High-Pressure Phase Transformations of Ramp-Compressed Aluminum and Sodium

by

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Biographical Sketch

Danae Nicole Polsin was born in Syracuse, NY. She graduated Summa Cum Laude from the State University of New York at Geneseo in 2013 with a Bachelor of Arts degree in Physics. She participated in nuclear physics undergraduate research at the University of Rochester’s Laboratory for Laser Energetics (LLE) under the supervision of Dr. Stephen Padalino and Dr. Thomas Sangster. Her experience at LLE motivated her to attend graduate school in the Department of Physics and Astronomy at the University of Rochester in 2013. As the head teaching assistant for mechanics laboratory experiments, she completed the final written examination for the Master of Arts degree in Physics in 2014. As a Horton and GAANN fellow, she pursued research at the LLE in the field of high-energy density (HED) physics under her advisor Dr. Thomas Boehly.

Publications as a result of doctoral study include:

First-Author Publications


Co-Author Publications


• C. McCoy, M. Gregor, D. N. Polsin, D. Fratanduono, P. Celliers, T. Boehly, and D. Meyerhofer, Measurements of the sound velocity of shock-compressed liquid silica to 1100 GPa, J. Appl. Phys. 120, 235901 (2016).

• C. McCoy, M. Gregor, **D. N. Polsin**, D. Fratanduono, P. Celliers, T. Boehly, and D. Meyerhofer, Shock-wave equation-of-state measurements in fused silica up to 1600 GPa, J. Appl. Phys. 119, 215901 (2016).
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Abstract

This thesis describes discoveries of new structural phase transitions in two of nature’s “simplest” metals, aluminum (Al) and sodium (Na). High-power lasers are used to ramp compress Al and Na into high-pressure solid states. These metals form face-centered cubic (fcc) and body-centered cubic (bcc) structures at ambient temperatures and pressures, respectively. Both are predicted to undergo a sequence of structural transformations to low-symmetry crystalline phases including insulating “electride” phases at high pressure. To explore this high-pressure behavior, Al and Na samples were ramp compressed over 10-20 nanoseconds by the high-power OMEGA EP laser. Nanosecond in-situ x-ray diffraction (XRD) was performed to determine the crystalline structure at pressures > 100 GPa and the absence of diffraction peaks was used to infer the onset of melting. Laser velocimetry was used to determine the in situ pressure of the Al and Na by measuring the particle or free-surface velocities in the samples. In Al, we show that a solid–solid phase transition to a hexagonal close-packed (hcp) structure, occurs at 216±9 GPa. At higher pressures, a transformation to a body-centered cubic (bcc) structure occurs at 321±12 GPa and persists to 547 GPa. This is the first in situ observation of bcc Al [1]. Additionally, the highest pressure solid x-ray diffraction and reflectivity data to date on Na are presented. Melting and resolidification of Na to an hP4 phase is observed for pressures greater than 300 GPa, and the melting curve is found to increase dramatically for pressures above 140 GPa. Simultaneous XRD and optical reflectivity measurements reveal that Na remains reflective to at least 290 GPa – in striking contrast to room-temperature static compression measurements.
Contributors and Funding Sources

This work was supervised by a dissertation committee consisting of Professors Eric Blackman and Lynne Orr of the Department of Physics and Astronomy, Professor Rip Collins, Dr. James Rygg, and Dr. Thomas Boehly [advisor] of the Department of Mechanical Engineering, and Dr. Dayne Fratanduono from Lawrence Livermore National Laboratory. Graduate study was supported by the Physics Department at the University of Rochester, and dissertation research by the Frank J. Horton Graduate Research Fellowship.

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1 Introduction

High energy density (HED) is defined as energy densities exceeding $100 \text{ GJ/m}^3$ which is equivalent to pressures of 100 Gigapascals, 1 Megabar, and 1 million atmospheres (purple shaded region in Fig. 1.1 [2]) and spans from ultra-dense matter to high temperature plasmas. Matter at HED conditions is found throughout our universe including Earth’s core (3.3 Mbar), the interiors of giant planets, the sun’s core (260 Gbar), and Inertial-Confinement-Fusion (ICF) capsules (100 Gbar). Laboratory HED physics is possible with the development of large-scale facilities (e.g. lasers [3–5], pulsed-power [6], particle accelerators, gas guns [7, 8], and explosives.)

The goal of achieving thermonuclear fusion within the laboratory entails many aspects of HED physics. This thesis work was performed at the OMEGA laser facility at the University of Rochester’s Laboratory for Laser Energetics (LLE) [4] that has a primary initiative of achieving fusion with high-power lasers [9] but has been used extensively to create and study HED physics. The main ICF concept pursued at LLE involves direct laser irradiation of a shell containing Deuterium-Tritium (DT) fuel to heat and compress the fuel to temperatures greater than 8 keV and densities of a few hundred g/cm$^3$ to create self-sustaining fusion burn or ignition (Blue curve in Fig. 1.1). This means the center of the fusion target reaches densities about 20 times greater than
the density at the center of the earth. The fuel undergoes the reaction,

\[ D + T \rightarrow He^4(3.5 \text{ MeV}) + n(14.1 \text{ MeV}), \]  

creating a total of 17.6 MeV of energy. Most of this ICF path is unconstrained by experimental benchmarks, and thus producing such benchmarks will likely be an important research direction in the coming decade, and is in part what motivates this thesis work. Furthermore, high-pressure materials research is important to stockpile stewardship science and the development of new techniques will add to that area of research. HED physics includes many disciplines: plasma physics, equation of state physics, condensed matter physics, nuclear physics, fluid dynamics, and astrophysics.

The work on Al was prompted by a need to understand the behavior of magnetically driven Al linear implosions on the Z-machine at Sandia National Laboratories [10]. To access the predicted high pressure states in Al and Na, they were near isentropi-
Figure 1.2: The predicted sequence of high-pressure phase of Al (top) and Na (bottom) that exhibit a trend of increasing structural complexity with increasing pressure [11–13].

cally compressed to several megabars, while maintaining a low enough temperature to achieve high pressure solid states.

Structure is a critical component in understanding the behavior of matter at extreme pressure. Al and Na are predicted to undergo a series of solid phase transformations with increasing pressure [Fig. 1.2] that exhibits a trend of increasing structural complexity with increasing pressure [11–13]. The sequence of pressure-induced transitions in Al is fcc–hcp (217 GPa, 298 K [14])–bcc (321 GPa, ∼920 K [1]), with the next phase transformation predicted at 3.2 TPa and 0 K to a Al16–I4/mcm host-guest structure [11]. Na transforms from simple cubic structures (bcc, fcc) to complex low-symmetry phases at high-pressure and low-temperatures (cI16, oP8, tI19, and hP4). Both materials are predicted to transform to incommensurate and electride phases. An incommensurate structure consists of a framework of host atoms and chains of guest atoms along the channels of the host structure. These structures have a non-integer number of atoms per unit cell. In electride structures, the electrons occupy the interstitial regions or voids between the atoms [15]. Electrides are associated with remarkable changes in electronic behavior; Na was observed to become transparent at 200 GPa [12]. The pre-
Figure 1.3: Theoretical and experimental phase diagram of Al based on Refs. [14, 16]. The phase boundaries are calculated using density functional theory methods [16] and are not constrained to match the experimental data [14].

The predicted and observed behavior of high-pressure Al and Na is in marked contrast to their typical free-electron-metal behavior where the ions are in a “sea” of free electrons.

At ambient conditions, Al and Na can be approximated as a periodic arrangement of positive ion cores embedded in a sea of conduction electrons. The assumptions of this free-electron model break down at high-pressures as the valence electrons are perturbed by the underlying ionic arrangement. In order to include many-electron effects, quantum mechanical density functional theory (DFT) calculations are needed to predict the high-pressure behavior of materials where no experimental data exist [11, 19]. This work constrains the high-pressure (> 100 GPa), low-temperature (< 10,000 K) phase diagrams of Al and Na and provides benchmarks for theory.

Figure 1.3 shows a theoretical and experimental phase diagram of Al where the phase boundaries (blue curves) are calculated using DFT methods [16] and diamond-anvil cell (DAC) experiments measured the fcc-hcp transition at 217 GPa and 297 K (red and black crosses). Along the principal Hugoniot, solid x-ray diffraction measure-
Figure 1.4: Experimental phase diagram of Na based on Refs. [12, 13, 17, 18]. The highest pressure data for Na, before this work, are at 200 GPa from DAC XRD experiments [12]. The melting curve above 140 GPa is extrapolated (black dashed curve), and in the pink-blue striped region, the existence of solid or liquid Na is unknown. The red curve is the principal isentrope; the model assumes the bcc phase to high-pressure. Reprinted figure with permission from M. Marqués et al., Physical Review B, Volume 83, 184106 (2011). Copyright 2018 by the American Physical Society.
ments are limited to 125 GPa due to shock melting, therefore ramp compression is used to investigate the fcc-hcp and hcp-bcc phase boundaries. No experimental data existed above 333 GPa while structural predictions exist to tens of terapascals.

An experimental phase diagram of Na is shown in Fig. 1.4 including structural [12, 13] and melting curve [18] measurements. Nominally, the principal isentrope (red curve) shows that in our experiments, Na will melt in the bcc phase and a solid phase will be observed if the melting curve continues to sharply increase at pressures greater than 140 GPa. Although structural and electronic predictions exist to tens of terapascals for Na, no data existed above 200 GPa.

In this thesis work, we present the highest pressure solid Al [Chapter 4] and Na [Chapter 5] structural data reported to date. Using ramp-compression and in situ x-ray diffraction measurements, the first observation of body-centered cubic Al was made at 321±12 GPa. A duplication of the fcc–hcp measurement was made at 216±9 on nanosecond timescales and at elevated temperatures. The highest pressure solid Na x-ray diffraction data were obtained at 418±45 GPa. The existence of a solid Na phase under ramp compression means the melting curve of Na increases dramatically for pressure above 140 GPa [Fig. 1.4] and in contrast to static-compression observations, we find from optical reflectivity measurements that Na remains reflective to at least 290 GPa.
2 Theory

X-ray diffraction (XRD) of near-isentropically compressed materials is performed in this thesis work. X-ray diffraction involves the elastic scattering of x rays off a periodic arrangement of atoms revealing information about the crystalline structure. The fundamentals of XRD including the geometry of crystals, Bragg’s law, and the intensity of the diffracted x rays are discussed in Sec. 2.1. The crystalline samples under investigation are compressed to millions of atmospheres of pressure and XRD is used to constrain the thermodynamic state of the crystal at these pressures. In Sec. 2.2.1, the conservation equations of fluid dynamics are derived and these equations are used to study shock compression [Sec. 2.2.3] and isentropic flow [Sec. 2.3.1]. A method based on hydrodynamic characteristics is discussed in Sec. 2.4 and is used to solve for the isentropic flow in this work.

2.1 X-Ray Diffraction

XRD is a quantitative tool for characterizing material structure at high pressures that exploits the periodicity of atomic arrangements to produce, by Bragg’s law, constructive interference of waves scattered from parallel planes of atoms. The Bragg condition can
be written as:

\[ 2d \sin \theta = n\lambda, \]  
\[ (2.1) \]

\[ \Delta k = G, \]  
\[ (2.2) \]

\[ 2k \cdot G = G^2, \]  
\[ (2.3) \]

where \( d \) is the spacing of the lattice planes, \( \theta \) is the scattering angle, \( n \) is a positive integer (order of reflection), \( \lambda \) is the wavelength of the incident radiation, \( G \) is the reciprocal lattice vector that maps points in the reciprocal lattice, \( k \) is the incident wave vector, and \( \Delta k \) is the scattering vector describing the change in direction of the incident and scattered waves. Using the cartoon in Fig. 2.1, it is clear that Eq. 2.1 states that the path difference of scattered x-rays between two adjacent planes \( (2d \sin \theta) \) must be equal to an integer number of wavelengths to give constructive interference. Eqs. 2.2 and 2.3 are alternative Fourier representations of the Bragg condition. The electron density in a lattice is spatially periodic and lends itself to a Fourier representation. Eq. 2.2 states that constructive interference occurs when the scattering wave vector matches a reciprocal lattice vector. The result is a diffraction pattern that is the Fourier transform of the periodic electron density distribution. Eq. 2.3 describes the diffraction condition assuming elastic scattering of the waves \( (k^2 = k'^2) \).

The relative intensities of the scattered waves depend on the electron density distribution within each cell and the geometrical structure factor. The x-ray diffraction data in this study usually do not have enough diffraction lines to uniquely define the crystal structure, rather one or more lattice parameters are used as free parameters to match the observed data. For a particular crystal structure, densities are calculated and the possible crystal structures are narrowed down by eliminating structures that result in an
Figure 2.1: The Bragg condition (Eq. 2.1) specifies the scattering angle ($\theta$), wavelength ($\lambda$), and interplanar spacing ($d$) for constructive interference of scattered x rays. The incident and scattered wavevectors are given by $\mathbf{k}$ and $\mathbf{k}'$, respectively.

unphysical increase in density or density decrease with increased pressure. The x-ray diffraction pattern analysis is discussed in Sec. 3.2.

These experiments utilize powder x-ray diffraction with a (quasi) mono-energetic x-ray source. Considering the Bragg condition (Eq. 2.1), this technique can be conceptualized as varying the angle $\theta$ with a fixed wavelength $\lambda$. Powder refers to a powdered sample where a sufficiently large number of crystallites are randomly oriented to uniformly span $\theta$ space to satisfy the Bragg condition. Mono-energetic x-rays scatter off planes with a given $d$ spacing at an angle $2\theta$ to form a cone about the incident beam. This is in contrast to single-crystal Laue diffraction where the planes are not randomly oriented and a single reflected beam results in a spot in the diffraction pattern.

### 2.1.1 Defining a Crystal

A crystal is defined by a lattice, a periodic array of points, and a basis, the group of atoms attached to each lattice site. The repeating unit of a crystal is the unit cell [Fig. 2.2]. The unit cell is defined by the crystallographic axes $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ or the lattice parameters $a$, $b$, $c$, $\alpha$, $\beta$, $\gamma$. The volume of the parallelepiped is defined
Figure 2.2: A unit cell labeled with its crystallographic axes and lattice parameters.

by \( V = |\vec{a} \cdot (\vec{b} \times \vec{c})| \). There are 7 crystal systems: cubic, tetragonal, orthorhombic, rhombohedral/trigonal, hexagonal, monoclinic, and triclinic. There are 14 possible Bravais lattices in three-dimensions: simple cubic (P), body-centered cubic (I), face-centered cubic (F), simple tetragonal (P), body-centered tetragonal (I), simple orthorhombic (P), body-centered orthorhombic (I), base-centered orthorhombic (C), face-centered orthorhombic (F), rhombohedral (R), hexagonal (P), simple monoclinic (P), base-centered monoclinic (C), and triclinic (P). The combination of the 32 crystallographic point symmetry groups and the 14 Bravais lattices results in 230 unique space groups describing all possible crystal symmetries.

The Miller indices, \( h, k, \) and \( l \), are used for defining the planes in a Bravais lattice. Three intersection points of the plane with the crystallographic axes are used to define the plane. The procedure for determining the Miller indices of a lattice plane is to first define the crystallographic axes, then determine the point of intersection of the plane with each axis in terms of the lattice constants. An example of plane is shown in Fig. 2.3, the plane intersects the axes at 3 \( \vec{a} \), 2 \( \vec{b} \), and 2 \( \vec{c} \). The \( hkl \) is determined from the reciprocals of these intersections reduced to the three smallest integer numbers. For
the example shown in Fig. 2.3, the reciprocals $1/3, 1/2, 1/2$ are reduced to determine the $hkl$ plane, (233). An index of 0 means the plane does not intersect that axis. If a plane intersects an axis at a negative value, the index is written with a bar over it: ($\bar{h}kl$).

