one-dimensional diffusion limited model.

also be used to simulate the effects of translation rate changes on the axial compositional distribution during growth and is well suited for choosing proper growth parameters prior to actual growth experiments. Based on the capabilities stated above and in view of the fact that no two or three-dimensional theoretical treatment of transient segregation exists in the open literature, the one-dimensional model by Clayton and colleagues appears currently the best analytical segregation analysis tool available for solid solution crystal growth and will be used in this work.

Figure 5-14 is a comparison of the axial compositional profile obtained for the MCT-D2 ingot and the axial profile as predicted by the one-dimensional model of
Clayton et al. The experimental data for MCT-D2 indicates that the expected initial transient and a steady state region followed by a final transient are present. Data agreement with the one-dimensional model indicates that the compositional distribution of CdTe was dominated by diffusion (Note: In figure 5-14 the first 1.5 cm of growth occurs at a temperature below the equilibrium solidification temperature and is termed 'supercooled length'. Supercooling is a common phenomena in unseeded growth experiments and was expected). This axial compositional distribution also compares well with the previous experimental results discussed in section 5.1.

5.2.3 Radial Compositional Distribution

Although the axial compositional distribution for HgCdTe appears diffusion dominated there exist large radial non-uniformity. Figure 5-15 shows the radial composition for wafers from the initial transient region of ingot MCT-D2 (zero field) as determined by IR transmission-edge measurements. The pattern of low CdTe content at the center is consistent with other results obtained previously in the absence of a magnetic field. This radial segregation can be explained by considering the growth process.

As growth is initiated, a crystal-melt interface is generated which is concave into the solid and is a result of the differences in the thermal conductivities of the melt, solid and confining silica ampoule (see figure 2-3). Simultaneously, the solute field evolves from a uniform state to establish gradients that are consistent with the rejection of the more dense HgTe component at the crystal-melt interface. The concave interface leads to thermosolutal convection that carries the HgTe to the center of the ampoule. Because the solidus temperature of the alloy decreases with increasing HgTe concentration (see figure A-1), the interface temperature at the center will decrease with respect to the edges, causing the interface to become more concave. Therefore, the crystal-melt interface will increase in curvature as the solutal boundary layer is established during the initial transient portion of crystal growth. Once the solutal boundary layer is established the crystal-melt interface no longer changes and the radial segregation in the steady state region of crystal growth is nearly con-
Figure 5-15: Radial compositional variations during the initial transient for ingot MCT-D2 (zero field) as determined by IR transmission-edge measurements; (a) 1.9 cm; (b) 2.1 cm and (c) 2.2 cm from the first to freeze end.
Figure 5-16: Radial compositional variations in the steady state portion of crystal growth for ingot MCT-D2 (zero field) as determined by EDS measurements; (a) 4.1 cm; (b) 5.1 cm and (c) 7.1 cm from the first to freeze end.

stant as indicated in figure 5-16. The final transient regime is a result of the depletion of the CdTe content of the bulk melt, i.e., the bulk melt is approaching the dilute limit and the crystal-melt interface curvature decreases. As illustrated in figure 5-17, the radial composition becomes more uniform in the final transient portion of crystal growth as expected.
Figure 5-17: Radial compositional variations in the final transient region for ingot MCT-D2 (zero field) as determined by EDS measurements.
5.2.4 Growth Interface Morphology

To further investigate the effect of convection on interface morphology, an experiment was performed to mark the crystal-melt interface. This was accomplished by directionally solidifying a sample for 65 mm with the same growth parameters as listed in table 5.1 and with zero magnetic field. The interface morphology in the steady state section was then captured by quenching the sample via a rapid translation rate increase. The resulting interface is shown in figure 5-18. The interface curvature was symmetric (in this cut plane) and concave toward the solid with a maximum deflection of 3.25 mm. This curvature of the crystal-melt interface is indicative of convection near the interface which gives rise to the large radial segregation shown in figures 5-15, 5-16 and 5-17. However, the excellent fit of the diffusion limited model to the data for the axial compositional distribution in figure 5-14 suggests that the
The axial compositional distribution of $CdTe$ for the quenched sample as determined from EDS measurements is shown in figure 5-19. The data shown are from longitudinal scans located 1 mm from the left edge, along the ingot centerline and 1 mm from the right edge. The differences in composition along the centerline and outer edge indicates that radial segregation is, again, non-uniform for growth without an applied magnetic field. The scatter in the data in the quenched part of the ingot is due to microvoids formed as a result of quenching, see figure 5-18. Since the EDS
measurements were taken at evenly spaced intervals using a beam size of 1 \( \mu m \) one can not miss the microvoids. Therefore, the data will be scattered. A technique of avoiding this scattering is to conduct EDS scans on larger area sizes which is effectively averaging the composition on that area. Results using this technique of weighted area averaging for determination of the composition in the quenched portion are presented in the next section.

The radial compositional variations during the steady state portion of growth are shown in figure 5-20. This figure shows that radial segregation is consistent and suggest that the system was experiencing steady state growth conditions.

5.3 Comparison with Microgravity Crystal Growth System

The experimental setup used for magnetic growth experiments was as similar as possible to the Advanced Automated Directional Solidification Furnace (AADSF). This was done in order to permit a direct comparison between microgravity crystal growth and magnetic crystal growth. The AADSF is basically a two-zone Bridgman-Stockbarger furnace with an adiabatic zone consisting of interchangeable thermal barriers and a heat extraction plate. A detailed description of the AADSF furnace can be found in reference [89]. Using this furnace a \( Hg_{0.8}Cd_{0.2}Te \) alloy crystal was grown in microgravity aboard the space shuttle during the Second United States Microgravity Mission (USMP-2) in March 1994 [64].

The results from the ground based portion of the flight experiment are described below and are compared to zero field results obtained during this research. Additionally, the results from the crystal grown in microgravity will be directly compared to magnetic field results in chapter 6.

5.3.1 Ground Based Results from USMP-2

Figure 5-21 depicts the experimental data for the axial composition profile and a
Figure 5-20: Radial segregation at axial positions 55 mm, 60 mm and 62 mm from the first to freeze portion of the ingot. Radial segregation is nearly constant indicating that the crystal-melt interface is not changing significantly in the steady state region of crystal growth.
Figure 5-21: Axial compositional profile from a $Hg_{0.8}Cd_{0.2}Te$ crystal grown in the AADSF.
Figure 5-22: Radial compositional profile of a $Hg_{0.8}Cd_{0.2}Te$ crystal grown in the AADSF.

The graphic presentation of the solution of one-dimensional theory for an ingot grown in the AADSF on the ground. It should be noted that the experimental data obtained by density measurements is in excellent agreement with theory and is almost identical to the axial profile obtained for growth with the magnetic crystal growth system at zero magnetic field (figure 5-14).

An arbitrary radial segregation profile from the steady state portion of this growth experiment is shown in figure 5-22. Again, there is excellent agreement with the data from the magnetic crystal growth system shown in figure 5-20. This finding suggests that the interface morphology produced in both growth systems must be very similar.
Indeed, a quenching experiment performed in the AADSF revealed that the crystal-melt interface shape was concave toward the solid with an interface deflection of 3.0 mm.

It is of interest to note that the microvoids in the quenched portion of the ingot grown in the AADSF caused a scatter of the compositional data in that region. By taking the EDS measurements over a larger area and averaging the data Lehoczky and colleagues were able to obtain viable data for the distribution of CdTe in the quenched region. The corresponding compositional profile, shown in figure 5-23, is compared with the theory of steady state solidification as derived by Tiller et al [49] in equation 2.15. The experimental data and theory appear in good agreement. This result is not surprising when considering that the system exhibits axial diffusion controlled growth.

5.4 Summary of Zero Field Results

It has been shown that the $Hg_{0.8}Cd_{0.2}Te$ growth system is characterized by destabilizing thermal and stabilizing solutal gradients. These two phenomena lead to double-diffusive or thermo-solutal convection near the crystal-melt interface which dominates the alloy segregation. As the melt temperature of $HgCdTe$ is highly compositional dependent, fluid flow near the interface which is sufficient to change the composition, can exacerbate interface curvature. This leads to large radial compositional non-uniformity, although the axial compositional variations exhibits diffusion controlled behavior. This subtle interaction of convection with the interface morphology and, hence, radial segregation is studied by growing crystals in the presence of applied magnetic fields.
Figure 5-23: Average axial compositional profile in quenched portion of crystal compared with the theory of steady state solidification as derived by Tiller et al [49] in equation 2.15.
Chapter 6

Segregation Results in the Presence of Magnetic Melt Stabilization

This chapter discusses four different sets of experiments that were conducted with the application of a magnetic field. The first set of experiments was conducted with the growth system and growth parameters identical to the zero field baseline results presented in the previous chapter. The only variable that was changed was the magnetic field strength from 0 to 50 kG. In the second set of experiments with a 50 kG field, the translation rate was decreased to investigate constitutional supercooling effects with all other growth parameters held constant. The third set of experiments involved the marking of the growth interface morphology in a 50 kG magnetic field. During the final series of experiments, ingots were grown at different field strengths. Again, all of the other growth parameters were held constant and were the same as those values used in the zero field results. It is important to note that in all magnetic field experiments the sample was first melted and then the magnetic field was set to the desired strength and held constant throughout the entire experiment. The melts were then allowed to reach equilibrium before growth was initiated by translating the furnace. This allowed the sample to remain in the homogeneous region of the field during growth.
Figure 6-1 shows the axial composition distribution profiles for three crystal growth experiments. Curves MCT-D2 and MCT-4 were obtained from growth with 0 $kG$ and 50 $kG$ magnetic fields, respectively. The translation rate for both crystals was 0.2 $\mu m/sec$. The theoretical curve based on a one-dimensional diffusion equation is also shown.

The curve for MCT-D2 (discussed in detail in the previous chapter) indicates that during solidification in zero field the distribution of $CdTe$ undergoes an initial transient, then a steady-state region followed by a final transient. This compares well
with the curve calculated from an exact numerical solution to the one-dimensional diffusion equation [88]. The curve for MCT-4 (50 kG field) shows a similar initial transient and steady-state section. However, a sharp increase in the CdTe content is observed near the last-to-freeze end just before the final transient. To ensure that this rise was not due to measurement error, IR compositional measurements were taken at various axial locations. There was excellent agreement between the two measurement techniques, see figure 6-1. This rise in CdTe content is attributed to constitutional supercooling ahead of the interface. Figure 6-2 shows a schematic of the solute boundary layer configurations for the no-field and field cases. In the no-field case, a region with intense convection caused by radial thermal gradients is assumed to occur between a bulk of diffusion-controlled melt and the growth interface as proposed by Kim and Brown [90] to explain axial segregation patterns seen in HgCdTe crystal growth experiments by Szofran and Lehoczky [91]. For this case, it is assumed that convection near the crystal-melt interface modifies the solute boundary layer in the melt such that the compositional dependent (see figure A-1 melt temperature, $T_m$, is less than the imposed thermal gradient, $T_A$, and normal solidification proceeds. However, during growth in the presence of a stabilizing magnetic field, the elimination or reduction of convection allows for the build up of the diffusion-controlled solute boundary layer closer to the crystal-melt interface. As the axial temperature gradient is held constant, this solutal boundary layer produces a region in the liquid ahead of the interface that is at an actual temperature below its equilibrium liquidus temperature. Accordingly, this can lead to phase separation of solid particles, richer in Cd (higher $x$) than the bulk melt, these float upwards because their densities are less than those of the melts. This less dense material is then solidified near the end of the ingot resulting in a CdTe rich section. To test this hypothesis a growth experiment based on the criteria for constitutional supercooling as derived by Rutter and Chalmers [37] was performed. The criteria for constitutional supercooling is given by:

$$\frac{G}{R} > \frac{-mC_o(1 - k)}{kD_l}$$

(6.1)
Applied Magnetic Field

Furnace temperature, $T_A$, is larger than melt temperature, $T_M$. Thus, stable growth occurs.

No Magnetic Field

Cd rich areas form due to nucleation ahead of the crystal—melt interface. These Cd rich areas, being less dense than surrounding environment, rise to the top of the ampoule where they remelt and remain until the end of growth. This results in a Cd rich band at end of boule.

Figure 6-2: Schematic presentation of the solute boundary layers for directional solidification growth of $HgCdTe$ with and without magnetic stabilization.
where $G$ is the axial temperature gradient in the melt, $R$ is the growth velocity, $m$ is the slope of the liquidus line from the phase diagram, $C_o$ is the starting composition and $D_I$ is the diffusion coefficient. One way to increase the $G/R$ ratio is to decrease the solidification velocity, $R$. To this end, an ingot was grown at a translation rate of 0.154 $\mu$m/sec. The resulting axial composition distribution is labeled as MCT-D5 in figure 6-1. It was observed that the 25% decrease in translation rate significantly reduced the compositional rise near the end of the crystal. This suggests that the sharp rise in $CdTe$ was most likely due to constitutional supercooling brought about by the reduction of fluid flow associated with magnetic stabilization. Indeed, this phenomenon of buoyant rising of solid particles, or Stokes migration, has been observed during vertical Bridgman-Stockbarger growth experiments of $HgCdTe$ [75],[92] and $HgCdSe$ [83] where the growth velocity was large enough to violate the constitutional supercooling criteria.

### 6.2 Radial Compositional Distribution

Figure 6-3 compares the radial compositional variations for wafers from the initial transient portions of ingots MCT-D2 (zero field) and MCT-4 (50 $kG$ field) as determined by IR transmission-edge measurements. The order of magnitude improvement in radial homogeneity achieved on application of an axial 50 $kG$ field clearly indicates that the magnetic field is effective in suppressing convective effects on segregation during the initial transient where the mass boundary layer is building up to its steady state value.

A radial compositional profile obtained from the steady state portion of experiment MCT-4 (50 $kG$) is shown in figure 6-4. The radial segregation is approaching the starting composition of $x = 0.2$ and is very uniform. Again, indicating that the magnetic field has a significant stabilizing effect on convection in the melt.
Figure 6-3: Compositional profiles for (a) MCT-D2 2.5 cm from first-to-freeze, grown without a magnetic field, (b) MCT-4 2.5 cm from first-to-freeze, grown with a 50 kG stabilizing magnetic field and (c) comparison of radial profiles.
Figure 6-4: Radial compositional profile for growth with a 50 kG applied magnetic field.
6.3 Growth Interface Morphology

The same quenching experiment used to mark the crystal-melt interface morphology during growth in zero field was also performed during growth in the presence of a 50 kG magnetic field. The resulting interface morphology is shown in figure 6-5. For growth under the influence of the magnetic field the interface curvature was also symmetric and concave toward the solid. However, the maximum deflection was 1.1 mm which is a factor of three less than that obtained in the zero field case. This suggests that the magnetic field had a significant influence on the fluid flow in the system during solidification and on radial segregation as can be seen in figure 6-6.

Also, it is of interest to note that the crystal-melt interface was located on the peripheral at a distance of 65 mm from the tip of the grown ingot for both the zero field and 50 kG field case. This evidence suggests that the phenomena associated
Figure 6-6: Typical radial segregation in the steady state section observed in the quenched ingot grown in a 50 kG magnetic field.
with the interface morphology change is due to compositional (i.e., constitutional) changes brought about by the reduction of fluid flow in the liquid and not due to changes in the overall heat transfer. Recall, in section 2.2.2 it was shown that for most semiconductor systems $Pe_i < 1$ which indicates heat transfer is dominated by conduction not convection.

The tendency of the crystal-melt interface shape to become more planar due to the influence of an applied magnetic field was first predicted by Oreper and Szekely [93] and subsequently by Kim and Brown [94]. Additionally, similar effects on the interface morphology were reported by Matthiesen et al [41] for gallium doped germanium grown in the presence of a 30 kG magnetic field. The basic physics behind the flattening of the crystal-melt interface can be understood by considering two limiting cases as discussed by Han et al [95]:

First consider the case where there is no magnetic field. Solutal damping of convection in the melt is achieved through establishment of convection induced horizontal solutal gradients which counteract the destabilizing horizontal thermal gradients. This requires that prior to growth, $Pe_s$, be larger than one to promote convective mixing and establish horizontal solutal gradients, which is generally the case for all non-capillary growth conditions on earth. As growth is initiated, a crystal-melt interface is generated which is usually concave into the solid and is a result of the differences in the thermal conductivities of the melt, solid and containing crucible. Simultaneously, the solute field evolves from a uniform state to establish gradients that are consistent with the rejection of $HgTe$ (more dense component) at the crystal-melt interface. The concave interface leads to thermosolutal convection that carries $HgTe$ to the center of the ampoule, which lowers the melting temperature (melting temperature is highly compositional dependent) and further increases the interface deflection.

Now consider growth in a magnetic field which is sufficient to suppress the convective intensity in the melt prior to growth to the point that $Pe_s$ is less than one. As growth is initiated, a crystal-melt interface (concave into the solid) will again be generated due to the differences of thermal conductivities. However, the convective
transport of $HgTe$ to the center of the ampoule will not take place and the resulting interface curvature will be less than that without a magnetic field. Also, horizontal solutal gradients will not be established, and a classically-defined diffusion controlled growth will be obtained where the radial segregation should be proportional to the curvature of the melt interface. This proportionality will be examined in detail in section 6.4.2.