Similarly, a crystal direction is denoted by $[uvw]$ where $u, v,$ and $w$ for a vector $\vec{r}$ is defined by $\vec{r}_{uvw} = u \vec{a} + v \vec{b} + w \vec{c}$. Therefore, the $x, y,$ and $z$ crystallographic axes are defined by $[100], [010],$ and $[001]$.

### 2.1.2 Scattering by an Electron – Thomson formula

The diffracted x-ray intensity is related to the positions of the atoms in the unit cell. The problem can be solved in pieces: scattering by a single electron, by an atom, and by the atoms in a unit cell [20].

X rays are scattered by an electron due to the oscillation (acceleration) of the electron in the electric field of the x ray, resulting in the emission of radiation. Coherent scattering is a special case where the scattered beam has the same frequency as the incident beam causing a one to one correlation between the phases of the two beams and resulting in interference effects applicable to diffraction.
J. J. Thomson worked out the intensity of a beam elastically scattered by a single electron. This Thomson scattering is the low photon energy \((h\nu < m_e c^2)\) limit of relativistic inelastic Compton scattering. This does not contribute to diffraction because the incident and scattered beam cannot interfere because their phases have no fixed relation. An electron scatters incident x rays via electromagnetic dipole radiation, emitting radiation with an angular distribution proportional to \(\sin^2 \phi\) where \(\phi\) is the angle between the axis of the dipole and an observer (or scattering direction). In this way, the scattered light appears polarized with respect to the observer. Thompson found the intensity of the scattered beam, \(I\), a distance \(r\) from the electron, is given by

\[
I = I_0 \frac{K}{r^2} \sin^2 \phi,
\]

where \(I_0\) is the incident intensity, \(K\) is a constant \(\left[\frac{\mu_0 e^4}{16\pi^2 m_e^2}\right]\), \(\mu_0\) is the permeability of free space, \(e\) is the electron charge, and \(m_e\) is the electron mass [20]. The unpolarized incident beam electric field vector, \(E\), can be broken up into two components, \(E^2 = E_y^2 + E_z^2\), and if the direction of \(E\) is random then, \(E_y^2 = E_z^2 = (1/2)E^2\) and \(I_{0y} = I_{0z} = (1/2)I_0\). Eq. 2.4 can be written as,

\[
I = \frac{1}{2} \left[I_{0y} \frac{K}{r^2} \sin^2(\alpha = \pi/2) + I_{0z} \frac{K}{r^2} \sin^2(\alpha = \pi/2 - 2\theta)\right]
\]

\[
= I_0 \frac{K}{r^2} \left( \frac{1 + \cos^2(2\theta)}{2} \right),
\]

where written this way, the term in the parentheses is called the polarization factor, due to the fact that the beam is randomly unpolarized. The scattered intensity decreases as \(r^{-2}\) and scatters preferentially in the forward and backward direction with respect to the incident beam. The constant \(K\) is related to the classical electron radius, \(r_e\), where \(r_e = \frac{\mu_0 e^2}{4\pi m_e}\).
The Thompson intensity can be written as a differential cross section,

\[
\frac{d\sigma_e}{d\Omega} = r_e^2 \left( \frac{1 + \cos^2(2\theta)}{2} \right),
\]

(2.6)

where \( \sigma_e \) is the cross section for elastic scattering by a single electron and \( \Omega \) is the solid angle.

### 2.1.3 Scattering by an Atom - Atomic Form Factor

The intensity of the scattered radiation depends on the scattering from each electron in the atom and is given by the atomic scattering factor or atomic form factor, \( f \). The scattering is inversely proportional to the mass of the scattering particle \( m_e \) (in the formula for the electron radius). Therefore, it can be assumed that scattering occurs due to the electrons and scattering from the nucleus, with a large mass \( m_p/m_e = 1836 \), can be neglected. This is because the nucleus is too massive to oscillate on the time scale of the frequency of the incident x-ray beam.

The atomic scattering factor, \( f \), is the efficiency of the scattering by an atom in a given direction, \( \theta \), at a wavelength, \( \lambda \). The atomic scattering factor is the ratio of the amplitude of the wave scattered by an atom to the amplitude scattered only by a single electron. It is called the “form” factor because it depends on the form of the electron distribution around the nucleus.

The atomic form factor is calculated by keeping track of the phase differences between the waves scattered by all electrons around the nucleus and Fig. 2.4 shows the atomic scattering factor for Al [21]. In the limiting case of forward direction scattering \( (2\theta = 0) \), the amplitudes of the scattered waves can simply be added because the waves are all in phase and \( f = Z \) where \( Z \) is the atomic number. However, \( f \) decreases as \( \theta \) increases because the scattered waves acquire larger differences in path length and hence, phases. The form factor also depends on the wavelength\( (\lambda) \), and \( f \) increases as \( \lambda \) increases because the phase difference acquired by the waves scattered by the different
electrons is smaller relative to the wavelength of the radiation. The form factor is often plotted as a function of $\sin(\theta)/\lambda$ due to the dependence on direction and wavelength.

By keeping track of the phase, the form factor is given by the Fourier transform of the spatial electron density distribution in the atom, $\rho(r)$. The distribution is assumed to be spherically symmetric and written as a function of $r$. The atomic form factor, $f_0$, is given by

$$f_0(r^*, Z) = 4\pi \int_0^\infty \frac{\rho(r) \sin(r^* r) r^2 \, dr}{r^* r}.$$  \hspace{1cm} (2.7)

where $r^*$ is the magnitude of the reciprocal lattice vector [22].

### 2.1.4 Scattering by a Unit Cell - Structure Factor

The structure factor, $F_{hkl}$, is the scattering amplitude resulting from scattering from all the atoms in the unit cell assuming Bragg’s law is satisfied. A crystal, with its periodic arrangement of atoms, causes scattered radiation to be directed in limited directions, forming diffracted beams. The procedure for calculating the structure factor is similar to the procedure for the form factor calculation except the phase of the scattered
Figure 2.5: A schematic of an incident wave ($\mathbf{k}$) scattered by a crystal producing an outgoing wave ($\mathbf{k}'$) from Kittel et al. [23]. The difference in path length between the wave scattered from $dV$ at $\mathbf{r}$ and the wave scattered at $O$ is $r \sin \phi$ and the difference in phase factor is $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$.

light from all the atoms in the unit cell is calculated as a function of direction.

The structure factor is derived by first considering the phase difference between two different volume elements of a crystal as shown in Fig. 2.5. The phase difference between waves scattered a distance $\mathbf{r}$ apart is given by $\frac{2\pi}{\lambda}[(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$, where $\mathbf{k}$ and $\mathbf{k}'$ are the wavevectors defining the incident and scattered beams. Now the Bragg condition, $\mathbf{k} + \mathbf{r}_{hkl}^* = \mathbf{k}'$, can be substituted into the phase difference. The phase is now written in a more compact form $-2\pi \mathbf{r}_{hkl}^* \cdot \mathbf{r}$. The structure factor is the summation of the phase from each atom in the unit cell and can be written as $F = \sum_j f_j \exp(-2\pi i \mathbf{r}_{hkl}^* \cdot \mathbf{r}_j)$ where $\mathbf{r}_j$ is the vector describing the position of the $j$th atom, $\mathbf{r}_{hkl}^*$ is the reciprocal lattice vector for a given $hkl$ plane and $f_j$ is the form factor of the $j$th atom. The reciprocal lattice vector for the $hkl$ lattice plane is given by $\mathbf{r}_{hkl}^* = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*$ and $\mathbf{r}_j = u_j \mathbf{a} + v_j \mathbf{b} + w_j \mathbf{c}$ is the position of the $j$th atom in the unit cell. These vectors are substituted into the structure factor and the identities, $\mathbf{a} \cdot \mathbf{a}^* = 1$, $\mathbf{b} \cdot \mathbf{a}^* = 0$, are used.

The structure factor for an $hkl$ plane due to scattering from all the atoms in the unit
cell, \(N\), is given by

\[
F_{hkl} = \sum_{j=1}^{N} f_j \exp[-2\pi i (h u_j + k v_j + l w_j)],
\]

(2.8)

where \(h\), \(k\), and \(l\) are the Miller indices for the lattice plane, and \(u_j, v_j, w_j\) are the fractional coordinates of the atom in the unit cell. The corresponding diffracted intensity is proportional to the square of the modulus of Eq. 2.8, \(|F_{hkl}|^2\), and contains no phase information.

2.1.5 Relative Intensities of Powder Diffraction Lines

There are many factors in addition to the structure factor that must be taken into account to understand the intensity of the diffracted x-rays including: polarization, multiplicity, absorption, temperature, etc. A few of these factors are derived here but techniques such as Rietveld refinement determines the best-fit crystal structure and instrumental parameters based on a full diffraction pattern fit including peak heights, widths, and positions.

Cullity et al. [20] gives a simplified expression for the relative integrated intensity of a diffraction reflection in a powder pattern, \(I\), for a Debye-Scherrer geometry

\[
I = |F|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right),
\]

(2.9)

where \(F\) is the structure factor given by Eq. 2.8, \(p\) is the multiplicity factor, and \(\theta\) is the Bragg angle.

Lorentz-Polarization Factor

The term in the parentheses in Eq. 2.9 is the Lorentz-polarization factor \((L)\). The Lorentz factor is a geometric factor introduced because the intensity of a reflection is influenced by angles deviating slightly from the Bragg angle. Two factors are introduced
due to the range of angles that influence the breadth and maximum intensity, $I_{\text{max}}$, of a given reflection. $I_{\text{max}}$ is proportional to $1/\sin(\theta_B)$ and the breadth is proportional to $1/\cos(\theta_B)$ as derived from the Scherrer formula where $\theta_B$ is the Bragg angle. Another geometrical factor is folded into the Lorentz factor that considers the number of crystal grains oriented at the Bragg angle of interest even if the crystals are considered to be oriented randomly. The number of crystals oriented for reflection is dependent on the Bragg angle and is proportional to $\cos(\theta_B)$. The forth geometrical factor is due to the geometry of a typical x-ray film where the film records more diffraction cone from a forward scattering beam, $2\theta = 0^\circ$, than $2\theta = 90^\circ$ and varies as $1/\sin(2\theta_B)$.

All four factors multiply to give the Lorentz factor for the specific XRD geometry:

$$L \propto \frac{1}{\sin(\theta)} \frac{1}{\cos(\theta)} \frac{\cos(\theta)}{\sin(2\theta)} \propto \frac{\cos(\theta)}{\sin^2(2\theta)} \propto \frac{1}{\sin^2\theta \cos\theta}. \quad (2.10)$$

The Lorentz-polarization factor includes an additional factor, the polarization factor, that is due to the beam being unpolarized [Eq. 2.5]:

$$L \approx \frac{1 + \cos^2(2\theta)}{\sin^2(2\theta) \cos(\theta)}. \quad (2.11)$$

**Structure Factor**

The structure factor [Eq. 2.8] can be calculated for any $hkl$ plane and therefore reveals reflections not allowed due to destructive interference, i.e. where $F = 0$. For example, the structure factor for a body-centered cubic (bcc) unit cell is derived by

Figure 2.6: The body-centered cubic (bcc) unit cell with lattice parameter, $a$. 
Table 2.1: Structure factor “rules” for simple, base-centered, body-centered and face-centered structures. Here mixed means both even and odd Miller indices and unmixed means only even or odd.

<table>
<thead>
<tr>
<th>Bravais Lattice</th>
<th>Reflections possibly present</th>
<th>Reflections necessarily absent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple</td>
<td>all</td>
<td>none</td>
</tr>
<tr>
<td>Base-centered</td>
<td>(h) and (k) unmixed</td>
<td>(h) and (k) mixed</td>
</tr>
<tr>
<td>Body-centered</td>
<td>((h + k + l)) even</td>
<td>((h + k + l)) odd</td>
</tr>
<tr>
<td>Face-centered</td>
<td>(h, k,) and (l) unmixed</td>
<td>(h, k,) and (l) mixed</td>
</tr>
</tbody>
</table>

first determining that the two atoms in the unit cell are located at \((0, 0, 0)\) and \((1/2, 1/2, 1/2)\) shown in Fig. 2.6. Substituting into Eq. 2.8, the structure factor for bcc is \(F_{hkl} = f(1 + \exp[2\pi i (h/2 + k/2 + l/2)])\). If \((h + k + l)\) is even, \(F = 2f\), however reflections with odd \((h + k + l)\) are not allowed because \(F = f - f = 0\). Notice that no information about the crystal system (cubic, tetragonal, etc.) or the lattice parameters are inputs into the structure factor, therefore it is independent of shape and size. An example of some of the rules that govern the possible reflections, derived from the structure factor, are given in the Table 2.1.

**Multiplicity Factor**

The multiplicity factor, \(p\), is the number of planes with the same spacing which increases the intensity by contributing to the same powder diffraction cone. For example, \(p = 8\) for the 111 planes because there are four sets of planes of the form \(\{111\}\): \((111)\), \((11\bar{1})\), \((\bar{1}1\bar{1})\), and \((\bar{1}11)\). The additional factor of two comes from the parallel planes counting separately if they have different Miller indices such as: \((111)\), \((\bar{1}11)\). The value \(p\) depends on the crystal system, and multiplicity factors are listed in the Table 2.2.
Table 2.2: Multiplicity factors for the cubic, hexagonal and rhombohedral classes from Appendix 13 in [20].

<table>
<thead>
<tr>
<th>Cubic</th>
<th>hkl</th>
<th>hhl</th>
<th>0kl</th>
<th>0kk</th>
<th>hhh</th>
<th>00l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>48</td>
<td>24</td>
<td>24</td>
<td>12</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hexagonal and Rhombohedral</th>
<th>hk \cdot l</th>
<th>hh \cdot l</th>
<th>0k \cdot l</th>
<th>hk \cdot 0</th>
<th>hh \cdot 0</th>
<th>0k \cdot 0</th>
<th>00 \cdot l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>6</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

2.2 Fluid Dynamics

The governing equations of fluid dynamics are the Euler equations which are used to describe the conservation of mass (the continuity equation), momentum (Newton’s second law), and energy (the first law of thermodynamics) with the relevant equations of state (EOS). The Navier Stokes equations are a coupled system of equations that includes dissipative terms due to viscous effects. The familiar Euler equations for fluid flow are recovered from the Navier Stokes equations by assuming no viscosity or thermal conductivity. The Euler equations of fluid dynamics are derived following the conventions of Riccardo Betti’s Hydrodynamic Instabilities course (ME536).

2.2.1 Fluid Equations

Conservation of Mass

The first conservation law states that the mass of a material volume is a conserved quantity, and is often called the continuity equation. A material volume, \( V \), and its material surface, \( S \), can be considered using the continuum model for fluids. The mass, \( M \), in the volume enclosed by the surface is the integral of the density, \( \rho \), over the volume, \( M = \int_V \rho \, dV \). The rate of change of mass in the volume is given by, \( \frac{dM}{dt} = \frac{d}{dt} \int_V \rho \, dV \). The volume is fixed as a function of time so the derivative can be brought into the integral, \( \frac{dM}{dt} = \int_V \frac{\partial \rho}{\partial t} \, dV \). If mass is flowing through the surface with a velocity \( \vec{u} \), then the mass flowing through a differential surface element, \( dS \), in the time interval, \( dt \), can be calculated by considering the volume shown in Figure 2.7.
Figure 2.7: The differential mass, $dm$, flowing through the surface element $dS$ in a time interval $dt$ is $\rho dS \hat{u} \cdot \hat{n} dt$.