Overall, the experimental data presented in chapters 5 and 6 tend to support this phenomenological argument. The next section will review the applicable numerical models and develop the basic physics associated with thermo-solutal convection. The derived scaling laws will be used to provide quantitative evidence to support the above conclusions.

### 6.4 Computational Fluid Dynamic Analysis

One of the first models of Bridgman-Stockbarger growth of $HgCdTe$ was by Kim and Brown [90]. They conducted a steady state analysis of the growth system shown schematically in figure 6-7. The governing equations were put into dimensionless forms by scaling lengths with the length of the ampoule, $L$, velocity components with the thermal diffusion velocity, $\frac{a_m}{L}$, pressure with $\frac{\rho_m a_m^2}{L}$, composition with $C_o$ and the temperature field with $T_h - T_c$ where $m, h, c$ represent melt, hot and cold, respectively. Their results showed that a strong cellular motion exists near the interface, but flow away from it is damped by the stabilizing dependence of the melt density on the heavier component of $HgTe$ which is rejected at the interface. Large radial segregation caused by incomplete mixing near the interface was predicted. However, the axial segregation was qualitatively similar to the results for diffusion only. This model does predict some of the basic phenomena observed during the no-field portion of this study. However, there are several shortcomings of the model. Namely, the thermophysical properties were taken independent of temperature and composition. This is an extreme simplification and as noted by the authors these dependencies must be accounted for in a quantitative analysis. Another shortcoming is the way
Figure 6-7: Schematic of vertical Bridgman crystal growth system modeled by Kim and Brown [90].
Kim and Brown varied the solutal Rayleigh number, $Ra_s$ during their analysis. They held the dimensionless liquidus slope fixed during the sequence of calculations. This does not correspond to varying the solute concentration, but is strictly equivalent to examining alloys with different values of the coefficient of solutal expansion, $\beta_s$. Multiple solutions were obtained for a given set of parameters which indicated that the steady state solver was perhaps not the best technique for thermo-solutal convective problems. Additionally, as pointed out by Motakef [96], Brown and co-workers have defined their non-dimensional parameters on physical characteristics of the system using the ampoule length and the overall temperature difference in the system. Motakef went on to derive the scaling laws which proved that convection intensity in the melt during growth in a gravitational field perpendicular to the growth surface is controlled by the non-planarity of the growth interface and the axial temperature gradient in the melt and that the correct scaling for the length was the crystal radius, $r_{cr}$. Therefore, the use of the ampoule length and the overall temperature difference in the system fails to identify the controlling scales of the solidification process.

In a subsequent paper [94] Kim and Brown addressed some of the shortcomings of their previous paper by performing a transient analysis on the growth of $Hg_{0.8}Cd_{0.2}Te$. They modeled the experimental setup of Lehoczky and colleagues [70] and used the crystal radius as the length scale. However, they still used the overall temperature difference in the system as their temperature scale. They included the segregation coefficient change (via the phase diagram), and accounted for the temperature and solutal dependence of density in their model. All other thermophysical properties were held constant. The authors rationalized that the sparsity of data did not justify attempts at incorporating very detailed correlation's of temperature and composition dependence of other thermophysical properties. They further argued that since the simulations covered a fairly narrow composition range, the properties should remain relatively constant.

The transient analysis was carried out for 1 cm of crystal growth and demonstrated the evolution from a well-mixed melt at the beginning of $HgCdTe$ growth to the diffusion-controlled solute segregation observed experimentally by Lehoczky.
and colleagues. Most importantly, the results show that, although the bulk of the flow field evolves on the slow time-scale for solute diffusion, the changes near the crystal-melt interface occur quickly enough that the solute field there is almost entirely controlled by diffusion after only a small fraction of the melt has been solidified (i.e., the build up of the solute boundary layer significantly damps convection). The only measurable effect of convection is to increase the radial segregation and interface deflection during the initial stages of growth.

This model predicts the basic phenomena of convective interference with radial segregation that is described in this thesis and several plots of the flow patterns during growth are given. However, these plots only give the stream function values and no further data is given to calculate a maximum flow velocity. Information on the fluid flow velocities and fluid flow patterns are necessary to draw definitive conclusions about the convective effects on interface morphology and segregation.

### 6.4.1 Order of Magnitude Estimates for Flow Velocity

One method to obtain the relative magnitude of flow velocity of the melt is to bound the value based on the 'basic physics' of the problem. To estimate flow regime transitions one can set the $Re \sim O(1)$ (see appendix E for meanings of non-dimensional parameters). This yields a velocity of $89 \mu m/sec$, using the radius of the crystal as the length scale. Therefore, for velocities $< 89 \mu m/sec$ the melt is experiencing a creeping or Stokes flow regime (lets not worry about the laminar to turbulent transition, as you will see later, the flow in this system does not approach this transition).

Similarly, setting $Pe_t$ and $Pe_s \sim O(1)$ will give an upper and lower bounds for the flow velocities in the system. The upper bounds will be when there is convective interference with heat transfer and the lower bounds will be when convection interferes with segregation. $Pe_t \sim O(1)$ calculations indicate that for velocities above $250 \mu m/sec$ convection is interfering with heat transfer. $Pe_s \sim O(1)$ calculations indicate for flow velocities greater than $1 \mu m/sec$ there will be convective interference with segregation. As indicated by this analysis, the flow velocity can be bounded by 1
\( \mu m/sec < V_{\text{max}} < 250 \mu m/sec \) and must be very small (well within the Stokes flow regime) in order for the mass transfer to be diffusion limited (see figure 2-2).

Consider also the driving forces for convection. It was shown in chapter 2 that the severity of convection is governed by equation 2.1, namely, the ratio of the thermal and solutal buoyant forces to the viscous forces. The ratio of these forces is given by the Rayleigh number,

\[
Ra_t = \frac{g \beta_t \Delta T_r L^3}{\nu \alpha} \quad \text{and} \quad Ra_s = \frac{g \beta_s \Delta C L^3}{\nu \alpha}
\]

(6.2)

where \( L^3 \) is the characteristic length scale of the system (for vertical Bridgman-Stockbarger growth the length scale is the crystal radius, \( r_c \)), \( \nu \) is the kinematic viscosity, \( \alpha \) is the thermal diffusivity and \( \Delta T_r \) is the radial temperature gradient. The relative magnitude of the thermal and solutal Rayleigh number is important for determining the amount of convection in the melt. Given Motakef's [44] scaling for the radial temperature gradient,

\[
\Delta T_r = \left( \frac{\partial T}{\partial Z} \right)_m \Delta \xi
\]

(6.3)

it would appear that all the parameters are known to calculate the \( Ra_t \). However, there is now a new unknown, the axial temperature gradient of the melt, \( \left( \frac{\partial T}{\partial Z} \right)_m \). The temperature gradient of the melt for \( HgCdTe \) can not be measured \textit{in situ} due to the high vapor pressure of \( Hg \) (\( \sim 30 \) ATM) at the processing temperature. However, Andrews et al [97] experimentally determined that for the \( Hg \) based II-IV systems the axial temperature gradient in the melt scales as one third the temperature gradient of the furnace bore,

\[
\left( \frac{\partial T}{\partial Z} \right)_m = \frac{1}{3} \left( \frac{\partial T}{\partial Z} \right)_f
\]

(6.4)

Substituting the above scaling laws for the radial temperature gradient into equation 6.2 gives an expression for the thermal Rayleigh number in terms of known physical

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quantities,

\[ Ra_t = g \beta \frac{1}{3} \left( \frac{\partial f}{\partial z} \right) \frac{\Delta \xi r_{cr}^3}{\nu \alpha}. \] (6.5)

Consider the stabilizing forces which are characterized by the solutal Rayleigh number. By analogy the solutal gradients should be proportional to the interface deflection, \( \Delta \xi \), and the axial solutal gradient in the melt, \( \frac{\partial C}{\partial z} \|_m \). Since the axial compositional profile in \( HgCdTe \) indicates diffusion limited growth (see figures 5-14, 5-23), the axial composition in the melt can be determined by the solution to the steady state continuity equation with appropriate boundary conditions. The solution to this equation is given by equation 2.15 and yields an expression for the axial composition of the melt as a function of the axial distance, \( z' \), from the crystal-melt interface. Differentiating equation 2.15 with respect to \( z' \) yields the following expression:

\[ \left( \frac{\partial C}{\partial z'} \right) = C_0 \left( \frac{k - 1}{k} \frac{R}{D_t} \exp^{-\left( \frac{g_{D_t}}{D_t} \right)} \right). \] (6.6)

Evaluating equation 6.6 at \( z' = \Delta \xi \) and multiplying by the crystal radius gives a representative value for the solutal difference, \( \Delta C \) as

\[ \Delta C = \left( \frac{\partial C}{\partial z'} \right)_{z' = \Delta \xi} \tau_{cr}. \] (6.7)

It should be noted that this will be an underestimate of the solutal gradient, by reason of its exponential nature, the real gradient is higher near the interface. Substituting equation 6.7 into equation 6.2 gives an expression for the solutal Rayleigh number in terms of known physical quantities,

\[ Ra_s = \frac{g \beta_s \left( \frac{\partial C}{\partial z} \right)_{z' = \Delta \xi}}{\nu \alpha} \tau_{cr}^4. \] (6.8)

Now using the thermophysical properties as listed in appendix A, the measured interface deflections and radial segregation from experiments MCT-D4 and MCT-D6 estimations for the thermal and solutal driving forces are given in table 6.1. The two
Table 6.1: Estimation of thermal Rayleigh numbers for growth with and without an applied magnetic field

<table>
<thead>
<tr>
<th></th>
<th>MCT-D6 (zero field)</th>
<th>MCT-D4 (50 kG field)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on interface deflection</td>
<td>Based on interface deflection</td>
<td></td>
</tr>
<tr>
<td>$\Delta \xi = 3 \text{ mm}$</td>
<td>$\Delta \xi = 1 \text{ mm}$</td>
<td></td>
</tr>
<tr>
<td>$Ra_t = 2300$</td>
<td>$Ra_t = 800$</td>
<td></td>
</tr>
<tr>
<td>Based on radial segregation</td>
<td>Based on radial segregation</td>
<td></td>
</tr>
<tr>
<td>$\Delta T_r = 15 \degree C$</td>
<td>$\Delta T_r = 3 \degree C$</td>
<td></td>
</tr>
<tr>
<td>$Ra_s = 4000$</td>
<td>$Ra_s = 900$</td>
<td></td>
</tr>
<tr>
<td>$Ra_s = -2.0 \times 10^6$</td>
<td>$Ra_s = -1.9 \times 10^6$</td>
<td></td>
</tr>
</tbody>
</table>

estimates of the $Ra_t$ given in table 6.1 were determined from different methods.

First the measured interface deflection obtained from the quenching experiments was used in equation 6.5 which yields an estimate of $Ra_t = 2300$ for the MCT-D6 experiment (zero field). The second estimate of $Ra_t = 4000$ was obtained by using the measured radial segregation shown in figure 5-20 and the phase diagram to calculate the radial temperature gradient, $\Delta T_r$. This radial temperature was then used in equation 6.2 to calculate the Rayleigh number. The two methods should produce the same results when the radial segregation is proportional to the interface curvature. Thus, the difference in the Rayleigh numbers in the zero field case indicates that the radial segregation is not proportional to the interface curvature. This difference is probably due to convective interference with segregation. For growth in a 50 kG magnetic field (MCT-D4) the two methods produced similar results for the Rayleigh numbers indicating that the magnetic field suppressed convection to the point that the measured radial segregation was proportional to the interface curvature. The estimate for the solutal Rayleigh numbers for the zero field and 50 kG field case were $-1.9 \times 10^6$ and $-2.0 \times 10^6$, respectively. The $Ra_s$ is approximately the same for both cases due to the fact that the crystal-melt interface deflection is much smaller than the solute boundary layer, $\Delta \xi \ll \frac{D_t}{R}$ (this important fact will be used later).
Figure 6-8: Geometry and boundary conditions for Hart’s problem. The box initially contains a linearly stratified salt solution.

**6.4.2 Analytical Results**

In order to quantify the amount of convection in the HgCdTe system the analytical model for double-diffusive convection by Hart [98] was utilized. This model was originally developed to study salinity gradients but has been shown to be applicable to non-dilute crystal growth systems [99]. Hart studied the stability of motion generated in a differentially heated vertical slot filled with a linearly stratified salt solution. The geometry and boundary conditions employed by Hart are shown in figure 6-8. The fluid is assumed to be initially linearly stratified and superimposed velocity, temperature and salinity fields are set up by imposing a quasi-statically increasing temperature difference across the plates. Hart also assumes that the aspect ratio, \( L/r \), is sufficiently large that for measurements conducted near the center of the apparatus the assumption of steady parallel mean flow is valid and that the Boussinesq approximation holds. With the infinite channel assumption the governing equations (equations 2.1, 2.4, 2.5) become linear and Hart gives the solution for the
non-dimensional velocity, $W_o$, across the channel as

$$W_o(x) = \frac{cosh M x \sin M x - Asinh M x \cos M x}{2M^3 B},$$

(6.9)

where $A$, $B$, and $M$ are given by

$$A = \frac{\tan \frac{M}{2}}{\tanh \frac{M}{2}},$$

(6.10)

$$B = \frac{\sin \frac{M}{2}}{\sinh \frac{M}{2}} + \frac{\cosh \frac{M}{2}}{\cos \frac{M}{2}},$$

(6.11)

$$M = \left(-\frac{Ra_s}{4}\right)^{\frac{1}{4}}$$

(6.12)

Figure 6-9 shows how the profiles change as $M$ increases (i.e., larger stabilizing
It should be noted that there is always a motion field although this becomes small as $M$ becomes large. Based on Hart’s scaling a dimensional form of velocity can be determined from the relationship,

$$ V(x) = \frac{W_0 g \beta_\tau \Delta T r^2}{v} $$

Using Hart’s analysis and the parameters ($Ra_s$ and $\Delta T_r$) for the HgCdTe system given in table 6.1, velocity profiles for the zero field and 50 kG field cases are shown in figure 6-10. The maximum fluid velocity for growth without an applied magnetic field is approximately 10 $\mu m/s$. This is one order of magnitude greater than the velocity required for diffusion limited growth as determined from $Pe_s \sim O(1)$ calculations and convective interference with radial segregation is expected, see figure 5-16. The maximum velocity for growth with a 50 kG magnetic field is 2 $\mu m/s$ which is on
the same order as the diffusion limited velocity and corresponding radial segregation is nearly uniform, see figure 6-4. An important question to raise is how accurate is Hart's analysis in predicting the maximum flow velocities in the HgCdTe system. One way to check this is to compare Hart's analytical work to computational fluid dynamic modeling results. As previously mentioned, Kim and Brown [94] do not present their results in a suitable manner to determine the maximum velocity in the system. However, they do state that their results agree with Hart's analysis to the extent that there is a semi quiescent region near the center of the melt where the solutal stabilizing forces effectively damp convection and the maximum velocities occur near the ampoule wall. From private communication with Alexander [100], his CFD model for the Hg0.8Cd0.2Te system predicts maximum velocities on the order of 25 μm/s. Therefore, it appears that Hart's analysis is capable of predicting the maximum fluid velocities in the melt.

It is of interest to note that if the flows in the HgCdTe system are indeed as slow as predicted by this analysis a smaller magnetic field should produce uniform radial segregation. To this end, growths with magnetic field strengths of 20, 10 and 5 kG were performed and in all cases the radial segregation was as uniform as that obtained with a 50 kG magnetic field.

Figure 6-11 shows the radial segregation obtained with an applied 5 kG magnetic field. This clearly shows that an order of magnitude change in field strength still produced a radially uniform crystal. Thus, it appears that the fluid is sufficiently damped by the application of a relatively small field.

In an effort to further quantify the effects of the magnetic field on the radial segregation, the experimental results were compared to the analysis of the lateral solute segregation associated with a curved crystal-melt interface during steady-state unidirectional solidification of a binary alloy as derived by Coriell and Sekerka and described in detail in references [57], [58]. Briefly, they solved the species continuity equation (equation 2.5) for the radial solute concentration in the solid crystal at the crystal-melt interface with the assumptions of no convection in the liquid and that the crystal-melt interface could be represented by a Fourier series. Their work
Figure 6-11: Radial composition distribution obtained for growth with an applied 5 \textit{kG} magnetic field. A reduction in field strength by an order of magnitude is found to result in uniform radial segregation.
Table 6.2: Comparison of experimental and the calculated diffusion-limited radial segregation according to the Coriell and Sekerka theory

<table>
<thead>
<tr>
<th>Radial segregation</th>
<th>MCT-D6 (zero field)</th>
<th>MCT-D4 (50 kG field)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\Delta C}{C_o} )_theory</td>
<td>0.38</td>
<td>0.13</td>
</tr>
<tr>
<td>( \frac{\Delta C}{C_o} )_expt</td>
<td>0.45</td>
<td>0.10</td>
</tr>
</tbody>
</table>

showed that in the limiting case \( \Delta \xi \ll \frac{D_l}{R} \), the transverse segregation in the solid is proportional to the deviation of the interface from planarity, the proportionality factor being just the product of the unperturbed concentration gradient and the distribution coefficient given by

\[
\frac{\Delta C}{C_o} = \frac{(k - 1)R}{D_l} \Delta \xi
\]

where \( \Delta C \) is the difference in composition at the edge and center of the crystal, \( k \) is the equilibrium segregation coefficient, \( R \) is the translation rate and \( \Delta \xi \) is the interface deflection. These calculations are applicable for crystal growth in a stabilizing magnetic field where the field strength is sufficient to suppress convection. The crystal-melt interface deflection necessary for the calculations was determined experimentally from the quenching experiments as shown in figures 5-18 and 6-5.