The mass rate of change now becomes $\frac{dM}{dt} = \int_V \frac{\partial \rho}{\partial t} dV = -\int_S \rho \hat{u} \cdot \hat{n} dS$. Only the normal component of the velocity contributes to the mass leaving the volume. Gauss’s theorem, or equivalently the divergence theorem, states that the integral of the divergence of a vector field $\mathbf{F}$ over a volume is equal to the surface integral of the vector field over the boundary of the volume $\int_V (\nabla \cdot \mathbf{F}) dV = \int_{\partial V} \mathbf{F} \cdot dS$. In this case, the vector field is $\rho \hat{u} n$ and using Gauss’s theorem results in the equation,

$$\int_S \rho \hat{u} \cdot \hat{n} dS = \int_V \nabla \cdot (\rho \hat{u}) dV, \quad (2.12)$$

and leads to an integral over the volume,

$$\int_V \left[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \hat{u}) \right] dV = 0. \quad (2.13)$$

Because the volume chosen was arbitrary, the conservation of mass can be written in the differential form,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \hat{u}) = 0. \quad (2.14)$$
Figure 2.8: A fluid element moving in one dimension.

The equivalent integral form of the continuity equation is given by,

\[
\frac{d}{dt} \int_V \rho \, dV = - \int_S \rho (\bar{\mathbf{u}} \cdot \hat{n}) \, dS. \tag{2.15}
\]

In cases where the fluid is incompressible, the density will be a constant in both space and time. From Eq. 2.14, the first two terms go to zero for incompressible flow, \( \frac{\partial \rho}{\partial t} + \bar{\mathbf{u}} \cdot \nabla \rho + \rho \nabla \cdot \bar{\mathbf{u}} = 0 \). This gives the condition for incompressible fluids, \( \nabla \cdot \bar{\mathbf{u}} = 0 \).

**Conservation of Momentum**

Conservation of momentum is derived by considering Newton’s second law in an inviscid fluid and yields a vector equation, or a system of three equations, for the flow velocity. The equations can be solved for the simple case of 1D fluid flow along the \( \mathbf{x} \) direction shown in Figure 2.8.

The differential mass of the volume element is \( dm = \rho(t) S dx(t) \), where \( S \) is the surface area. The velocity of the fluid element is \( u(x, t) = u[x(t), t] \) where \( x(t) \) is the trajectory of the fluid element. Therefore, the acceleration is given by \( a = \frac{d}{dt} [u(x(t), t)] = \)
\[ \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \] Newton’s second law, \( F = dm \times a \), gives the force, \( F = \rho(t)Sdx(t) \) \((\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x})\). If the fluid element is removed and replaced with a force, then the force is given by \( F = P\big|_{x-\frac{dx}{2}} - P\big|_{x+\frac{dx}{2}} S \) where \( P \) is the pressure at the fluid boundaries in the \( \pm x \) directions and \( S \) is the surface area. The momentum equation can be rewritten considering the pressure forces,

\[ \rho(t)dx(t)\left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x}\right)S = P\big|_{x-\frac{dx}{2}} - P\big|_{x+\frac{dx}{2}} S, \quad (2.16) \]

giving the 1D momentum equation,

\[ \rho \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x}\right) = -\frac{\partial P}{\partial x}. \quad (2.17) \]

Other forces, such as viscous stresses, could be included but are not considered here. When the effect of viscosity is taken into account, the momentum equations become the Navier Stokes equations. The viscous term in the Navier Stokes equations arises from the application of shear stresses to the fluid element, and for Coutte-type flow the shear stresses are proportional to velocity gradients.

An example of an additional force, includes the presence of gravity in the fluid flow,

\[ \rho \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x}\right) = -\frac{\partial P}{\partial x} + \rho \vec{g} \cdot \hat{e}_x, \quad (2.18) \]

where the last term on the right hand side includes the gravitational forces on the fluid.

For flow in three dimensions, conservation of momentum yields three equations

\[ \rho \left(\frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \nabla)\vec{u}\right) = -\nabla P + \rho \vec{g}. \quad (2.19) \]

**Conservation of Energy**

The first law of thermodynamics is equivalent to the conservation of energy. The conservation of energy states that the total energy of a closed system is conserved.
A simple version is $\Delta U = Q + W$. This intuitively describes energy conservation by stating the change in internal energy of a system is equal to the energy added as heat to the system minus work done by the system.

In thermodynamics, the conservation of energy is often written as generalized force-displacement pairs or conjugate variables. The most familiar conjugate variables describe mechanical work as $dW = -PdV$, where $P$ is the pressure defined by the derivative, $P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$. Here pressure is the change in the energy of the system per change in volume of the system when the entropy $S$ and number of particles $N$ are held constant.

The pressure is an intensive property (one that goes to a constant in the thermodynamic limit) because it is a derivative with respect to an extensive parameter (one that grows proportional to the size of the system). The definition, $dW = -PdV$, is consistent with the idea that pressure is the force per unit area ($F^{\text{total}} \Delta x = PA\Delta x = P\Delta V$). This force-displacement pair states that the internal energy of the system must decrease by the mechanical work done by the system. Similarly, the heat absorbed by the system is given by $dQ = TdS$, where $T$ is the temperature defined by the thermodynamic derivative, $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$. Also, if the system is permeable to particles that may have chemical reactions, then the change in energy must include the chemical potential, $\mu = \left(\frac{\partial E}{\partial N}\right)_{V,S}$, that gives the change in energy with respect to the change in the number of particles.

Putting these sources and sinks of energy all together gives the first law of thermodynamics, $dE = TdS - PdV + \mu dN$.

These same concepts can be applied to a fluid element by equating the total rate of energy stored in a fluid volume to the rate of energy flowing into the volume, and including the rate of heat transfer across the boundary, the rate work is done on the volume by the surroundings, and the rate energy is produced within the volume.

First, the rate of energy storage in the fluid volume is given by the internal energy ($U$ is internal energy per unit mass) and kinetic energy, $\frac{d}{dt} \left(\rho U + \frac{1}{2} \rho u^2\right) \Delta x \Delta y \Delta z$. Across
all the volume faces, the rate of energy change per volume is given by,

$$\frac{\partial}{\partial t} \left( \rho U + \frac{1}{2} \rho u^2 \right) \Delta x \Delta y \Delta z = - \nabla \cdot \left[ \rho \bar{u} \left( U + \frac{u^2}{2} \right) \right] \Delta x \Delta y \Delta z,$$

(2.20)

where \((\bar{u} = u \hat{e}_x + v \hat{e}_y + w \hat{e}_z)\). Next, heat transfer across the volume boundary arises from heat conduction and can be written in terms of the heat flux \(\bar{q}\) (where \(\bar{q}\) has units of Energy/Area/time). The Fourier law for heat conduction says that the heat flux is proportional to temperature gradients, \(\bar{q} = -\kappa \bar{V} T\), assuming the temperature scale length is much larger than the mean free path of the particles (collisions) and where \(\kappa\) is the coefficient of thermal conductivity. The rate of energy transfer in the volume along the \(x\)-direction is given by the heat inflow by conduction across the \(x\)-face, \(\frac{\partial}{\partial x} \| \bar{q} \| dydz\) minus the heat outflow across the \(x + \Delta x\) face, \(\frac{\partial}{\partial x} \| \bar{q} \|_{x+\Delta x} dydz\). This is the definition for the gradient, so the net heat flow across the \(x\)-face is given by \(-\frac{\partial \bar{q}}{\partial x} dx dydz\). Across all the faces, the heat transferred by heat conduction is given by \(\frac{\partial}{\partial t} \left( \rho U + \frac{1}{2} \rho u^2 \right) \Delta x \Delta y \Delta z = - \bar{V} \cdot \bar{q} dx dydz\).

The work done on the fluid element by surface and gravitational forces must be considered. The net rate of work done on the volume element by the surfaces is given by,

\[ - \left[ \frac{\partial}{\partial x} (\bar{u} \cdot \bar{F}_x) + \frac{\partial}{\partial y} (\bar{u} \cdot \bar{F}_y) + \frac{\partial}{\partial z} (\bar{u} \cdot \bar{F}_z) \right] dx dydz. \]

Similarly, the force of gravity on the fluid element gives a rate of work, \(\rho \bar{g} \cdot \bar{u} dx dydz\). In addition, there can be sources of energy, such as nuclear reactions or chemical reactions, in the volume that would create a rate of work given by \(\dot{Q} dx dydz\).

Putting together the energy added as heat to the system minus work done by the system gives the conservation of energy equation. Dividing all the rate of work terms by the arbitrary volume \((\Delta V = dx dydz)\), gives

$$\frac{\partial}{\partial t} \left[ (\rho U + \frac{1}{2} \rho u^2) \right] =$$

\[ - \nabla \cdot \left[ \rho \bar{u} \left( U + \frac{u^2}{2} \right) \right] + \bar{V} \cdot (\kappa \bar{V} T) - \left[ \frac{\partial}{\partial x} (\bar{u} \cdot \bar{F}_x) + \frac{\partial}{\partial y} (\bar{u} \cdot \bar{F}_y) + \frac{\partial}{\partial z} (\bar{u} \cdot \bar{F}_z) \right] + \dot{Q}. \]

(2.21)
Together the mass, momentum, and energy conservation equations are 5 equations with 7 unknowns. In the highest moment equation for energy, the Fourier assumption for the heat flux was required to write heat flux as a function of temperature. An equation of state provides the final two unknowns in order to close the system of equations and allows for the fluid equation of motion to be solved as a function of space and time.

### 2.2.2 Thermodynamic Equations of State

A thermodynamic equation of state (EOS) is a relation between state variables, such as temperature, pressure, volume, \( f(P, V, T) = 0 \). An EOS characterizes a material under various physical conditions and phases including solid, liquid, molecular fluid, gas, etc.

The familiar ideal gas law is a simple example of an EOS for ideal gases, \( PV = Nk_B T \), where \( P \) is the pressure, \( N \) is the particle number density, \( T \) is the temperature, \( k_B \) is the Boltzmann constant, and \( V \) is the volume.

The fundamental thermodynamic function is the entropy, \( S(E,V,N) \), from which all thermodynamic behavior can be determined. This is also true of the internal energy, \( E(S,V,N) \). The partial derivatives,

\[
\left( \frac{\partial E}{\partial S} \right)_{V,N} = T(S,V,N) \quad (2.22)
\]

\[
\left( -\frac{\partial E}{\partial V} \right)_{S,N} = P(S,V,N) \quad (2.23)
\]

\[
\left( \frac{\partial E}{\partial N} \right)_{S,V} = \mu(S,V,N) \quad (2.24)
\]

give three equations of state. If the EOS are known then this is equivalent to knowing the fundamental thermodynamic function using the Euler relation, \( E = TS - PV + \mu N \). The Gibbs-Duhem relation, \( SdT - VdP + Nd\mu = 0 \), can be used to determine the third EOS if two of the three EOS are known.
For example, for an ideal gas two of the equations of state can be used to find the third. Consider an ideal monatomic gas, with EOS \( PV = Nk_B T \) and \( U = \frac{3}{2} Nk_B T \). These can be rewritten as \( \frac{P}{T} \frac{1}{V} = \frac{k_B}{N} \) and \( \frac{1}{T} = \frac{3}{2} k_B \frac{N}{U} = \frac{3}{2} \frac{k_B}{u} \), where \( u \) is the energy per particle and \( v \) is the volume per particle. The Gibbs-Duhem relation can be rewritten as

\[
d\left( \frac{\mu}{T} \right) = ud\left( \frac{1}{T} \right) + vd\left( \frac{P}{T} \right).
\] (2.25)

Substituting the EOS for an ideal gas gives,

\[
d\left( \frac{\mu}{T} \right) = u\frac{3}{2} k_B d\left( \frac{1}{u} \right) + v k_B d\left( \frac{1}{v} \right) = -\frac{3}{2} k_B \frac{d}{u} du - k_B \frac{d}{v} dv.
\] (2.26)

Upon integration, the chemical potential is known with respect to a reference state, \( u_0 \) and \( v_0 \),

\[
\left( \frac{\mu}{T} \right) - \left( \frac{\mu}{T} \right)_0 = -\frac{3}{2} k_B \ln\left( \frac{u}{u_0} \right) - k_B \ln\left( \frac{v}{v_0} \right).
\] (2.27)

Now, one can solve for the entropy using the Euler relation,

\[
S(E,V,N) = \frac{E}{T} + \frac{P}{T} V - \frac{\mu}{T} N = \frac{N}{N_0} S_0 + N k_B \ln \left[ \left( \frac{E}{E_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \left( \frac{N}{N_0} \right)^{-5/2} \right]
\] (2.28)

Therefore, from the equations of state for an ideal gas, the entropy was derived from which all behaviors of an ideal gas can be deduced [24].

### 2.2.3 Rankine-Hugoniot Relations

Using the conservative forms of the Euler equations, one can assume discontinuous solutions to derive the Rankine-Hugoniot (R-H) equations. The conservative form of an equation is written as the rate of change of a conserved quantity, \( Q \), plus the divergence of the fluxes, \( \vec{F} \),

\[
\frac{\partial Q}{\partial t} + \vec{\nabla} \cdot \vec{F} = 0.
\]

Integrating over a differential volume gives,

\[
\int dV \frac{\partial Q}{\partial t} = -\int \vec{F} \cdot \vec{n} = -\int dV \vec{F} \cdot \vec{n}.
\]

Using Gauss’s theorem, the equation can be written in integral form,

\[
\int dV \frac{\partial Q}{\partial t} = -\int dS (\vec{F} \cdot \vec{n}).
\]

This states that the rate of change of a quantity in a volume is...
given by fluxes through the surface of that volume. The conservative form of the energy conservation equation derived in the Sec. 2.2.1, ignoring heat flux, viscous terms, and sources and sinks is given by

$$\frac{\partial}{\partial t} \left[ \left( \frac{\gamma P}{\gamma - 1} + \frac{1}{2} \rho v^2 \right) \right] + \nabla \cdot \left[ \vec{v} \left( \frac{\gamma P}{\gamma - 1} + \frac{\rho v^2}{2} \right) \right] = 0,$$

(2.29)

where $\gamma$ is the adiabatic index or the ratio of specific heats, $\frac{C_p}{C_v}$, and is equal to $\frac{5}{3}$ for an ideal gas. This equation can be rewritten into a non-conservative form for the adiabat or entropy, $\frac{P}{\rho \gamma}$,

$$\frac{\partial}{\partial t} \left( \frac{P}{\rho \gamma} \right) + \vec{v} \cdot \nabla \left( \frac{P}{\rho \gamma} \right) = 0.$$

(2.30)

This was rewritten in a conservative form by taking the dot product of $\vec{v}$ and the momentum equation and then subtracting it from the energy equation. This is a conservative equation along the fluid motion and can be proven by transforming the equation from Eulerian to Lagrangian coordinates or mass coordinates. The material derivative in Eulerian coordinates is $D/Dt = \partial/\partial t + \vec{v} \cdot \nabla$ and in Lagrangian coordinates is $D/Dt = \partial/\partial t$. Therefore, the non-conservative form of the energy equation can be rewritten in mass coordinates into this simple form,

$$\frac{\partial}{\partial t} \left( \frac{P}{\rho \gamma} \right) = 0$$

(2.31)

This form of the energy equation is significant because it states that the entropy or adiabat, $\alpha = \frac{P}{\rho \gamma}$, is a constant along the particle motion. The conclusion that entropy is a conserved quantity is under the assumption of no heat flux, sources and sinks.