Table 6.2 is a comparison of the experimental and theoretical results. For this calculation, the steady-state equilibrium segregation coefficient, \( k = 4.2 \), was determined experimentally by measuring the compositional change across a quenched interface in the steady-state region of crystal growth and compares well with the value of 4.0 as determined from the equilibrium phase diagram. The mass diffusion coefficient, \( D_l = 5.5 \times 10^{-5} \text{ cm}^2/\text{s} \), was determined by a best fit of the experimental axial compositional data to the one-dimensional diffusion-limited model of Clayton et al [88] and is consistent with the value obtained by Lehoczky et al [70]. The comparison of the various experimental and calculated results suggest that the radial segregation for the zero field case slightly exceeds the value predicted by the non-planarity of the crystal-melt interface, whereas, the growth in the magnetic field agrees well with the theory.
The Coriell formalism is developed for a 2-D rectangular geometry which does not completely describe the crystal growth geometry in the $HgCdTe$ system. To rectify this problem a numerical code based on the Coriell formalism was developed by Wang and Watring [101] to predict the radial compositional distributions in $HgCdTe$. The configuration used was a cylindrical system at steady-state growth conditions and the crystal-melt interface was expressed in terms of a series combination of Bessel’s functions. The details of this analysis are given in appendix B.

Figure 6-12 is a comparison of the zero field experimental data and the theory based on the Coriell formalism. There is good agreement in the center of the wafer.
However, there is an approximately 20% disagreement near the edge of the wafer. The agreement near the center is probably due to the fact that the melt velocity near the center of the crystal is essentially zero and the disagreement near the edge is due to the maximum flow velocities occurring near the ampoule wall as predicted by Hart [98] and Kim and Brown [94]. The radial segregation for growth in a 50 kG magnetic field is shown in figure 6-13. There is excellent agreement with the theory and indicates that the radial segregation is approaching the diffusion limited regime.
6.5 Comparison with Microgravity Crystal Growth Results

A $Hg_{0.8}Cd_{0.2}Te$ alloy crystal was grown in the microgravity environment aboard the space shuttle during the Second United States Microgravity Mission in March 1994. The grown ingot was approximately 16 cm long and 0.72 cm in diameter. During the mission portions of ingot were grown while the orbiter was in different attitudes. The influence of orbiter attitude and, hence, the residual drag acceleration on the growth process was investigated by examining the radial composition of the ingot during the $+YVV/-ZLV$ and $-ZVV/-XLV$ portions of the mission, see figure 6-14. It is imperative to note that this is the one and only $HgCdTe$ experiment performed in microgravity. Thus, conclusions based on the results of the microgravity experiment, are made with the caveat that they are based on one experiment and additional microgravity data is necessary to draw definitive conclusions.

The radial compositional profiles for the different attitudes are shown in figure 6-15. These measurements were taken at 15 degree intervals at circumferences within the sample at progressively increasing distances from the edge, and starting at 100 $\mu$m in from the edge. As can be seen, the asymmetry in the compositional variation across the 63 mm wafer ($+YVV/-ZLV$ attitude) shown in figure 6-15a shows a definite correlation with the direction of the residual acceleration vector resolved on this plane. This growth configuration is unstable in that there is a residual acceleration component in the direction of solid to liquid of 0.28 $\mu g$. This coupled with the 0.55 $\mu g$ transverse component lead to an asymmetric compositional distribution. In the 106 mm wafer ($-ZVV/-XLV$ attitude), the material is more homogeneous, this being presumable due to the stabilizing effect of the vector from liquid to solid of 0.50 $\mu g$, even though there is a high transverse vector of 1.55 $\mu g$. In figure 6-16, the radial segregation of the 106 mm wafer is compared to the diffusion limited theory developed in appendix B. The experimental data agrees with the theory in the center of the wafer. However, there is a large discrepancy near the edge of the crystal. This can be attributed to the maximum flow velocities being near the ampoule wall as predicted.
Figure 6-14: Components of residual acceleration at AADS during USMP-2.
Figure 6.15: (a) Radial compositional map for the +YVV/-ZLV attitude (63 mm), (b) radial compositional map for the -ZVV/-XLV attitude (106 mm), (c) radial compositional map for a sample grown in a 50 kG magnetic field (69 mm).
by the numerical model of Kim and Brown [94] and analytically by Hart's model [98]. The temperature of the interface based on the phase diagram is also plotted in figure 6-16. Due to the asymmetry of the data the radial temperature gradient ranges from 15 °C to 25 °C. This gradient is on the same order as the radial gradients obtained during the zero magnetic field portion of this work which indicates that the interface deflection and maximum velocities were also on the same order. Thus, the data suggest that radial composition distribution in low gravity is highly sensitive to the orientation and magnitude of the residual acceleration forces. Any misalignment of the gravity vector can produce fluid flow on the same order as experienced on earth.

The compositional profile for growth in a 50 kG magnetic field is shown in figure 6-15c for comparison. The compositional distribution is more uniform and symmetric which indicates that the magnetic field is effective in suppressing convection that may result from any misalignment with the gravity vector under 1 g conditions.

6.6 Summary of Magnetic Field Results

The effects of applied magnetic fields on segregation in HgCdTe can be summarized as follows:

The axial compositional profile remained relatively unaffected during the initial transient and steady state portions of crystal growth. However, an abrupt rise in CdTe content was observed during solidification near the end of the ingot. This rise was attributed to the build up of a diffusion controlled solute boundary layer (close to the crystal-melt interface) which leads to constitutional supercooling. Experimental results for growth in magnetic fields published in the open literature confirm this phenomena. Interface curvature decreased threefold with a corresponding decrease in radial segregation which agreed well with the diffusion limited theory. Order of magnitude scaling and analytical analysis estimated the velocity for conventional growth to be an order of magnitude greater than that required for diffusion limited growth and large radial segregation was predicted and confirmed in the zero field experiments. For growth in an applied magnetic field the maximum flow velocity was
Figure 6-16: Radial compositional distribution for growth of $HgCdTe$ in microgravity during the USMP-2 mission.
on the same order as the diffusion limited velocity and uniform radial segregation that was proportional to the curvature of the crystal-melt interface was achieved.

In microgravity crystal growth a strong correlation was observed between radial segregation and the relative magnitude and orientation of the residual acceleration due to drag. If the drag vector is not aligned parallel to the growth direction (liquid to solid) three dimensional fluid flow will result which destroys the symmetry of the system and leads to non-uniform radial segregation.
Chapter 7

Conclusions and Recommendations for Future Work

In order to achieve homogeneous semiconductor crystals through melt stabilization during the crystal growth process, $Hg_{1-x}Cd_xTe$ crystals were grown by the Bridgman-Stockbarger method in space and on the ground in the presence and absence of magnetic fields up to $50 \, kG$. A crystal growth system was designed with a thermal environment similar to that of the NASA microgravity crystal growth furnace to permit a direct comparison with results observed in a microgravity environment. The influence of convection, by magneto hydrodynamic damping, on mass transfer in the melt was investigated by measuring axial and radial compositional variations in the grown samples. The results of the no-field and field growths were then compared with existing computational fluid dynamic models and analytical analysis in order to quantify the effects of the imposed magnetic field on convection and segregation in the $HgCdTe$ system.

The principal finding of the work may be summarized as follows:

(1) For conventional growth in a vertical Bridgman-Stockbarger configuration, the axial compositional profile of the resolidified charge experienced an initial transient,
then a steady state behavior of relatively constant composition followed by a final transient. This axial composition distribution compares well with the results calculated with a one-dimensional model and suggests that the axial composition profile of CdTe is dominated by diffusion. This axial composition also compares well with the results discussed in the open literature for the past 15 years and with the results obtained during the ground based portion of a microgravity experiment. The results indicated that the furnace was well characterized and the results could be directly compared with those obtained in a microgravity growth experiment.

(2) Radial segregation profiles obtained during growth in the absence of magnetic melt stabilization showed large radial variations which were not proportional to the crystal-melt interface curvature. This effect was attributed to intense convection (as compared to the growth velocity) near the crystal-melt interface interfering with radial segregation.

(3) The crystal-melt interface obtained during growth without a magnetic field was symmetric and concave toward the solid with a maximum deflection of 3.25 mm for a crystal radius of 4 mm. This curvature is attributed to double-diffusive convection resulting in the accumulation of Hg-rich material at the center of the melt just ahead of the growth interface. This phenomenon, in turn, increases the interface curvature because of the nature of the pseudo binary HgTe-CdTe phase diagram.

(4) Axial magnetic fields were applied during crystal growth in order to reduce the velocity of the melt via magneto hydrodynamic interactions. The achieved reduction in convection significantly altered the overall segregation process associated with growth. Axial compositional distribution was relatively unaffected during the initial transient and steady state growth portions of the solidification process. However, an abrupt rise in the CdTe content was observed near the end of the ingot, an effect, which was attributed to constitutional supercooling brought about by the magnetic suppression of convection near the crystal-melt interface. It, in turn, results in an
increase in the slope of the diffusion-controlled solute boundary layer. Experiments with decreased growth rates verified this "hypothesis".

(5) It was found that growth in a 5 kG magnetic field was sufficient to suppress the convective intensity in the melt prior to growth to the point where $Pe_s \sim O(1)$. As growth is initiated, a crystal-melt interface (concave into the solid) is generated due to the differences in thermal conductivities of the melt, solid and confining crucible. However, no convective transport of $HgTe$ to the center of the ampoule takes place and the resulting interface deflection (1.1 mm) was a factor of three smaller than that obtained without the magnetic field.

(6) The radial segregation for all growth experiments in the magnetic field was proportional to the crystal-melt interface curvature as predicted by diffusion limited theory.

(7) During crystal growth in a microgravity environment, a pronounced correlation exists between the relative magnitude and orientation of the residual acceleration due to drag and the segregation behavior. If the drag vector is not aligned parallel to the growth direction (liquid to solid) three dimensional fluid flow will result which destroys the symmetry of the system and leads to non-uniform radial segregation.

Perhaps the most interesting finding of this research is that convective interference with segregation and the growth interface morphology in the $HgCdTe$ system is quite subtle. By reducing fluid flow from 10 $\mu m/s$ (no magnetic field) to 2 $\mu m/s$ (magnetic field), the crystal-melt interface deviation from planarity was reduced significantly. This is attributed to the large separation of the liquidus and solidus phases in the $HgCdTe$ system which produces a highly composition dependent crystal-melt interface and segregational behavior. The importance of the solutal term compared to the thermal term on density should be noted. A change of 5% in composition has the same effect on density as a 150 °C change in temperature. Therefore, a small reduction in fluid flow (i.e., reducing the build-up of the solute at the sample center)
will tend to produce a more planar crystal-melt interface. This effect can be minimized by judiciously choosing the thermal boundary conditions. Additionally, this study indicates that the interaction of the thermal, solutal and momentum fields in HgCdTe systems are highly coupled. The modification of these complex interactions, through, for example, the application of a magnetic field or processing in space, can significantly alter the interface morphology and compositional homogeneity. Therefore, any attempts at modeling these systems should involve the fully coupled form of the governing equations.

7.1 Recommendations for Future Work

As this work dealt only with the compositional uniformity, there are several areas were this work should be continued. For example:

(1) A detailed analysis of the carrier concentration and electron mobility of the grown crystals should be conducted.

(2) Microstructural analysis should be performed on the samples to determine if there is a correlation between homogeneity and defect location, defect densities, low angle grain boundaries and second phase inclusions.

(3) It is recommended that several additional crystal growth experiments be performed with the magnetic field. Suggested studies include: Determination of the minimal magnetic field required to produce uniform radial segregation for the geometry studied in this thesis. The furnace and crystal growth parameters should be refined in order to produce a more planar crystal-melt interface. Control schemes should be incorporated into the growth procedure which could be used to keep the crystal-melt interface at a fixed location relative to the furnace during growth by automatically compensating for unavoidable transient effects. For example, this could be accomplished through appropriate changes in power input to the heaters [109].
In order to improve the computational fluid dynamic models, better values of the thermophysical properties are necessary. Therefore, it is recommended that an extensive program be developed to determine thermophysical properties and their dependence on temperature and composition. This should include electrical conductivity of the melt as this parameter is critical to determine relative effectiveness of the magnetic field in suppressing convection.

Once the pertinent thermophysical properties are known numerical simulations which explore the effect of magnetic fields on the suppression of convection in vertical Bridgman-Stockbarger crystal growth of $HgCdTe$ should be carried out. These simulations should utilize the proper scaling parameters and include the specific furnace geometry. Furthermore, the semitransparency of the containing quartz ampoule must be taken into account in the models. By including a specific furnace/ampoule geometry, these models, once validated with experimental results, can be used to develop an approach which permits active control of the interface morphology and radial segregation.
Appendix A

Thermophysical Properties of HgCdTe

The choice material for IR applications has long been $Hg_{1-x}Cd_xTe$. In order obtain quality crystals by optimization of the crystal growth parameters, detailed thermophysical property data is necessary.

One of the most complete studies of $HgCdTe$ properties has been the work of Lehoczky and colleagues. They have determined many of thermophysical properties such as: the effective mass diffusion coefficient [70]; liquid thermal diffusivity [76]; kinematic viscosity [77]; liquid density [79]; heat capacity, enthalpy of mixing, thermal conductivity [80] and the establishment of the phase diagram [78]. Another excellent reference on the properties of $HgCdTe$ is the text "Properties of Mercury Cadmium Telluride," edited by J. Brice and P. Capper [102]. If detailed relationships for the thermophysical property dependence on temperature and composition is necessary, the reader should review the above references.

For this thesis, the values of the thermophysical properties used in the scaling/analytical analysis are listed in table A.1 and the corresponding phase diagram, temperature dependence of the $CdTe$ segregation coefficient and composition dependence of the $CdTe$ segregation coefficient are shown in figures A-1, A-2, A-3, respectively. The values listed in table A.1 were evaluated at specific temperatures in order to have a direct comparison of the analytical/scaling analysis developed in
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Thermal Conductivity, $K_m$ @ 800 °C</td>
<td>$1.88 \times 10^{-2} \text{ W cm}^{-1} \text{K}^{-1}$</td>
<td>[80]</td>
</tr>
<tr>
<td>Solid Thermal Conductivity, $K_s$ @ 600 °C</td>
<td>$8.37 \times 10^{-3} \text{ W cm}^{-1} \text{K}^{-1}$</td>
<td>[80]</td>
</tr>
<tr>
<td>Melt Density, $\rho_m$ @ 810 °C</td>
<td>$7.55 \times 10^{-3} \text{ g cm}^{-3}$</td>
<td>[79]</td>
</tr>
<tr>
<td>Solid Density, $\rho_s$</td>
<td>$7.65 \times 10^{-3} \text{ g cm}^{-3}$</td>
<td>[103]</td>
</tr>
<tr>
<td>Melt Specific Heat, $C_{p,m}$</td>
<td>$2.04 \times 10^{-1} \text{ J g}^{-1} \text{K}^{-1}$</td>
<td>[80]</td>
</tr>
<tr>
<td>Solid Specific Heat, $C_{p,s}$</td>
<td>$1.64 \times 10^{-1} \text{ J g}^{-1} \text{K}^{-1}$</td>
<td>[102]</td>
</tr>
<tr>
<td>Kinematic Viscosity, $\nu$ @ 800 °C</td>
<td>$3.57 \times 10^{-3} \text{ cm}^{2} \text{sec}^{-1}$</td>
<td>[77]</td>
</tr>
<tr>
<td>Latent Heat of Solidification, $\Delta H_{sl}$</td>
<td>$130 \text{ J g}^{-1}$</td>
<td>[105]</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient, $\beta_t$ @ 800 °C</td>
<td>$1.5 \times 10^{-4} \text{ cm} \text{K}^{-1}$</td>
<td>[94]</td>
</tr>
<tr>
<td>Solutal Expansion Coefficient, $\beta_s$ @ 800 °C</td>
<td>$-0.3 \text{ mole frac CdTe}$</td>
<td>[94]</td>
</tr>
<tr>
<td>Melt Thermal Diffusivity $\alpha_m$ @ 800 °C</td>
<td>$1.2 \times 10^{-2} \text{ cm}^{2} \text{sec}^{-1}$</td>
<td>[102]</td>
</tr>
<tr>
<td>Electrical conductivity, $\sigma_{HgCd}$ @ 800 °C</td>
<td>$1.6 \times 10^{-3} \text{ S cm}^{-1}$</td>
<td>[104]</td>
</tr>
</tbody>
</table>

Table A.1: Thermophysical properties of $Hg_{0.8}Cd_{0.2}Te$ for use in scaling/analytical analysis.