Discontinuous solutions to the Euler equations can be assumed in order to derive the R-H jump conditions. The conservative forms of the equations can be rewritten in the frame of reference of the discontinuity. Using the substitution $\vec{w} = \vec{v} - U_S$, where $U_S$ is the velocity of the discontinuity (assumed to be a constant), $\vec{v}$ is the velocity in the
laboratory frame, and $\mathbf{w}$ is the velocity in the frame of reference of the discontinuity, the Euler equations become the following,

$$
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{w}) = 0,
$$

(2.32)

$$
\rho \left( \frac{\partial \mathbf{w}}{\partial t} + (\mathbf{w} \cdot \nabla) \mathbf{w} \right) = -\nabla P + \rho \frac{\partial \dot{\mathbf{U}}_S}{\partial t},
$$

(2.33)

and

$$
\frac{\partial}{\partial t} \left[ \left( \frac{\gamma P}{\gamma - 1} + \frac{1}{2} \rho w^2 \right) \right] + \nabla \cdot \left[ \mathbf{w} \left( \frac{\gamma P}{\gamma - 1} + \frac{\rho w^2}{2} \right) \right] = \rho \mathbf{w} \cdot \frac{\partial \dot{\mathbf{U}}_S}{\partial t}.
$$

(2.34)

In the momentum and energy equations, the two terms on the right hand side, $\rho \frac{\partial \dot{\mathbf{U}}_S}{\partial t}$ and $\rho \mathbf{w} \cdot \frac{\partial \dot{\mathbf{U}}_S}{\partial t}$, are the inertial force and the work done by the inertial force, respectively. This is for the case where $U_S$ is not a constant, therefore the system is in a non-inertial reference frame. For the purposes of deriving the jump conditions, these terms will be neglected and rewritten in 1D,

$$
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial z} (\rho w) = 0,
$$

(2.35)

$$
\rho \left( \frac{\partial w}{\partial t} + w \frac{\partial}{\partial z} w \right) = \frac{\partial}{\partial z} P,
$$

(2.36)

and

$$
\frac{\partial}{\partial t} \left[ \left( \frac{\gamma P}{\gamma - 1} + \frac{1}{2} \rho w^2 \right) \right] + \frac{\partial}{\partial z} \left[ w \left( \frac{\gamma P}{\gamma - 1} + \frac{\rho w^2}{2} \right) \right] = 0.
$$

(2.37)

The momentum equation can be rewritten by bringing $\rho$ into the derivative, $\delta_t (\rho w) - w \delta_t \rho + \delta_z (\rho w^2) - w \delta_z (\rho w) = 0$. The second and fourth terms cancel from the continuity equation giving a new form of the momentum equation,

$$
\frac{\partial (\rho w)}{\partial t} + \frac{\partial}{\partial z} (\rho w^2 + P) = 0.
$$

(2.38)
Now integrate these equations over the left and right side of discontinuity of an infinitely small thickness, \( \varepsilon \). Eq. 2.35 now becomes,

\[
\int_{-\varepsilon}^{\varepsilon} \left[ \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial z} (\rho w) \right] dz = \frac{\partial \rho}{\partial t} 2\varepsilon + (\rho w) \big|_{-\varepsilon}^{+\varepsilon} = 0.
\] (2.39)

In the limit of \( \varepsilon \) going to zero gives the jump condition for conservative of mass,

\[
\lim_{\varepsilon \to 0} \left[ \frac{\partial \rho}{\partial t} 2\varepsilon + (\rho w) \big|_{-\varepsilon}^{+\varepsilon} \right] = [\rho w] = 0,
\] (2.40)

where the notation, \([Q]\), means the jump in the quantity, \(Q\), across the shock front.

This jump condition is intuitive because the mass leaving one side of the discontinuity must equal the mass entering the other side. The same procedure can be applied to Eq. 2.38 and 2.37 for momentum and energy giving,

\[
[|P + \rho w|] = 0,
\] (2.41)

\[
[\left| \frac{\gamma P}{\gamma - 1} + \frac{\rho w^2}{2} \right] = 0.
\] (2.42)

These two equations state that the forces on one side of the discontinuity must equal the forces on the other side and the energy fluxes are equal across the discontinuity.

The jump conditions can be applied to a fluid that experiences a discontinuity with velocity, \( U_S \). In Figure 2.9, a fluid at rest or any known state has conditions \( u_1, P_1, \) and \( \rho_1 \). The discontinuity passes through the fluid and leaves behind a fluid in “State 2” \((u_2, P_2, \) and \( \rho_2)\). This leaves 3 equations with 3 unknowns because the initial conditions are known \((u_1, P_1, \rho_1)\) and \( P_2 \) is known from launching the discontinuity. This can be better understood by considering the method of launching the discontinuity. One way to increase the pressure on one side of the fluid is by applying a pressure \((P_2)\) with a piston, laser ablation, gas gun, pulsed-power, etc..
Figure 2.9: A piston applying a pressure $P_2$ into a fluid with known initial conditions, $u_1$, $P_1$, and $\rho_1$. As the shock propagates through the fluid, the material behind the shock are in a state, $u_2$, $P_2$, and $\rho_2$.

 Returning back into the laboratory frame of reference, the jump conditions can be used to relate the fluid before and after the discontinuity called the Rankine-Hugoniot equations,

$$\frac{U_s - u_1}{C_{S1}} = \left[1 + \frac{\gamma + 1}{2\gamma} Z\right]^{\frac{1}{2}},$$  \hspace{1cm} (2.43)

$$\frac{u_2 - u_1}{C_{S1}} = \frac{Z}{\gamma\left[1 + \frac{\gamma + 1}{2\gamma} Z\right]^{\frac{1}{2}}},$$  \hspace{1cm} (2.44)

$$\frac{\rho_2}{\rho_1} = \frac{1 + \frac{\gamma + 1}{2\gamma} Z}{1 + \frac{\gamma - 1}{2\gamma} Z},$$  \hspace{1cm} (2.45)

$$\frac{C_{S2}}{C_{S1}} = \left[\frac{(1 + Z)(1 + \frac{\gamma - 1}{2\gamma} Z)}{1 + \frac{\gamma + 1}{2\gamma} Z}\right]^{\frac{1}{2}}$$  \hspace{1cm} (2.46)

where $Z$ is the shock strength [$Z = \frac{P_2 - P_1}{P_1}$] and $C_S$ is the sound speed $C_S = \sqrt{\frac{\gamma P}{\rho}}$. The discontinuity is referred to as a shock front. There are many forms of the R-H equations. This form is particularly interesting because all the right hand sides of the
equations only depend on shock strength. Therefore, if the applied pressure, $P_2$, is known, then the various thermodynamic parameters can be calculated easily.

An interesting limit is for strong shocks or large $Z$ and Eq. 2.45 becomes,

$$\frac{\rho_2}{\rho_1} = \frac{\gamma + 1}{\gamma - 1}. \quad (2.47)$$

This states that compression asymptotes for strong shocks and for an ideal gas ($\gamma = \frac{5}{3}$) the compression is limited to a factor of 4.

It is also informative to calculate the change of entropy for the case of strong shocks. Returning to Eq. 2.31, the adiabat or entropy in this case is defined as $\alpha = (P/\rho^\gamma)$. The ratio of the entropy before and after the shock front in the limit of strong shocks is

$$\frac{\alpha_2}{\alpha_1} = \left(\frac{P_2}{P_1}\right) \left(\frac{\rho_1}{\rho_2}\right)^\gamma = \left(\frac{\gamma - 1}{\gamma + 1}\right) \left(\frac{P_2}{P_1}\right). \quad (2.48)$$

This implies that shock waves significantly increase the entropy when the shock strength is large, and shock formation is a highly irreversible, dissipative process.

Other commonly used forms of the Rankine-Hugoniot Equations for a material initially at rest are,

$$\rho_0 U_s = \rho_1 (U_s - u_p), \quad (2.49)$$

$$P_1 - P_0 = \rho_0 U_s u_p, \quad (2.50)$$

and

$$E_1 - E_0 = \frac{1}{2}(P_0 + P_1)(\frac{1}{\rho_0} - \frac{1}{\rho}) \quad (2.51)$$

where $u_p$ is the particle velocity or the velocity of the material behind the shock front.
2.3 Isentropic Flow and The Riemann Invariants

Near-isentropic or ramp compression [Sec. 3.1] is used in these experiments to produce high pressures and densities, but at lower temperatures than those accessible by shock-compression [Sec. 2.2.3]. Using the fluid equations derived in Sec. 2.2.1, the solutions to planar isentropic flow are provided in Sec. 2.3.1, and the method of characteristics is used to solve for the isentropic fluid flow [Sec. 2.3].

2.3.1 Acoustic Waves and Planar Isentropic Flow

Perturbations in pressure \( P = P_0 + \tilde{P} \), density \( \rho = \rho_0 + \tilde{\rho} \), and velocity \( U = U_0 + \tilde{U} \) are applied to the one-dimensional mass and momentum fluid equations [Eqs. 2.14 and 2.17]. The naught and tilde denote the initial state and the perturbation, respectively. When the perturbations are assumed to be infinitesimally small and the equations are linearized with no initial velocity \( U_0 = 0 \), the result is 2 equations with 3 unknowns,

\[
\frac{\partial \tilde{\rho}}{\partial t} + \rho_0 \frac{\partial \tilde{U}}{\partial x} = 0, \quad (2.52)
\]

and

\[
\rho_0 \frac{\partial \tilde{U}}{\partial t} + \frac{\partial \tilde{P}}{\partial x} = 0. \quad (2.53)
\]

An equation of state (EOS) must be assumed in order to close the system of equations. In general, the state relation can be expressed as a thermodynamic variable as a function of two other variables. Because we are interested in isentropic compression where the entropy is assumed to be conserved, the EOS of choice is \( P(\rho, S) \), where \( S \) is
the entropy. The EOS is simplified by expanding about the initial density and entropy,

\[ P(\rho, S) = P(\rho_0, S_0) \approx P(\rho_0, S_0) + (\rho - \rho_0) \left( \frac{\partial P}{\partial \rho} \right)_S + (S - S_0) \left( \frac{\partial P}{\partial S} \right)_\rho + \ldots \]  \quad (2.54)

Assuming the disturbances are small and that fluid evolves isentropically gives,

\[ \tilde{P} = P - P_0 = \left( \frac{\partial P}{\partial \rho} \right)_S \tilde{\rho}. \]  \quad (2.55)

Combining Eqs. 2.52, 2.53, and 2.55 yields wave equations

\[ \frac{\partial^2 \tilde{\rho}}{\partial t^2} = C_E^2 \frac{\partial^2 \tilde{\rho}}{\partial x^2}, \]  \quad (2.56)

\[ \frac{\partial^2 \tilde{U}}{\partial t^2} = C_E^2 \frac{\partial^2 \tilde{U}}{\partial x^2}, \]  \quad (2.57)

and

\[ C_E^2 = \left( \frac{\partial P}{\partial \rho} \right)_S, \]  \quad (2.58)

where the acoustic disturbances travel at the local Eulerian sound speed \( C_E \).

The solution to the wave equation is a superposition of two waves propagating at \( \pm C_E \) where

\[ \tilde{U} = f_1(x - C_E t) + f_2(x + C_E t), \]  \quad (2.59)

and

\[ \tilde{\rho} = f_1(x - C_E t) + f_2(x + C_E t). \]  \quad (2.60)

The above equations describe the acoustic wave solution where it is assumed entropy is conserved and perturbations in pressure, density, and velocity are small. The
disturbances of all the fluid parameters travel at the sound speed along a pathline or characteristic, \((\frac{dx}{dt})_\pm = U \pm C_E\).

The wave equation for planar isentropic flow removes the assumption of small perturbations. Conservation of mass and momentum give

\[
\left[ \frac{\partial U}{\partial t} + (U \pm C_E) \frac{\partial U}{\partial x} \right] \pm \left[ \frac{1}{\rho C_E} \left( \frac{\partial P}{\partial t} + (U \pm C_E) \frac{\partial P}{\partial x} \right) \right] = 0. \tag{2.61}
\]

Defining the characteristics as \((\frac{dx}{dt})_\pm = U \pm C_E\),

\[
\frac{dU}{dt} \pm \frac{1}{\rho C_E} \frac{dP}{dt} = 0 \tag{2.62}
\]

where the total derivative along the forward and backward propagating characteristics is

\[
\left( \frac{d}{dt} \right)_\pm = \frac{\partial}{\partial t} + (U \pm C_E) \frac{\partial}{\partial x}. \tag{2.63}
\]

The Riemann invariants for isentropic flow are defined by

\[
J_\pm = U \pm \int \frac{dP}{\rho C_E}, \tag{2.64}
\]

where \(\rho(P)\) and \(C_E(P)\) are functions of pressure. The Riemann invariants are constant along their respective characteristic: \(J_+\) is constant along the \(C_+\) characteristics. Therefore, \(C_+\) depends only on the \(J_-\) invariant. Writing the equations for isentropic flow in terms of the Riemann invariants is a mathematical transformation that allows the equations to be solved more easily.

For an ideal gas with constant specific heats \((P = \rho_0 \rho^\gamma\) and \(C_E^2 = \gamma \rho_0 \rho^{\gamma-1}\)), the Riemann invariants become

\[
J_\pm = U \pm \int \frac{\sqrt{\gamma \rho_0 \rho^{\gamma-1}}}{\rho} d\rho = U \pm \frac{2}{\gamma-1} C_E. \tag{2.65}
\]
The velocity and sounds speed can be written in terms of the Riemann invariants,

\[ U = \frac{J_+ + J_-}{2}, \quad (2.66) \]

and

\[ C_E = \frac{\gamma - 1}{4} (J_+ - J_-), \quad (2.67) \]

where \( \gamma \) is the ratio of the specific heats. This illustrates that if the Riemann invariants are known, then the fluid flow can be solved.

### 2.3.2 Lagrangian Coordinates

These equations, so far, have been derived in the Eulerian frame of reference. In an Eulerian flow field, the fluid motion is described at specific locations in space as the fluid moves in time. The Lagrangian representation of fluid flow, on the other hand, describes the fluid motion from the frame of a fluid element evolving in both space and time. Oftentimes, Lagrangian coordinates provide a more simplified solution to a problem.

The isentropic flow equations can be transformed into Lagrangian coordinates. In Eulerian coordinates, the fluid is represented by \( x(h,t) \) while Lagrangian coordinates describe the fluid position, \( h \), and time, \( t \). The conservation of mass can be used to relate the two frames of reference,

\[ \rho(t) dx = \rho_0 dh. \]

The convective derivative is the derivative along the fluid motion and in Eulerian coordinates, it is defined as

\[ \frac{D}{Dt} = \frac{\partial}{\partial t} + U \cdot \nabla. \]

The derivative is \( \frac{D}{Dt} = \frac{\partial}{\partial t} \) in Lagrangian coordinates.

Conservation of mass and momentum in Lagrangian coordinates for isentropic flow give,

\[ \left[ \frac{\partial U}{\partial t} + C_L \frac{\partial U}{\partial h} \right] \pm \frac{1}{\rho_0 C_L} \left( \frac{\partial P}{\partial t} + C_L \frac{\partial P}{\partial h} \right) = 0, \quad (2.68) \]
where \( h \) is the Lagrangian coordinate and \( C_L \) is the Lagrangian sound speed, \( C_L = \frac{\rho}{\rho_0} C_E \).

A new form for the characteristics equations are given by,

\[
dU \pm \frac{1}{\rho_0 C_L} dP = 0,
\]

and

\[
\left( \frac{dh}{dt} \right)_\pm = C_L
\]

along \( C_{L \pm} \).

The Riemann invariants in Lagrangian coordinates become,

\[
J_\pm = U \pm \int \frac{dP}{\rho_0 C_L},
\]

where \( C_L(P) \).