This thesis contributes to the CFD work of Kim and Brown [94].
Figure A-1: Phase diagram of $\text{Hg}_{90.8}\text{Cd}_{0.2}\text{Te}$ as determined by Szofran and Lehoczky [91].
Figure A-2: Temperature dependence of the CdTe segregation coefficient as determined by Lehoczky et al [70].
Figure A-3: Compositional dependence of the CdTe segregation coefficient as determined by Szofran and Lehoczky [70].
Appendix B

Diffusion Limited Theory

The purpose of this appendix is to present a calculation of the radial segregation associated with a non-planar crystal-melt interface during directional solidification of a binary alloy. For these calculations it is assumed that there is no convection in the liquid. A condition which should be applicable for crystal growth in a stabilizing magnetic field and in the reduced gravity environment of space. The central premise of our model is the same as that used by Coriell and Sekerka [57]. That is, the radial segregation can be calculated solely from a knowledge of the interface morphology and a consistent solution of the diffusion equation. As the basic physics of heat flow are represented by the interface morphology, this allows for the uncoupling of the governing equations and significantly simplifies the solution.

B.1 Theory

The system under study is an azimuthal symmetric cylindrical system with a curved crystal-melt interface shape at uniform unidirectional solidification shown schematically in figure B-1. Assuming the system is under steady state diffusion limited growth and scaling the solute concentration by the bulk concentration, $C_0$ and the length by the crystal radius, $r_{rc}$, the governing equation for diffusion limited growth is

$$\frac{\partial^2 C(r, z)}{\partial r^2} + \frac{1}{r} \frac{\partial C(r, z)}{\partial r} + \frac{\partial^2 C(r, z)}{\partial z^2} + \beta \frac{\partial C(r, z)}{\partial z} = 0$$  (B.1)
Figure B-1: Geometry associated with unidirectional solidification with a non-planar crystal-melt interface.

\[
C(r,z) = 1; \quad z \to \infty
\]

\[
\beta(k-1)C_1(r,z) = \frac{\partial C_1(r,z)}{\partial z} - \frac{\partial C_1(r,z)}{\partial r} \frac{\partial \Psi(r)}{\partial r}
\]

\[
\frac{\partial C(r,z)}{\partial r} = 0 \quad @ \quad r = 1
\]
where \( \beta = \frac{V}{D} \) in which \( V \) is the growth velocity and \( D \) is the diffusion constant of the solute in the liquid. The boundary conditions are

\[
C(r, z) = 1, \quad \text{for} \quad z \to \infty; \tag{B.2}
\]

\[
\frac{\partial C(r, z)}{\partial r} = 0 \quad \text{at} \quad r = 1; \tag{B.3}
\]

\[
\beta(k - 1)C_I(r, z) = \frac{\partial C_I(r, z)}{\partial z} - \frac{\partial C_I(r, z)}{\partial r} \frac{\partial W(r)}{\partial r} \tag{B.4}
\]

where \( W(r) \) is the crystal-melt interface shape and \( k \) is the equilibrium segregation coefficient.

First, let's consider the special case where the interface is planar i.e., \( W(r) = W_0 \) where \( W_0 \) is a constant. In this case equation B.1 reduces to

\[
\frac{\partial^2 C(r, z)}{\partial z^2} + \beta \frac{\partial C(r, z)}{\partial z} = 0 \tag{B.5}
\]

which is a homogenous second order P.D.E. with constant coefficients. The solution of equation B.5, as first given by Tiller and colleagues [49] and as readily obtained with the aid of boundary conditions B.2 and B.4, is

\[
C(z) = \frac{(1 - k)}{k} \exp^{-\beta(z - W_0)} + 1. \tag{B.6}
\]

To solve equation B.1 for the more general case we will use the separation of variables technique which assumes as a working hypothesis that

\[
C(r, z) = R(r)Z(z) \tag{B.7}
\]

is a solution to equation B.1. Taking the respective partial derivatives and substituting them into equation B.1 gives

\[
Z(z) \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} \right] + R(r) \left[ \frac{\partial^2 Z(z)}{\partial z^2} + \frac{\partial Z(z)}{\partial z} \right] = 0 \tag{B.8}
\]
dividing the above equation by $R(r)Z(z)$ and then separating variables yields

$$
\frac{1}{R(r)} \left[ \frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} \right] = \frac{-1}{Z(z)} \left[ \frac{\partial^2 Z(z)}{\partial z^2} + \frac{\partial Z(z)}{\partial z} \right]
$$

(B.9)

which is a necessary condition that $C(r, z) = R(r)Z(z)$ be a solution. Now the left hand side of equation B.9 is clearly independent of $z$. Hence (in spite of its appearance) the right hand side of equation B.9 must also be independent of $z$, since it is identically equal to the expression on the left. Similarly, each member of equation B.9 must be independent of $r$. Therefore, being independent of both $r$ and $z$, each side must be a constant, say $u$. This constant can be positive, negative or zero. Thus, each case must examined to see when the solution has physical meaning.

### B.2 Case 1 ($u = 0$)

For the case when $u = 0$, equation B.9 yields

$$
\frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} = 0
$$

(B.10)

whose solution is

$$
R(r) = A_1 \ln(r) + A_2
$$

(B.11)

and

$$
\frac{\partial^2 Z(z)}{\partial z^2} + \beta \frac{\partial Z(z)}{\partial z} = 0
$$

(B.12)

whose solution is

$$
Z(z) = B_1 \exp^{-\beta z} + B_2.
$$

(B.13)

Therefore, the solution from $C(r, z) = R(r)Z(z)$ is

$$
C(r, z) = (A_1 \ln(r) + A_2)(B_1 \exp^{-\beta z} + B_2)
$$

(B.14)

As this solution can not satisfy the boundary condition B.3, $u = 0$ is not a possible solution.
B.3 Case 2 \((u > 0)\)

If \(u > 0\) we can write \(u = \eta^2\) \((\eta > 0)\). In this case the two differential equations are

\[
\frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} - \eta^2 R(r) = 0
\]

which is a modified Bessel equation whose solution is given by

\[
R(r) = A_1 I_0(\eta r) + A_2 K_0(\eta r)
\]

and

\[
\frac{\partial^2 Z(z)}{\partial z^2} + \beta \frac{\partial Z(z)}{\partial z} + \eta^2 Z(z) = 0
\]

whose solution is

\[
Z(z) = B_1 \exp^{\eta_1 z} + B_2 \exp^{\eta_2 z}
\]

where

\[
q_{1,2} = -\frac{\beta}{2} \left[1 \pm \sqrt{1 - \left(\frac{2\eta}{\beta}\right)^2}\right].
\]

Again, a solution of the form

\[
C(r, z) = R(r)Z(z) = [A_1 I_0(\eta r) + A_2 K_0(\eta r)][B_1 \exp^{\eta_1 z} + B_2 \exp^{\eta_2 z}]
\]

can not satisfy the boundary condition B.3 (i.e., \(\frac{\partial I_0(\eta r)}{\partial r} = 0\) can not have real roots).

B.4 Case 3 \((u < 0)\)

Finally, if \(u < 0\), we can write \(u = -\alpha^2(\alpha > 0)\). Then the component differential equations and their solutions are

\[
\frac{\partial^2 R(r)}{\partial r^2} + \frac{1}{r} \frac{\partial R(r)}{\partial r} - \eta^2 R(r) = 0
\]

\[
\frac{\partial^2 Z(z)}{\partial z^2} + \beta \frac{\partial Z(z)}{\partial z} + \eta^2 Z(z) = 0
\]
which is a zero order Bessel equation whose solution is

\[ R(r) = A_1 J_0(\alpha r) + A_2 Y_0(\alpha r). \]  

(B.22)

Since \( Y_0(0) = -\infty \), we need \( A_2 = 0 \) for meaningful solutions and for the second differential equation

\[ \frac{\partial^2 Z(z)}{\partial z^2} + \beta \frac{\partial Z(z)}{\partial z} - \alpha^2 Z(z) = 0 \]  

(B.23)

the solution is

\[ Z(z) = B_1 \exp q_1 z + B_2 \exp q_2 z \]  

(B.24)

where

\[ q_{1,2} = -\frac{\beta}{2} \left[ 1 \pm \sqrt{1 + \left(\frac{2\alpha}{\beta}\right)^2} \right]. \]  

(B.25)

For large \( z \), \( Z(z) \) will grow exponentially due to the second term. Thus, we must set \( B_2 = 0 \) for meaningful solutions. This equation will then satisfy the boundary conditions given in equations B.2 and B.3.