In ramp compression experiments, is it assumed compression information is carried by hydrodynamic characteristics propagating at the local sound speed. These derivations are taken from Chapter 1 of Zel’dovich and Raizer [25].

### 2.3.3 Numerical Equations of State

A numerical equation of state model typically stores thermodynamic functions such as internal energy, pressure, and entropy on a density-temperature grid. From this “EOS surface”, other thermodynamic properties can be calculated from various derivatives. Figure 2.10, shows an example of an EOS surface from Kerley 3600.

Numerical equations of state, such as SESAME [26] or Quotidian Equation of State (QEOS) [27], have the challenging problem of generating tables that are valid over a wide range of densities, temperatures, and phases, or creating a “global” EOS. This often involves interpolating between various theoretical models in different regions of validity while maintaining thermodynamic consistency. This motivates experimental data in these regions to benchmark these calculations.
Figure 2.10: An EOS pressure surface as a function of density and temperature for Kerley 3600 for Al. The global EOS is shown here for only a small range of pressures, temperatures, and densities relevant to this high pressure research. The black lines are the principal isentrope and principal Hugoniot. From this graphical representation, isentropic compression achieves high pressure, low temperature states while shock compression achieves high pressure, high temperature states.
Generation of a theoretical equation of state model will be discussed in the context of aluminum. There are many approaches to model the behavior of Al under shock loading and unloading, melting, and in the plasma fluid and solid phases, etc. This discussion will look at the chemical model used in Kerley 3600 [28]. A solid EOS model and a fluid EOS model are calculated separately. For the solid model, the Helmholtz free energy \( F = E - TS \) or equivalently the pressure is the sum of three contributions given by,

\[
F_{\text{solid}}(\rho, T) = F_c(\rho) + F_l(\rho, T) + F_e(\rho, T)
\]

(2.72)

and

\[
P_{\text{solid}}(\rho, T) = P_c(\rho) + P_l(\rho, T) + P_e(\rho, T),
\]

(2.73)

where the \( c \) stands for “cold,” \( l \) stands for “lattice”, and \( e \) stands for “electron.” The first term is the contribution to the internal energy from the cold curve. The cold curve, or the energy on the \( T = 0 \) K isotherm, represents the ground state energy. The cold curve gives the contribution to the energy for fixed ions. The other two terms include contributions to the free energy from thermal ions and thermal electrons. \( F_l(\rho, T) \) is the energy due to the lattice vibrations or other ionic excitations. \( F_e(\rho, T) \) is the energy due to the electronic excitations and ionization [29].

The cold curve was constructed using a universal metal EOS analytical form [30] to fit experimental data so that the cohesive energy, density, and bulk modulus of the solid could be determined at 0 K. The cold curve can also be computed using density functional theory (DFT) of the Al crystalline system to determine the volume and bulk modulus from a Vinet equation of state fit to the DFT output. These methods are two of many options. The results for the 0 K isotherm must be connected to higher densities to match the Thomas-Fermi-Dirac (TFD) statistical model.

In Al, the contribution to the EOS from lattice vibrations was accounted for using the Debye model. The Debye model treats lattice vibrations as phonons, discrete energy
quanta associated with sound waves, in a box. The vibrations of the lattice take on collective modes inside the box. By treating the phonons using Bose-Einstein statistics, the contribution to the internal energy and pressure is,

\[ F_l(\rho, T) = \frac{R}{W} \left[ \frac{9}{8} \Theta + 3T \ln(1 - e^{-\Theta/T}) - TD(\Theta/T) \right] \]  

(2.74)

and

\[ P_l(\rho, T) = \frac{R}{W} \Gamma(\rho) \rho \left[ \frac{9}{8} \Theta + 3TD(\Theta/T) \right] , \]  

(2.75)

respectively. \( R \) is the gas constant, \( W \) is the molecular weight, \( \Gamma \) is the Grüneisen function, and \( \Theta \) is the Debye Temperature. Rotational and vibrational degrees of freedom (DOF) should be considered for solids as these DOFs have an important role in the vibrational spectrum. The sum over the lattice vibrational modes is cut off for large amplitudes. For solids, the \( F_l(\rho, T) \) term can be calculated using either the Debye or Einstein models. The Einstein model treats the atoms in the solid as individual non-interacting quantum harmonic oscillators with the same frequency. These models are extrapolated to high temperatures and low densities (the ideal gas limit).

For \( F_e(\rho, T) \), the behavior of the core and valence electrons must be captured at higher densities as the core electrons begin to influence the structure of the solid. For Al, the \textit{INFERNO} code [31] was used to calculate the contribution to the internal energy from the thermal electrons. \textit{INFERNO} computes the wave functions and energy levels for both the bound and continuum electrons in a dense plasma. At lower densities, an Ionization Equilibrium Theory (IET) model was used to take into account bound and free electrons configurations. This technique includes effects from continuum lowering, where the ionization energy for bound electrons decreases with increasing density, as the free electron continuum lowers relative to the bound energy levels. This has important implications to the metal-insulator transition and other high pressure phenomenon.

The fluid Al was modeled using contributions from the thermal motion of the molecules and intermolecular forces to the free energy. The melt curve is determined
by the combination of the fluid and solid models where the free energies are equal. From these models, it is predicted that melting occurs at 125 GPa on the Hugoniot for Al.

### 2.4 The Method of Characteristics

In high-pressure ramp-compression experiments, the free-surface velocity or the velocity of a reflective interface behind an optical window is used to make an *in situ* measurement of the material confined by that window. To deduce the pressure in the material, a calculation based on the method characteristics [Sec. 2.3] is used to backwards propagate the measured velocities using the equations of motion of isentropic flow [32, 33]. The free-surface or interface produces backward characteristics that interact with the forward characteristics by modifying the sound speed. The slope of the forward propagating characteristics will change at the point of intersection with a back propagating characteristic. The wave interactions can be taken into account to determine the state of the sample.

As derived in Sec. 2.3, hydrodynamic characteristics are a locus of points satisfying the mass and momentum Euler equation’s for isentropic fluid flow. They have the property that they travel at the Lagrangian sound speed [Eq. 2.70] with the quantity given by the Riemann invariant [Eq. 2.71]. The Riemann invariant can alternatively be defined as $J_\pm = u_p \pm \sigma$, where $\sigma = \int dP/(\rho_0 C_L)$. The characteristics are often drawn in an x-t diagram with forward-propagating characteristics, $R = u_p + \sigma$, and back-propagating characteristics, $S = u_p - \sigma$. From these definitions, relations for the particle velocity and the pressure term at the intersection of a forward and backward characteristic are

$$u_p = \frac{R + S}{2} \quad (2.76)$$
Figure 2.11: (b) The pressure temporal profile applied to an undisturbed infinitely thick diamond slab shown in (a). (c) The characteristics are drawn in an h-t diagram. The pathlines have a slope proportional the Lagrangian sound speed $C_L(P)$. Since sound speed increases with pressure, the high-pressure characteristics will overtake the lower speed ones, forming a shock in an infinitely thick sample.

$$\sigma = \frac{R - S}{2}.$$  \hfill (2.77)

2.4.1 Example: Simple Waves

An example of the characteristics analysis applies a temporal applied pressure profile, $P_0(t)$, to an undisturbed diamond sample at $h = 0$, shown in Figure 2.11. The Riemann invariants are determined by the boundary conditions of the problem. In this case, the negative characteristics originating downstream have $S = 0$ because the particle velocity and pressure are zero. Therefore, Eqs. 2.76 and 2.77 are now equal with a value $u_p = \sigma = R/2 = (u_p + \sigma)/2$. There are no negative characteristics, $S = 0$, to interact with the incoming flow, therefore the flow is unaltered and the characteristics are straight lines. Since sound speed increases with pressure, the high-pressure characteristics will overtake the lower speed ones, forming a shock in an infinitely thick sample.
Figure 2.12: (a) The applied pressure temporal profile. (b) The applied pressure can be thought of as a piston on the left side of the sample where the sample has a finite thickness, \(d\), and initial density, \(\rho_0\). (c) \(P(u_p)\) for the EOS used for the diamond sample.

### 2.4.2 Example: Characteristics at a Free-Surface

Another example, applies the same temporal pressure profile to a finite thickness sample. In this case, the free surface acts as a downstream disturbance that produces negative characteristics interacting with the incoming flow. This problem is solved numerically using a characteristics algorithm.

The inputs to the analysis are an applied pressure as a function of time [Fig. 2.12 (a)], the initial conditions of the sample (including ambient density and thickness [Fig. 2.12 (b)]), and a model for the EOS of the sample material [Fig. 2.12 (c)]. The isentrope with values of Lagrangian sound speed and particle velocity is used to calculate pressure (\(P\)), sigma (\(\sigma\)), and density (\(\rho\)) for an initial density (\(\rho_0\)) using [34],
\[ d\sigma = \frac{dP}{\rho_0 C_L(P)}, \]
\[ dP = \rho_0 C_L(u_p) du_p, \]
\[ dV = -V_0 \left( \frac{du_p}{C_L} \right). \] 

(2.78)

The fluid flow is mapped as a grid of intersections of positive and negative characteristics. The indexing for this problem is shown in Fig. 2.13. The point \((i,j)\) can be solved for when points \((i,j-1)\) and \((i-1,j+1)\) are known. For the indexing chosen for this problem, a loop over the \(i\) and \(j\) indices is done over \(1:N\) and \(1:N-i+1\), respectively, where \(N\) is the number of time steps in the applied pressure profile. The boundary conditions for this problem are at the applied pressure (piston) surface and the free-surface. Therefore, the piston surface needs to be treated as a special case in the for-loop and the forward characteristics must be defined before the entire grid can be solved. If \(i = 1\), then \(R = u_p(P_j) + \sigma(P_j)\), where \(P_j\) is the applied pressure and the EOS provides the values of \(u_p\) and \(\sigma\) at those pressures. After the forward characteristics are defined, the free-surface boundary conditions must be specified. If \(j = 1\) (free-surface), then \(S = R\) from Eq. 2.77 because \(P = 0\) and \(\sigma = 0\). Otherwise, if \(j \neq 1\), then \(S\) can be determined from the previous point, \(S = u_p(i,j-1) - \sigma(i,j-1)\). After \(S\) and \(R\) for all \(i = 1\) are specified, \(u_p, \sigma, \) and \(C_L\) are determined at the intersection points from,
Figure 2.13: A $h$-$t$ plot of the calculated intersection points of forward and backward characteristics in a 100-$\mu$m diamond sample. The pressure is applied at $h = 0$ $\mu$m and the free-surface is at $h = 100$ $\mu$m. The characteristics are approximated as straight lines and only a few characteristics are drawn to show the indexing. The color of the points represents the pressure at the intersection in GPa. The characteristics indexed $(1,j)$ are all simple waves until they intersect a back-propagating characteristic. The characteristics labeled $(i,1)$ are at the free-surface and have a value $P = 0$ GPa. This indexing allows for the grid to be mapped out by looping over $i = 1:N$ and $j = 1:N-i+1$. 
Figure 2.14: (a) The intersections of forward and backward characteristics. The color of the point is proportional to the value of the pressure in GPa in the colorbar. (b) The values of the pressure at the intersection points are interpolated onto a uniform grid. The results show the pressure is low near the free surface where the release wave propagates back into the material, isentropically releasing the pressure in the diamond. The pressure is maximum near the end of the pulse (∼10 ns) where the applied pressure is at a maximum value. After the applied pressure is turned off, the release wave decreases the pressure throughout the target.

\[
    u_p(i, j) = \frac{R + S}{2},
    \sigma(i, j) = \frac{R - S}{2},
    C_L(i, j) = C_L(\sigma(i, j)),
    P(i, j) = P(\sigma(i, j)).
\]

The values for the pressure and Lagrangian sound speed are solved for the entire grid. The generic update for the next intersection has \( R \) determined from the previous point \( R = u_p(i - 1, j + 1) + \sigma(i - 1, j + 1) \) and \( S = u_p(i, j - 1) - \sigma(i, j - 1) \) or \( S = R \) at the free surface. Eqs. 2.79 are used to calculate the thermodynamic values at the intersection points.

The thermodynamic properties are known at the intersection points, but the loca-
tions in time and space of the intersection points need to be calculated. The coordinates of the points of intersection are solved using the equations for the trajectories of the characteristics from the two previous points. The average sound speeds on the previous segments can be defined as 

\[ c_+ = \frac{(C_L(i-1,j+1) + C_L(i,j))}{2} \] and 

\[ c_- = \frac{(C_L(i,j-1) + C_L(i,j))}{2}. \]

The characteristic to the new point \((i,j)\) is approximated as a straight line with a value equal to \(1/c_+\) or \(1/c_-\) which is the inverse of the average sound speed between the current point and the previous one. The special case for \(c_+\) is for \(i = 1\) where \(c_+ = C_L(\sigma_j)\), where \(\sigma_j = 0\). At the piston surface \((h = 0 \ \mu m)\), the time is equal to the time stamp of the applied pressure temporal profile. At the free surface, \(h\) is equal to the thickness of the target and the time of intersection at \(i = 1\) and \(j = 1\) is given by, 

\[ t(i = 1, j= 1) = \text{thickness}/c_+. \]

The previous times and positions can be defined as 

\[ t_- = t(i, j-1) \] and \(t_+ = t(i-1, j+1)\) and \(h_- = h(i,j-1)\) and \(h_+ = h(i-1,j+1)\). At the free surface where \(i \neq 1\) and \(j = 1\), 

\[ t(i,j) = (\text{thickness} - h_+)/c_+ + t_+. \]

From these positions, times, and slopes, the intersection point of the two characteristics can be calculated. The result of the characteristics analysis is a grid of intersections with values of pressure at intersection times and Lagrangian positions. The results are shown in Fig. 2.14.

### 2.4.3 Example: Characteristics at a Material Interface

In laser-driven compression experiments, the targets consist of many layers with the most basic package consisting of an ablator, sample, and window. Characteristics reaching a material interface produce negative characteristics that propagate upstream and interact with the incoming flow. Therefore, a material interface is another boundary condition that needs to be taken into account in a characteristics calculation.

At an ablator-sample or sample-window boundary, the particle velocity and pressure are continuous. In the limiting case of an infinitely thin sample layer between an ablator and window, the ramp wave immediately passes through the sample and the pressure is applied directly to the window. With this assumption, the pressure in the sample is
equal to the pressure in the window material at the sample location. For the sample thicknesses used in these experiments, this assumption is not valid because throughout the thickness of the sample there are spatial and temporal pressure gradients.

The next order correction takes into account the finite thickness of the sample by treating the sample as the window material but with an equivalent thickness. The equivalent thickness is given by the ratio of the Lagrangian sound speeds of the window and the sample to maintain the time the ramp wave would propagate through the sample. This is a good option if the sample EOS is not known.

To accurately determine the pressure state in these experiments, the in situ measurements are used to back propagate the loading pressure to determine the average pressure state of the sample. This assumes an EOS for both the sample and window, and propagates characteristics throughout the sample. The impedance matching boundary condition at the interface is continuity of particle velocity and normal stress. In this section, the subscripts on the variables correspond to the material on either side of the boundary where the characteristics are propagating from material 1 into material 2. From the continuity of particle velocity, \( u_p^1 = u_p^2 \), and using Eq. 2.76, then \( R_1 + S_1 = R_2 \) (\( S_2 \) is equal to zero because there are no upstream disturbances). Using Eq. 2.77 and \( R_1 + S_1 = R_2 \), a relation between \( \sigma_1 \) and \( \sigma_2 \) is given by \( \sigma_1 + \sigma_2 = R_1 \). Because \( \sigma_1(P) + \sigma_2(P) \) are know from the assumed EOS models and the value along the forward propagating characteristic in material 1 is known, \( R_1 \), then the pressure at the interface, \( P_{int} \), can be determined by \( \sigma_1(P_{int}) + \sigma_2(P_{int}) - R_1 = 0 \). The continuity of normal stress at the material interface defines the pressure across the boundary, \( P_{int} = P_1 = P_2 \).