In this case the solution is given by

\[ C(r, z) = R(r)Z(z) = A J_0(\alpha r) \exp -\frac{\beta}{2} \left[ 1 + \sqrt{1 + \left(\frac{2\alpha}{\beta}\right)^2} \right] z. \]  

(B.26)

Therefore, the most general solution to equation B.1 is a combination of equation B.26 and the solution for a planar interface given in equation B.6 i.e.;

\[ C(r, z) = 1 + \frac{(1 - k)}{k} \exp -\beta(z - W_0) + A J_0(\alpha r) \exp -\frac{\beta}{2} \left[ 1 + \sqrt{1 + \left(\frac{2\alpha}{\beta}\right)^2} \right] z. \]  

(B.27)

Applying the boundary condition \( \frac{\partial C(r, z)}{\partial r} = 0 \) at \( r = 0 \) on equation B.27 leads to

\[ \frac{\partial C(r, z)}{\partial r} = A \left[ \frac{\partial J_0(\alpha r)}{\partial r} \right] \exp -\frac{\beta}{2} \left[ 1 + \sqrt{1 + \left(\frac{2\alpha}{\beta}\right)^2} \right] z = 0. \]  

(B.28)

Therefore,

\[ \frac{\partial J_0(\alpha r)}{\partial r} = -\alpha J_1(\alpha r) = 0 \]  

(B.29)
which will give definite values for $\alpha$. Letting $\alpha = u_n$ for $n = 0 \to \infty$ and setting

$$P(n) = \sqrt{1 + \left(\frac{2\alpha}{\beta}\right)^2}$$  \hspace{1cm} (B.30)$$

the solution can be written as

$$C(r, z) = 1 + \frac{(1 - k)}{k} \exp^{-\beta(z-W_0)} + \sum_{n=1}^{\infty} A_n J_0(u_n r) \exp^{-\beta z [1 + P(n)]}.$$  \hspace{1cm} (B.31)$$

The final boundary condition that must be satisfied by equation B.31 is

$$\beta(k - 1) C_1(r, z) = \frac{\partial C_1(r, z)}{\partial z} - \frac{\partial C_1(r, z)}{\partial r} \frac{\partial W(r)}{\partial r}$$  \hspace{1cm} (B.32)$$

where the subscript $I$ denotes near the crystal-melt interface. If we assume that the crystal-melt interface can be expressed as a series combination of Bessel's functions given by

$$W(r) = W_0 + \sum_{n=1}^{\infty} \delta(n) J_0(u_n r); \quad \text{with} \quad J_1 = 0$$  \hspace{1cm} (B.33)$$

equation B.32, with the aid of equations B.31 and B.33, can be written as

$$\sum_{n=1}^{\infty} \left[\beta(1 - k) + \frac{\beta}{2} [1 + P(n)]\right] A_n J_0(u_n r) \exp^{-\beta z [1 + P(n)]}$$

$$- \sum_{n=1}^{\infty} u_n A_n J_1(u_n r) \exp^{-\beta z [1 + P(n)]} \frac{\partial W(r)}{\partial r}$$

$$= - \left[\beta(k - 1) + \beta(1 - k) \exp^{\beta(z-W_0)}\right].$$  \hspace{1cm} (B.34)$$

The solution of equation B.34 for the coefficients, $A_n$, is rather cumbersome. However, if the solution is restricted to the cases were:

1. $\beta << 1$ (i.e., the solutal boundary layer is thick as compared to the deviation of the interface from planarity) and $z << 1$ (i.e., we are considering results very near the crystal-melt interface) such that the exponential term can be approximated by

$$\exp^{-\beta(z-W_0)} \approx 1 - \beta \sum_{n=1}^{\infty} \delta(n) J_0(u_n r)$$  \hspace{1cm} (B.35)$$

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and the case where

\[ u_n \frac{\partial w(r)}{\partial r} << \left[ \beta(k - 1) + \frac{\beta}{2}[1 + P(n)] \right] \]

equation B.34 reduces to

\[ \sum_{n=1}^{\infty} \left[ \beta(k - 1) + \frac{\beta}{2}[1 + P(n)] \right] A_n J_0(u_n r) = \sum_{n=1}^{\infty} \beta^2(1 - k)\delta(n)J_0(u_n r). \quad (B.36) \]

Solving for \( A_n \) we obtain

\[ A_n = \frac{2\beta(1 - k)\delta(n)}{2k + P(n) - 2}. \quad (B.37) \]

By substituting equation B.37 into equation B.31 the expression for the composition of the solute in the liquid near the crystal-melt interface can be written as

\[ C_I(r, z) = 1 + \frac{(1 - k)}{k}\exp^{-\beta(z-w_0)} + \sum_{n=1}^{\infty} \frac{2\beta(1 - k)\delta(n)}{2k + P(n) - 2} J_0(u_n r) \exp^{-\frac{\beta}{2}[1+P(n)]z}. \quad (B.38) \]

Noting that \( C_{SI} = kC_I \) the expression for the solute concentration in the solid near the interface is

\[ C_{SI}(r, z) = k + (1 - k)\exp^{-\beta(z-w_0)} + \sum_{n=1}^{\infty} \frac{2\beta k(1 - k)\delta(n)}{2k + P(n) - 2} J_0(u_n r) \exp^{-\frac{\beta}{2}[1+P(n)]z}. \quad (B.39) \]

Equations B.38 and B.39 can now be solved using a numerical package such as MATLAB or MAPLE to determine the radial segregation in the grown ingots.
B.5 Further Simplifications/Limiting Cases

Applying the two restrictions used earlier to obtain the coefficients, $A_n$, to equations B.38 and B.39 we obtain

$$C_I = \frac{1}{k} - \frac{\beta(1-k)}{k} \sum_{n=1}^{\infty} \frac{\delta(n)J_0(u_nr)}{1 + \frac{2k}{P(n)-1}}; \quad (B.40)$$

and

$$C_{SI} = 1 - \beta(1-k) \sum_{n=1}^{\infty} \frac{\delta(n)J_0(u_nr)}{1 + \frac{2k}{P(n)-1}} \quad (B.41)$$

which are simpler expressions for the radial segregation.

It is of interest to note, that in the limiting case that $\frac{2k}{P(n)-1} << 1$, equation B.41 reduces to

$$C_{SI}(r) = 1 - \beta(1-k)[W(r) - W_0]; \quad (B.42)$$

which implies that the radial segregation is proportional to the deviation of the interface from planarity. This limiting case is consistent with the expression first derived by Coriell and Sekerka [57].
## Appendix C

### Scaling Laws

<table>
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<tr>
<th>Name</th>
<th>Meaning</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
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<td>Prandtl No.</td>
<td>Viscous diffusivity</td>
<td>$Pr = \frac{\nu}{\alpha}$</td>
</tr>
<tr>
<td>Schmidt No.</td>
<td>Viscous diffusivity</td>
<td>$Sc = \frac{\nu}{D}$</td>
</tr>
<tr>
<td>Thermal Peclet No.</td>
<td>Convective heat transfer</td>
<td>$Pe_t = \frac{V_L}{\alpha}$</td>
</tr>
<tr>
<td>Solutal Peclet No.</td>
<td>Diffusive heat transfer</td>
<td>$Pe_s = \frac{V_L}{D}$</td>
</tr>
<tr>
<td>Reynolds No.</td>
<td>Inertia force</td>
<td>$Re = \frac{V_L}{\nu}$</td>
</tr>
<tr>
<td>Thermal Grashof No.</td>
<td>Thermal buoyancy force</td>
<td>$Gr_t = \frac{g\beta \Delta T L^3}{\nu^2}$</td>
</tr>
<tr>
<td>Solutal Grashof No.</td>
<td>Solutal buoyancy force</td>
<td>$Gr_s = \frac{g\beta_s \Delta C L^3}{\nu^2}$</td>
</tr>
<tr>
<td>Hartman No.</td>
<td>Lorentz force</td>
<td>$Ha = BL \left( \frac{\sigma}{\nu \nu'} \right)^{\frac{1}{2}}$</td>
</tr>
<tr>
<td>Magnetic interaction parameter</td>
<td>Lorentz force</td>
<td>$N = \frac{g^2 L}{\nu \nu'}$</td>
</tr>
</tbody>
</table>

Table C.1: Dimensionless groups resulting from the scaling of the transport equations listed in section 2.1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Raliegh No.</td>
<td>$Ra_t = Gr_t Pr = \frac{g\beta \Delta T L^3}{\nu^2}$</td>
</tr>
<tr>
<td>Solutal Raliegh No.</td>
<td>$Ra_s = Gr_s Sc = \frac{g\beta_s \Delta C L^3}{\nu D}$</td>
</tr>
<tr>
<td>Thermal Peclet No.</td>
<td>$Pe_t = Re Pr = \frac{V_L}{\nu}$</td>
</tr>
<tr>
<td>Solutal Peclet No.</td>
<td>$Pe_s = Re Sc = \frac{V_L}{D}$</td>
</tr>
</tbody>
</table>

Table C.2: Important dimensionless relationships.
Bibliography


[68] Instruction Manual for Superconducting Magnet, Cryomagnetics, Inc., Oak Ridge, TN.


[72] H. Alexander (private communication).