The backward characteristics into material 1 can be defined by using \( \sigma_1(P) \) to find the value of \( \sigma_1(P_{int}) \) and find \( \sigma_2 = R_1 - \sigma_1(P_{int}) \). This defines \( S_1 = R_1 - 2\sigma_1(P_{int}) \). The forward characteristics into material 2 are defined by \( R_2 = u_p + \sigma_2(P_{int}) \) where \( u_p \) is determined from \( u_p = u_{p1} = u_{p2} \).

Figure 2.15 shows the grid of characteristics intersections in a diamond and alu-
Figure 2.15: (a) The forward and backward characteristics and their intersections from a material interface and a free surface. The colors of the intersection points are proportional to the value of the pressure in GPa in the colorbar. The applied pressure profile shown in Fig. 2.12 is applied to a 105-µm diamond ablator with a 20-µm aluminum sample attached. The algorithm applies continuity of particle velocity and normal stress at the C-Al interface and propagates characteristics into the aluminum sample. At the free surface, at 125 µm, the free surface boundary conditions are applied, \( P = 0 \), \( \sigma = 0 \) and \( R = S \). (b) The values of the pressure at the intersection points are interpolated onto a uniform grid showing the pressure throughout the C-Al target. The vertical white dashed lines show the location of the C-Al interface and the Al-free-surface interface. The white box shows a region of interest in the diamond target from 8 ns - 9 ns. (c) The pressure histogram in the region inside the white box. The pressure histogram provides the average pressure and the standard deviation due to spatial and temporal gradients. The method of characteristics allows one to determine the pressure throughout the target.
minimum target on the left. In this case, there is a C/Al interface and an Al/free-surface boundary. The values for the pressure at the intersection points are interpolated onto a uniform grid [Fig. 2.15 (top right)]. This analysis can be used to determine the pressure in space and time in the target. For example, a white box is drawn from 8 ns - 9 ns in the diamond sample. The pressure histogram in this region is shown on the bottom right and provides an average pressure in the sample and the standard deviation due to pressure gradients.

2.4.4 Back-Propagating Characteristics

In experiments where velocities of free-surfaces or window interfaces are measured, the hydrodynamic characteristics algorithm must back propagate the equations of motion using the measured velocities as a boundary condition. So far, only forward propagation of characteristics have been discussed. No further knowledge about isentropic waves in materials is required to solve the backwards propagation problem, however the ordering and indexing of the characteristics intersections is different because the boundary condition is now placed at the measurement surface.

This problem is covered extensively by Rothman et al. [33], but an alternative indexing scheme is shown here. This indexing allows for the intersections to be solved over two for-loops. The indexing is shown clearly in Fig. 2.16 and is different from the forward indexing in Fig. 2.13. In this example, a Al-window interface velocity is measured at 40 µm and the intersection points of forward and backward propagating characteristics in the 20 µm Al sample are shown. The pressure at the intersections indexed \((i,j)\) are given by the measured velocities and the EOS of the window and the following expressions are used to define the characteristics for points \((i,j)\),
Figure 2.16: (a) The Al-LiF interface velocity measured with VISAR that is used as a boundary condition in the characteristics code. (b) A Lagrangian position-time plot of the calculated intersection points of forward and backward propagating characteristics in a 20 µm Al sample using a measured sample-window interface velocity at 40 µm. The colors of the points denote the value of the pressure at each intersection in GPa. The pressure at the interface is given by $P(u_p)$ from the window EOS and the characteristics are propagated back to the front of the Al sample at 20 µm. The pressure at the intersections indexed (1,j) are given by the measured velocities and the EOS of the window. This indexing allows for the grid to be mapped out by looping over $i = 1:N$ and $j = 1:N-i+1$. The point (i,j) can be solved when points $(i-1,j+1)$ and $(i-1,j)$ are specified. (b) The pressure as a function of space and time in the Al sample. The velocity measurement surface is at 40 µm and the ablator is located at 20 µm. The white box shows the timing of a 1-ns x-ray probe. (c) The pressure histogram inside the white box. The average pressure is 339 GPa ± 1.4 GPa.
\[ u_p = u_{\text{interface}}(t_j), \]
\[ t = t_j, \]
\[ P_{\text{window}} = P_{\text{sample}}, \]
\[ u_p(\text{window}) = u_p(\text{sample}), \]
\[ S_{\text{window}} = 0, \]
\[ u_p(\text{window}) = \sigma(\text{window}), \quad (2.80) \]
\[ P_{\text{window}} = P_{\text{window}}(u_p = \sigma_{\text{window}}), \]
\[ P_{\text{sample}}(\sigma_{\text{sample}} = R_{\text{sample}} - u_p) = P_{\text{window}}(\sigma_{\text{window}} = u_{p\text{window}}) \]
\[ R_{\text{sample}} = u_p + \sigma_{\text{sample}}, \]
\[ S_{\text{sample}} = u_p - \sigma_{\text{sample}}, \]
\[ C_{L\text{sample}} = C_L(\sigma_{\text{sample}}), \]

where \( u_{\text{interface}} \) is the measured interface velocity. This indexing allows for the grid to be mapped out by looping over \( i = 1:N \) and \( j = 1:N-i+1 \). The point \((i,j)\) can be solved when points \((i-1,j+1)\) and \((i-1,j)\) are specified. The pressure at point \((i,j)\) of Fig. 2.16 can be calculated using the following expressions:
\[ R = u_p(i-1,j+1) + \sigma(i-1,j+1), \]
\[ S = u_p(i-1,j) - \sigma(i-1,j), \]
\[ u_p = \frac{R+S}{2}, \]
\[ \sigma = \frac{R-S}{2}, \]
\[ C_L(i,j) = C_L(\sigma), \]
\[ P = P(\sigma), \]
\[ c_+ = \frac{C_L(i-1,j+1) + C_L(i,j)}{2}, \]
\[ t_+ = t(i-1,j+1), h_+ = h(i-1,j+1), \]
\[ c_- = \frac{C_L(i-1,j) + C_L(i,j)}{2}, \]
\[ t_- = t(i-1,j), h_- = h(i-1,j), \]
\[ h(i,j) = \frac{(-1/c_-)h_+ - (1/c_+)(h_- + (-1/c_-)(t_+ - t_-))}{(-1/c_-) - c_+}, \]
\[ t(i,j) = \frac{(-1/c_-)t_- - (1/c_+)t_+ + h_+ - h_-}{(-1/c_-) - (1/c_+)} \]

The results for the pressure as a function of space and time in a 20-µm Al sample are shown in Fig. 2.16(c). The Al-LiF particle velocity measurement is made at 40 µm [Fig. 2.16(a)]. A white box shows the 1-ns duration of the x-ray probe and the corresponding pressure histogram throughout the sample during the probe time is shown [Fig. 2.16(d)]. The average pressure in the sample is 339 GPa and the standard deviation is only 1.4 GPa. The boundary condition at the ablator-sample interface is not taken into account in this analysis. The method of characteristics is used in these experiments to determine the average pressure in the samples as well as to characterize the presence of spatial and temporal gradients. The implementation of this technique is discussed in more detail in Sec. 3.4.
3 Experimental Methods

In this thesis, we looked to study the crystalline structure of dynamically compressed Al and Na. These materials are interesting because they are predicted to transform into numerous solid allotropes with increasing pressure but have no experimental validation. To compress these materials, infer their crystalline structure, and determine the stress state, we performed experiments at the University of Rochester’s OMEGA EP Laser System [35].

High-pressure solid-states were created by laser-driven ramp-compression using shaped UV pulses from OMEGA EP. The laser pulse shapes were designed using radiation-hydrodynamic simulations to achieve a uniform, high-pressure, solid-state [Sec. 3.1]. The Powder X-Ray Diffraction Image Plate (PXRDIP) [36] detected phase transformations and constrained the crystalline phase of the compressed solids [Sec. 3.2]. Laser velocimetry simultaneously measured the pressure of the compressed sample by measuring the particle or free surface velocities [Sec. 3.3]. The velocities were used as a boundary condition in a characteristics algorithm to infer the pressure in the sample [Sec. 3.4]. In addition, the amplitude of the VISAR signal provided time-dependent reflectivity measurements that were used to infer the optical properties of the compressed materials. These diagnostics provided measurements that constrain the high-pressure phase diagram for a wide range of materials. An image taken inside the OMEGA target chamber is shown in Fig. 3.1 where the PXRDIP, VISAR, an x-ray
3.1 Laser Driven Ramp-Compression

High-energy densities (HED) in the laboratory, in excess of 100 GJ/m$^3$, can be created using a number of techniques including: pulsed-power devices, gas guns, diamond anvil cells, and high-power lasers. These experiments used the OMEGA EP Laser System’s four long-pulse 351-nm beam lines that can deliver up to 5-kJ per beam in 10-ns pulses to generate high-energy-density (HED) conditions. The high-power laser beams deposit energy on the outer surface of a target and drive pressure via laser ablation. Laser ablation rapidly ejects material from the surface of the target and by conservation of momentum, the non-ablated region of the target accelerates inward. This process is analogous to a rocket where momentum is balanced between the exhausted fuel and the payload (target).
Figure 3.2: An example of the radial density, temperature, and pressure profiles in a typical laser driven target. The various regions of the ablating target include the corona (gray), conduction zone (yellow), shocked compressed material (green), and cold undriven material (purple). (Graph from LLE viewgraph database)
3.1.1 Laser Ablation

A laser interacts with a solid target by first creating a long-scale length (100-300 µm) coronal plasma in front of the target. The radial density, temperature, and pressure profiles in a typical laser-driven target are shown in Fig. 3.2. The laser is incident from the right, and the low-density, hot plasma outside the critical surface is referred to as the corona. Laser energy is coupled into the target by electron-ion collisional absorption or inverse-bremsstrahlung absorption. The electrons oscillating in the laser field collide with ions, redistributing their momenta and transferring the laser energy into the ions. The laser energy is deposited up to the plasma critical surface with a critical density, \(n_c\), where the frequency of the laser light is equal to the plasma frequency, \(\omega_{pe} = \sqrt{\frac{4\pi n_e e^2}{m_e}}\), where \(n_e\) is the electron density, \(e\) is the electron charge, and \(m_e\) is the electron mass. In a plasma, the refractive index, derived from the electromagnetic dispersion relation \((\omega^2 = \omega_{pe}^2 + k^2 c^2)\) is \(n = \sqrt{1 - \frac{\omega_{pe}^2}{\omega^2}}\). For \(\omega < \omega_{pe}\), the refractive index and wave number, \(k\), become imaginary, meaning the light propagating in the inhomogeneous plasma will reflect at the critical surface and the field beyond the critical surface will be evanescent.

Above the critical density, electron thermal conduction is responsible for the transport of energy to the cold, dense layer. The electrons mean-free-path will become small near the cold shell creating a steep thermal gradient at the ablation surface. Via conservation of momentum, the expansion of the cold shell forces the non-ablated material inwards and acts as a piston applying ablation pressure.

3.1.2 Ramp Compression

Laser ablation is used in this work to produce dynamic, shockless compression of materials by “ramping” the temporal profile of the laser power. This can produce high pressures and densities, but at lower temperatures than those accessible by shock-compression. Recall from Eq. 2.48 that the material behind a strong shock is at an
elevated entropy and temperature with respect to the unshocked material. Ramp compression can be approximated by an infinite number of weak shock waves, because the change in entropy is only third order in compression. This can be proven starting with the first law of thermodynamics differentiated with respect to the specific volume, \( V \),

\[
\frac{dE}{dV} = -P + T \frac{dS}{dV} \tag{3.1}
\]

Substituting in the Rankine-Hugoniot energy equation, Eq. 2.51, for \( dE/dV \) gives

\[
\frac{dE}{dV} = \frac{1}{2} (V_0 - V) \frac{dP}{dV} - \frac{1}{2} (P + P_0) = -P + T \frac{dS}{dV}, \tag{3.2}
\]

where all derivatives are evaluated at the initial state \( V = V_0 \).

By combining terms,

\[
T \frac{dS}{dV} = \frac{1}{2} (V_0 - V) \frac{dP}{dV} + \frac{1}{2} (P - P_0) \tag{3.3}
\]

can be differentiated with respect to specific volume two more times to determine \( (dS/dV)_{V=V_0} \) to the third order.

\[
T \frac{d^2S}{dV^2} + \frac{dT}{dV} \frac{dS}{dV} = \frac{1}{2} (V_0 - V) \frac{d^2P}{dV^2} \tag{3.4}
\]

\[
T \frac{d^3S}{dV^3} + 2 \frac{dT}{dV} \frac{d^2S}{dV^2} + \frac{d^2T}{dV^2} \frac{dS}{dV} = \frac{1}{2} (V_0 - V) \frac{d^3P}{dV^3} - \frac{1}{2} \frac{d^2P}{dV^2} \tag{3.5}
\]

Evaluating Eqs. 3.3, 3.4, and 3.5, at the initial state \( P_0 \) and \( V_0 \), we find that \( (dS/dV)_{V=V_0} = 0 \), \( (d^2S/dV^2)_{V=V_0} = 0 \), and \( (d^3S/dV^3)_{V=V_0} = -\frac{1}{27} (d^2P/dV^2) \), respectively. This can be substituted in the Taylor expansion of entropy with respect to specific volume, \( S = S_0 + (dS/dV)_{V=V_0} (V - V_0) + (1/2)(d^2S/dV^2)_{V=V_0} (V - V_0)^2 + (1/6)(d^3S/dV^3)_{V=V_0} (V - V_0)^3 \),
to get an expression for the change in entropy along the Hugoniot.

\[
S - S_0 \approx \frac{1}{12\gamma} \left( \frac{d^2 P}{dV^2} \right) V_0 (V - V_0)^3. \tag{3.6}
\]

From this equation, when \( P > P_0 \) and \( V < V_0 \), as it is for most fluids, then the entropy \( S > S_0 \) increases due to a shock wave and decreases for a rarefaction shock wave. Due to the second law of thermodynamics, this means it is impossible to have a rarefaction shock wave because most fluids have a positive isentropic curvature in \( P(V) \). From Eq. 3.6, the Hugoniot and isentropic curves have the same tangents and centers of curvature at the initial state, \( P_0 \) and \( V_0 \), because the entropy is the same for both curves for the first and second terms of \( (V - V_0) \) [25]. In Fig. 3.3, this can be displayed graphically in the \( P-V \) plane for Al [37, 38]. It shows the Hugoniot, Rayleigh line (line connecting initial and final states or equivalently conservation of momentum (Eq. 2.50)), isentrope, and 0-K isotherm for Al from Ref. [37]. The principal isentrope lies below the principal Hugoniot as expected from Eq. 3.6, for \( V < V_0 \). Also, the two curves nearly coincide until \( \sim 30 \) GPa, consistent with Eq. 3.6.

For strong shocks \( (P \gg P_0) \), the Rankine-Hugoniot equation for the total internal specific energy (2.51) becomes \( E_1 = (1/2)P_1(V_0 - V_1) \). Whereas the internal energy for isentropic compression is given by \( E_{\text{isen}} = -\int_{V_0}^{V_1} P_{\text{isen}} dV \), where \( P_{\text{isen}} \) is the pressure along the isentrope. Therefore in Fig. 3.3, the total internal energy is given by the area of the triangle under the Rayleigh Line (blue shaded region) and the internal energy due to isentropic compression is the area under the isentrope. This means the area between the Rayleigh Line and the isentrope (striped region) is the irreversible internal energy responsible for the entropy and temperature increase.

Laser ablation can be used to produce both shock and ramp compression by controlling the rate of rise of the laser pulse shape. Ramp compression is close to isentropic but not necessarily due to time-dependent phenomena including phase transformations and plastic flow. The applied ablation pressure is proportional to the laser intensity, \( I \), and
Figure 3.3: The Hugoniot, Rayleigh line, Isentrope, and 0-K isotherm for Al from Refs. [37, 38]. The total internal energy is given by the area of the triangle under the Rayleigh Line (blue shaded region).

Laser wavelength, $\lambda$, and scales as $\sim (I / \lambda)^{2/3}$, for stationary laser-driven ablation [39]. Therefore, one can control the dynamic loading of a target by designing a laser pulse shape suited for the specific target component thicknesses. The laser pulse is “ramped” as a function of time over a relatively long time scale, 10s of nanoseconds, compared to the rise time of a shock compression laser pulse shape, 10s of picoseconds.

A ramp wave can steepen to form a shock wave as it propagates depending on the rate of rise of the pulse shape and the material EOS. Recall from Sec. 2.3.1, the solutions to the wave equation for planar isentropic flow are sound waves propagating at $U \pm C_E$, where $C_E$ is the Eulerian sound speed $[C_E^2 = \left( \frac{\partial P}{\partial \rho} \right)_S]$ and $U$ is the flow velocity. $C_E^2 = \left( \frac{\partial P}{\partial \rho} \right)_S$ is positive for most materials in the absence of phase transitions, hence, the sound speed increases monotonically as a function of pressure. Therefore, the initial ramp wave, traveling at $C(\rho_0)$, will eventually be taken over by subsequent ramp waves traveling at $C(\rho > \rho_0) > C(\rho_0)$. 
3.1.3 Scaling of Ablation Pressure to Laser Intensity

The many mechanisms involved with laser-energy deposition including cross-beam energy, laser-plasma instabilities, and electron thermal transport complicate the scaling of ablation pressure with laser intensity. In practice, this makes it difficult to design laser-driven compression experiments with the goal of achieving a particular pressure and temperature state. However, experiments by Fratanduono et al. directly measured the instantaneous ablation pressure scaling with respect to laser intensity for diamond targets under ramp-compression up to 970 GPa at the OMEGA laser facility [40]. The experiments involved back propagating measured free-surface velocities in ramp-compressed diamond targets to the ablation front using the method of characteristics. The scaling, for intensities between $3.0 \times 10^{12}$ to $7.1 \times 10^{13}$ W/cm$^2$ and pressures
in the range of 95 to 870 GPa, was found to be,

\[ P(\text{GPa}) = 42(\pm 3)[I(\text{TW/cm}^2)^{0.71(\pm 0.01)}]. \]

This power law dependence deviates from the various theoretical models due to the complicated processes involved in the laser energy coupling. These results can be used to design ramp-compression experiments with diamond ablators. An example of a laser pulse shape used for ramp-compression is shown in Fig. 3.4 (blue line) and the corresponding applied ablation pressure (red) is calculated from Eq. 3.7. It reaches a peak applied pressure of \( \sim 270 \) GPa, giving an accurate estimation of the pressure achievable with this pulse shape. In Section 2.4, the applied pressure profiles were generated using this scaling.
3.1.4 Target Design

In these experiments, the sample under study was sandwiched between a plate of \(\langle 110 \rangle\)-oriented single-crystal diamond (the ablator/pusher) and a \(\langle 100 \rangle\)-oriented Lithium Fluoride (LiF), \(\langle 100 \rangle\)-oriented Magnesium Oxide (MgO) or another \(\langle 110 \rangle\)-oriented single-crystal diamond plate (rear window). Single-crystal tamper layers are used because the diffracted x-rays from the single-crystal create a pattern of spots and this is distinct from the diffraction from the polycrystalline sample that is a pattern of rings. The corresponding pulse shapes were designed using radiation–hydrodynamic simulations guided by the scaling found by Fratanduono et al. to avoid shock formation in the target. The simulation shown in Fig. 3.5 directly converts an input laser pulse shape into an applied pressure using the laser intensity scaling for diamond [40] (Eq. 3.7), resulting in much improved results compared to conventional ray-tracing algorithms. An example pressure contour from a simulation of a diamond-Al-diamond target is shown in Fig. 3.5 for the pulse shape shown in Fig. 3.4. The pressure (colormap) as a function of space and time is shown in the contour plot with the material interfaces called out. The Al pressure is designed to be maximum and uniform for at least 1-ns, represented by the vertical black dashed lines, for XRD. As seen in the simulation, the reverberations at the material interfaces increase or decrease the pressure depending on the material’s relative impedances. These reverberations drive the sample to a uniform high-pressure in diamond sandwich targets with Al samples.

Diamond was chosen as the ablator and window material for a number of reasons. First, diamond is ideal for ramp compression due to its high bulk modulus making it more resistant to shocking up. Second, diamond under ramp-compression is well understood. It’s ramp EOS was measured up to 5 TPa [41, 42] and, as mentioned, the ablation pressure scaling with laser intensity was measured [40]. It’s low atomic number results in low absorption of x-rays for diffraction while improving hydrodynamic efficiency including greater electron-heat conduction and lower radiation losses (therefore, less preheat of the sample).
Figure 3.6: A radiation-hydrodynamics simulation of a C-Al-LiF target used to design the laser pulse shape and determine the x-ray timing in x-ray diffraction experiments. Simulations performed by Ray Smith of Lawrence Livermore National Laboratory.
In some cases, LiF or MgO are used as the rear window material in the target. LiF was chosen because it is transparent to the VISAR probe laser, 532 nm, under ramp compression up to 800 GPa [43] and is transparent under shock compression to 215 GPa [44–46]. Similarly, the optical and mechanical responses of LiF under ramp compression have been well characterized at Sandia’s Z machine [46, 47]. MgO was chosen as a window material because it is also transparent to the VISAR probe beam but has a material impedance more similar to that of diamond. MgO was measured to be transparent under shock compression up to 226 GPa [48] and was found to be transparent under ramp compression to even higher pressures but undergoes a B1-B2 phase transformation at 600 GPa [49]. Therefore, MgO windows are only used for pressures less than 600 GPa in order to avoid complications in interpreting the XRD data.

Transparent LiF and MgO windows allows one to directly measure the sample–window interface velocity using VISAR. With knowledge of the optical and mechanical response of LiF or MgO under ramp compression [43, 46–48], the pressure at the sample–window interface can be deduced using the impedance matching boundary conditions without the need to back propagate from the free surface. On the other hand, single-crystal diamond windows become opaque to the VISAR probe laser under ramp-compression above $\sim$100 GPa [49, 50]. Therefore, only the velocity of the rear surface of the target, or free-surface velocity, is measured. The use of a transparent window eliminates the need to back-propagate a free-surface velocity and the systematic errors associated with the diamond EOS, strength effects, and assumptions of wave interactions within the window. A transparent window can also provide the sample reflectivity which can be used to study its optical properties under ramp compression.

A radiation–hydodynamic simulation for the C-Al-LiF target is shown in Fig. 3.6 for the same pressure loading as the simulation shown in Fig. 3.5. The use of a LiF window improves accuracy of the pressure determination in the Al sample targets because it has a wave-impedance much closer to that of Al compared to diamond, thus
only a small correction to the interface pressure is needed to obtain the pressure inside
the sample. This can be seen in Fig. 3.6 because the reverberations are not as strong
as the diamond window case. The optimal probe time for this target design is slightly
delayed compared to the diamond window case and the high-pressure is not held for
as long of a duration because of the relative impedances of the layers. For these very
reasons, simulations are used to understand these subtle but important differences that
depend on the target layer thicknesses, target layer materials, and total laser power.

3.2 Powder X-Ray Diffraction Image Plates (PXRDIP)

The x-ray diffraction diagnostic used in these experiments is called Powder X-Ray
Diffraction Image Plates (PXRDIP) [36]. This technique uses a mono-energetic x-
ray source (XRS) to probe a polycrystalline sample, the theory of which is discussed
in Sec. 2.1. The x-ray source is a laser-driven x-ray backlighter that produces He-α
radiation that forms a quasi-monoenergetic x-ray spectrum. The diffraction geometry
is calibrated using an in-situ reference diffraction pattern from a high-Z uncompressed
material. After measuring the 2θ diffraction angles, the crystal structure and density
are determined are determined from Bragg’s law (Eq. 2.1). Much of the discussion in
this section is based upon the work of Rygg et al. [36, 51].

3.2.1 Diffraction Geometry

X rays scattered from interatomic lattice planes with spacings, d, constructively in-
terfere when the Bragg condition, \( \lambda = 2dsin(\theta) \), is satisfied for an x-ray wavelength, \( \lambda \),
and x-ray incidence angle, \( \theta \). Diffraction from a crystal powder with a mono-energetic
x-ray beam will produce cones of diffracted x rays while a single-crystal will result in
a diffraction pattern of intense spots or no spots at all, shown in Fig. 3.7. To satisfy
the stringent Bragg condition, a powdered material (i.e. one with randomly orientated
Figure 3.7: Diffraction patterns produced from powdered (left) and textured (right) crystals.

crystal grains) is used with a monochromatic x-ray wavelength so that each of the crystals in the powder is randomly orientated so that each (hkl) plane has a crystallite which is at the correct angle to satisfy the Bragg condition. This will produce uniform cones of diffracted x rays for each allowed lattice plane for a material’s crystal structure. This geometry is shown in Fig. 3.7 (a). In contrast, a single crystal in a monoenergetic beam will not necessarily produce diffraction. Therefore, single-crystal diffraction typically uses a white light source in order to satisfy the Bragg condition. For single crystals, the diffraction pattern is an array of spots, or Laue reflections.

Texture is defined as the preferred orientation of the grains comprising a polycrystalline sample where the distribution of orientations is nonrandom. A diffraction pattern from a textured material is illustrated on the right in Fig. 3.7 (b). The result of the preferred orientations are Debye-Scherrer rings that have a variation in intensity around their circumference. In the case of rolled Al foils, the texture is so great that the intensity around the ring is discontinuous and parts of the ring are missing. The texture of the Al foil results from deformation during it’s production. Preferred orientation is common and usually unavoidable; a material with no texture is rare. The disadvantages of using an actual powder (not in the diffraction sense) sample is that the initial den-
Figure 3.8: The PXRDIIP box hardware [36].

...is difficult to characterize and, in the case of Al, the increased surface area of the powder can make the material pyrophoric.

Here powder diffraction is used to measure the scattering angle between the incident and diffracted beams, $2\theta$, and thereby determine the crystal structure. Under compression, the $2\theta$ for each lattice plane increases with decreasing interatomic spacing until a phase transformation occurs. When a new crystal structure is formed, an abrupt change in the scattering angles is observed as the symmetry, and therefore the structure factor (Eq. 2.8), changes for the new atomic arrangement. From the scattering angle, the interatomic $d$ spacing can be calculated from Bragg’s law when the x-ray wavelength is known.

The diffraction patterns are recorded on x-ray sensitive image plates (IPs) [52] placed on five sides of a stainless steel box shown in Fig. 3.8 [36]. The box is 50
Figure 3.9: The PXRDIP target assembly.

× 50 × 75 mm³ with a 10 × 10 mm² setting for the target assembly and a 25 mm-diam circular aperture on the back for the VISAR probe beam.

Fig. 3.9 shows the target assembly which comprises a pinhole baseplate made of tungsten, tantalum, or platinum (75–100 µm × 10 mm × 10 mm) with a 300 µm-diam pinhole [Fig. 3.9 (blue)]. The pinhole diameter can be increased if more throughput is desired but at the cost of broadening the diffraction lines. The pinhole aperture serves as a x-ray collimator so that only x rays diffracted from the center of the driven target reach the IPs. The pinhole also produces an in situ reference diffraction pattern used to determine the diffraction geometry. The sample assembly consisting of an ablator, sample, and window [Fig. 3.9 (gray and red)] is mounted on top of the pinhole aperture. A plate of Ta is placed around the 3 × 3 mm² main target, with the same thickness as the main target assembly [Fig. 3.9 (pink)] to provide additional shielding of the IPs from the ablation plasma radiation. Another Ta plate, with a 2 mm-diam circular aperture, is placed on top of the main target to keep the main target in place while providing
Figure 3.10: The IP arrangement in the PXRDIP box.

additional shielding [Fig. 3.9 (purple)]. Ideally, if the pinhole substrate is also made of Ta, the two shielding plates can be made of Tungsten or another high Z material to provide broader spectral coverage for the shielding. Then, a 25–50 mm layer of Kapton [Fig. 3.9 (orange)] is laid on top of the outermost Ta plate so that the wings of the laser spot do not hit the high-Z shielding and generate background x rays. Finally, a 3D printed plastic frame [Fig. 3.9 (black)] acts as a spacer to hold the entire assembly flush against the PXRDIP box in its setting shown in Fig. 3.8.

The IP arrangement inside the PXRDIP box is shown in Fig. 3.10. The IPs are referred to as up, down, left, right, and back depending on their location in the box. The magnetic IPs are held flush against the walls of the box. The IPs are also arranged in the box to minimize the number of degrees of freedom (DOFs). Looking through the back plate, the clockwise edge of each IP is pushed flush against the respective corner of the box. Therefore, IP rotational DOFs and one translational DOF are eliminated. The notches cut into the corners of the IPs are always facing the back plate in order to keep track of plate orientation when scanning.

The Debye-Scherrer rings trace out conic sections on the IPs as shown in Fig. 3.11.
The diffraction rings from the ambient density bcc W pinhole are labeled with their (hkl) plane and scattering angle for a Cu (8.37-keV) backlighter XRS. The other diffraction rings are from high-pressure Al. Positions along the pinhole diffraction rings are assigned their known $2\theta$ value and a least squares minimization routine is used to determine the best fit to IP, XRS, and pinhole locations relative to the diffraction lines. To optimize the diffracted x-ray scattering angular coverage, the XRS is typically 25 mm away from the main target and at a 23° angle with respect to the target normal. The diffraction scattering angle coverage shown here is 30°–98°. The pinhole image of the direct XRS is located on the down plate, in Fig. 3.11, labeled with 0° scattering angle. The down IP with the direct XRS image is usually saturated requiring multiple scans of the image plates to extract most of the x-ray excited photoelectrons. The position of the direct XRS image is more well defined in the IP scan that is less saturated, therefore the white rectangular box around the direct XRS is the second IP scan image superimposed on the first.

X-ray diffraction patterns for ambient density fcc Pt and high-pressure Si are shown in Fig. 3.12 using a Ge (10.25-keV) backlighter. The use of a higher energy, smaller wavelength XRS results in a smaller diffraction scattering angle for a given $d$-spacing (Eq. 2.1.) In Fig. 3.12, the scattering angles and (hkl) planes are labeled for the diffraction
Figure 3.12: Raw PXRDIP IP scans with a Pt pinhole and a Ge (10.25-keV) backlighter.

In designing a XRD experiment, it is important that the diffraction from the reference pinhole material does not overlap with the expected high-pressure sample diffraction. In the case of fcc Pt, shown in Fig. 3.12, there are more diffraction lines compared to bcc W (Fig. 3.11) which can increase the chances for overlapping the sample diffraction pattern.

Once the best fit geometric values are obtained, the diffraction patterns are projected into $2\theta$-$\phi$ space. A $2\theta$-$\phi$ projection for the same data as in Fig. 3.11 is shown in Fig. 3.13. Averaging along $\phi$ gives the typical intensity as a function of $2\theta$ plot for comparison with other diffraction patterns. There are a number of features on the IP data. First, the hole for the VISAR probe beam is on the back plate in Fig. 3.11 and at $\phi = 0^\circ$ and $2\theta = 20^\circ$ in Fig. 3.13. Diffraction from the single-crystal diamond and LiF plates manifest as intense spots on the IPs with a characteristic broad width in $2\theta$ (as seen at $\phi = \pm 140^\circ$ and $2\theta = 38^\circ$). The ablator and window were chosen to be single-crystal so that the diffraction would be distinct from the polycrystalline sample, however indexing the Laue spots is difficult because the diffracted x-ray wavelength is unknown because it originates from the quasi-monoenergetic XRS. The large $2\theta$ width of the Laue spots is caused by the large pressure gradients present in the ablator and window. The Laue spots are identified by their unique characteristics and masked out of the lineout, shown on the bottom of Fig. 3.13. The diffraction lines from the
Figure 3.13: Background subtracted $2\theta$-$\phi$ projection of IP data from shot 25789.
pinhole and sample are then distinguished (labeled as “W” and “Al”, respectively,) and
a Gaussian fit is performed on the diffraction peaks to determine the best-fit $2\theta$ and their
corresponding uncertainties. The minimum uncertainty in $2\theta$ is taken to be 0.2°, and
greater uncertainty is assigned to diffraction patterns with poor geometric parameter
fits. This error is propagated to lattice $d$-spacing using Bragg’s law. A systematic error
in $2\theta$ due to the offset in position of the aperture relative to the sample is discussed in
Sec. 3.2.4.

3.2.2 X-ray Source

Typically, x-ray sources for diffraction vary from high-voltage Cu x-ray tubes (Cu
$K_\alpha$ = 1.54 Å) to the brightest free-electron lasers (1 – 5 Å) and synchrotron radiation
sources (0.1 – 1 Å.) For convenience, the x-ray sources (XRS) for these experiments
were laser-driven Cu or Ge x-ray backlighters. Because laser-driven experiments last
only tens of nanoseconds, the XRS must be bright while only lasting a nanosecond or
less. The tolerable duration of the XRS is determined by the duration of the uniform
pressure state. Laser-driven x-ray backlighters satisfy these requirements. An x-ray
backlighter is a laser-driven foil made of a transition metal (e.g. Fe, Cu, Ge, Cr, Ni,
Zn) that is ionized to generate He$\alpha$ emission. The Cu (8.37-keV) and Ge (10.25-keV)
backlighters used in these experiments were 2 mm ʻ 2 mm ʻ 10 µm foils attached to
boron carbide stalks. Measurements of the x-ray conversion efficiency found that 2%,
0.6%, and 0.2% of the laser energy is converted into He$\alpha$ x-rays for Fe, Cu, and Ge
foils, respectively [53].

One or two laser beams irradiated the backlighter foil with a 1250-J (maximum en-
ergy), 351-nm, 1-ns, temporally square pulses with 200/250-µm or 280/360-µm focal-
spot sizes to optimize laser energy to x-ray conversion efficiency for a Ge or Cu back-
lighter foil, respectively. This corresponds to intensities of $4.0 \times 10^{15}$ or $2.5 \times 10^{15}$
W/cm$^2$. 
Crystal x-ray spectrometers are used to diagnose the spectral content of the x-ray source [54]. An example spectrum is shown in Fig. 3.14 for a Cu backlighter irradiated with two beams at an intensity of $2.4 \times 10^{14}$ W/cm$^2$. The strongest line in the spectrum is the He$_\alpha$ followed by the He$_\beta$. Because the XRS is only quasi-monoenergetic, additional filtering across the IPs is used to attenuate x-rays other than the He$_\alpha$. For Cu backlighters, K-edge filters comprised of Cu are used to filter x rays with energies higher than the material K edge and to attenuate background from the ablation plasma. For Ge backlighters, Al filters are used to attenuate low-energy (<4 keV) background, although preferably, expensive K edge Ge filters would be used.

Choice of XRS material dictates the x-ray wavelength and hence the attenuation in the sample and the location of Debye-Scherrer rings on the IPs. The $1/e$ optical depths or attenuation lengths at 23.5° for C, Al, and LiF are shown in Fig. 3.15 [55]. The ideal thickness of the XRD sample, from diffraction signal considerations only, is one optical depth [36]. For a Cu backlighter, the ideal thickness of an Al sample is 35 $\mu$m for a x-ray source at an angle of 23.5°. However, the choice of thickness must also
be optimized in order to prevent the ramp wave from steepening into a shock and to minimize errors in the pressure determination due to gradients. For these experiments, Al samples of 15 µm and 20 µm were chosen to trade off diffraction signal for pressure precision.

For the scattering angle coverage shown in Figs. 3.11 and 3.12 ($2\theta = 30^\circ–100^\circ$), the detectable $d$ spacings for Cu (8.37-keV) and Ge (10.25-keV) XRSs are 2.86–0.97 Å and 2.33–0.79 Å. Higher energy x-rays are capable of probing smaller lattice spacings and effectively squeezes the XRD rings together on the IPs. For instance, for the shots in the hcp phase, Cu backlighters were used to better resolve the hcp triplet [(100), (002), (101)].

### 3.2.3 Structure Determination and Phase Transformations

A crystal structure is assigned to a diffraction pattern based upon the presence and absence of the allowed reflections (Sec. 2.1.4). The two observables, lattice $d$-spacing
Figure 3.16: The measured lattice spacing for each observed diffraction ring versus the pressure measured via velocimetry (Sec. 3.4).

and pressure, for compressed Al are plotted and compared to the expected $d$ spacing, shown in Fig. 3.16. The Kerley 3700 principal isentrope [28] (black, red, and blue curves) is used to calculate the expected reduction of the lattice $d$ spacing with pressure and does not include phase transitions. The curves are calculated from the isentropic pressure-density curve by first calculating the volume, $V$, from the density, using

$$V = \frac{wA}{\rho N_A},$$ (3.8)

where $w$ is the atomic weight, $A$ is the number of atoms per cell for a specific crystalline structure, $\rho$ is the mass density, and $N_A$ is Avogadro’s constant. The atomic volume is simply $V/A$. The lattice parameters can be calculated from the volume for a
given unit cell, using

\[ V = a^3, \quad \text{(Cubic)} \]
\[ V = a^2c, \quad \text{(Tetragonal)} \]
\[ V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c, \quad \text{(Hexagonal)} \]
\[ V = a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}, \quad \text{(Rhombohedral)} \]
\[ V = abc, \quad \text{(Orthorhombic)} \]
\[ V = abc, \sin\beta \quad \text{(Monoclinic)}, \quad \text{and} \]
\[ V = abc \sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}. \quad \text{(Triclinic.)} \] (3.9)

Then the basis vectors, \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \), can be defined from the lattice parameters. For example, \( \mathbf{a}_1 = [a, 0, 0], \mathbf{a}_2 = [0, a, 0], \mathbf{a}_3 = [0, 0, a] \) for cubic lattices and \( \mathbf{a}_1 = [a, 0, 0], \mathbf{a}_2 = [a\cos(2\pi/3), a\sin(2\pi/3), 0], \mathbf{a}_3 = [0, 0, c] \) where \( c = \sqrt{8/3}a \) for hexagonal close packed (hcp) lattices. The volume of the primitive or Wigner-Seitz cell, the minimum volume cell to define the crystal, is \( V_p = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3| \) when \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) are the primitive basis vectors. The reciprocal lattice basis vectors are then defined by

\[
\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_p},
\]
\[
\mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V_p}, \quad \text{and}
\]
\[
\mathbf{b}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V_p} \] (3.10)

It is useful to work in reciprocal (k-space or Fourier) space in XRD. The reciprocal lattice vectors have the property that \( \mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij} \), therefore \( \mathbf{b}_1 \) is perpendicular to the
The vector perpendicular to a particular (hkl) plane is defined by

$$ \mathbf{R}^* = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3, $$

(3.11)

where the magnitude is equal to, $|\mathbf{R}^*| = 1/d_{hkl}$. Therefore, the curves for the lattice spacing, $d_{hkl}$, as a function of pressure can be calculated. Another useful expression is the angle between any two lattice planes $[(hkl)$ and $(h_1k_1l_1)]$,

$$ \cos \phi = \frac{\mathbf{R}^* \cdot \mathbf{R}^*_1}{|\mathbf{R}^*||\mathbf{R}^*_1|}, $$

(3.12)

For example, the initial spacing of the (111) planes of fcc Al can be calculated using Eqs. 3.8–3.11 with the following inputs: the initial density of Al (2.7 g/cc), 4 atoms per unit cell in fcc, atomic weight (26.98 g/mol), and Avogadro’s constant ($6.022 \times 10^{23}$ mol$^{-1}$). From Eq. 3.8, the initial volume is 66.37 Å$^3$ and for a cubic crystal, Eq. 3.9 gives the lattice parameter $a = 4.05$ Å. The lattice basis vectors are $\mathbf{a}_1 = [a,0,0], \mathbf{a}_2 = [0,a,0], \mathbf{a}_3 = [0,0,a]$ which give the reciprocal lattice vectors, $\mathbf{b}_1 = [1/a,0,0], \mathbf{b}_2 = [0,1/a,0], \mathbf{b}_3 = [0,0,1/a]$. Then $|\mathbf{R}^*| = \sqrt{(h/a)^2 + (k/a)^2 + (l/a)^2}$ and $d_{111} = 1/|\mathbf{R}^*| = 2.34$ Å. In Fig. 3.16, this corresponds to the zero pressure $d$ spacing of the fcc (111) plane (black line). The (111) plane spacing decreases with increasing pressure because the density increases. The $d$ spacing versus pressure curves for the other allowed lattice planes in the fcc, hcp, and bcc phases are calculated in the same manner. If the lattice parameters are known, the $d$ spacing for a particular lattice plane can be calculated directly from these simplified equations.
Figure 3.17: A map of $\chi^2$ as a function of lattice parameters $a$ and $c/a$. Contours of $\chi^2 = \chi^2_{\text{min}} + 1$ correspond to the confidence region of this fit.

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{(Cubic)},
\]
\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2 + c^2} \quad \text{(Tetragonal)},
\]
\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad \text{(Hexagonal)}, \quad \text{and}
\]
\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{(Orthorhombic)}. \quad (3.13)
\]

which are derived using the methods just described.

Examining Fig. 3.16, each black, red, and blue point represents a $d$ spacing derived from a observed diffraction line and it is plotted against the pressure determined by velocimetry (Sec. 3.4.) Multiple points plotted at the same pressure indicates that multiple diffraction rings were observed on a given shot. The points are compared to the black, red, and blue curves in order to determine the crystalline structure. The color of the points are based upon their indexed phase: fcc, hcp, or bcc.
After the diffraction peaks are indexed, the method of least squares is used to determine the best-fit lattice parameters from the measured \(d\)-spacing, and a \(\chi^2\) minimization routine is used to determine the uncertainty in the lattice parameters. For a cubic crystal, a one-parameter fit is performed to determine the lattice parameter, \(a\), while in a hexagonal crystal, a two-parameter fit is done to find \(a\) and \(c/a\). A least squares algorithm is used to find the lattice parameters that minimize

\[
\chi^2(a, c/a) = \sum_{i=1}^{N} \frac{(d_i - d_{\text{fit}}(a, c/a))}{\sigma_i^2},
\]

where \(d_i\) is the observed lattice spacing and \(\sigma_i\) is the uncertainty in \(d_i\). The parameter \(d_{\text{fit}}\) is calculated for an array of \(a\) and \(c/a\) and is given by

\[
d = \begin{cases} 
\frac{a}{\sqrt{h^2 + k^2 + l^2}} & \text{(Cubic),} \\
\frac{ac}{\sqrt{\frac{4}{3}c^2(h^2 + hk + k^2) + a^2l^2}} & \text{(Hexagonal)}
\end{cases}
\]

for cubic and hexagonal crystals. A map of \(\chi^2\) is shown on the left in Fig. 3.17 for a range of \(a\) and \(c/a\) for a hexagonal crystal. In this optimization, two diffraction peaks corresponding to the hcp phase were measured. Fig. 3.17 (left) shows a contour (white) of \(\chi^2 = \chi^2_{\text{min}} + 1\) and the tangents to that contour (white dashed lines). The tangents correspond to \(a_{\text{fit}} \pm \sigma_a\) and \(c/a_{\text{fit}} \pm \sigma_{c/a}\) where \(\sigma_a\) and \(\sigma_{c/a}\) are one standard deviation from the least squares estimates of \(a_{\text{fit}}\) and \(c/a_{\text{fit}}\) [56]. On the right, the \(\chi^2\) as a function of the lattice parameter, \(a\), is shown where the value of \(a\) that corresponds to a minimum \(\chi^2\) is the least squares estimator for \(a\). The uncertainty in \(a\) is the change in \(a\) necessary to increase the value of \(\chi^2\) by one. The three vertical dashed black lines are drawn at the least squares estimator of \(a\), and \(\pm \sigma_a\). This analysis is performed for all the diffraction patterns. If multiple phases are present in a single diffraction pattern, the peaks from each phase are fitted separately to determine the lattice parameters for
each phase.

This analysis can be cross checked with standard error propagation. The errors in \(a\) and \(c/a\) are given by

\[
\sigma_a = \sqrt{\left(\frac{\partial a}{\partial d}\right)_{d=d_{\text{obs}}}^2 \sigma_d^2},
\]

and

\[
\sigma_{c/a} = \sqrt{\left(\frac{\partial (c/a)}{\partial d}\right)_{d=d_{\text{obs}}}^2 \sigma_d^2 + \left(\frac{\partial (c/a)}{\partial a}\right)_{a=a_{\text{obs}}}^2 \sigma_a^2}, \tag{3.16}
\]

where \(d_{\text{obs}}\) is the observed \(d\) spacing and \(\sigma_d\) is the error in the \(d\) spacing. The analysis shown in Fig. 3.17 is checked here. The measured \(d\) spacing for the observed hcp (011) diffraction peak was \(d_{011} = 1.7038 \pm 0.0015 \text{ Å}\) and for hcp (100), \(d_{100} = 1.916 \pm 0.002 \text{ Å}\). The hcp(100) peak can be used to determine \(a = 2.213 \pm 0.002 \text{ Å}\).

This is calculated using Eq. 3.13,

\[
a = \frac{d}{\sqrt{\frac{4}{3}(c/a)^2(h^2 + hk + k^2) + l^2}} \frac{c}{a}, \tag{3.17}
\]

and the error in \(a\) is derived by taking the derivative of Eq. 3.17 with respect to \(d\),

\[
\sigma_a = \sqrt{\left(\frac{\partial a}{\partial d}\right)_{d=d_{\text{obs}}}^2 \sigma_d^2} = \sqrt{\left(\frac{\sqrt{\frac{4}{3}(c/a)^2(h^2 + hk + k^2) + l^2}}{c/a}\right) \sigma_d^2}. \tag{3.18}
\]

This is in agreement with the \(\chi^2\) minimization analysis that gets \(a = 2.213 \pm 0.003 \text{ Å}\). The \(c/a\) and \(\sigma_{c/a}\) can now be calculated using the value and error in \(a\) and substituting
into Eqs. 3.13 and 3.16 giving,

\[
c/a = \frac{dl}{\sqrt{a^2 - \frac{4}{3}d^2(h^2 + hk + k^2)}} \tag{3.19}
\]

and

\[
\sigma_{c/a} = \sqrt{\left(\frac{3\sqrt{3}a^2l}{(3a^2 - 4d^2(h^2 + hk + k^2))^{3/2}}\right)^2 \sigma^2_d + \left(\frac{3\sqrt{3}adl}{(3a^2 - 4d^2(h^2 + hk + k^2))^{3/2}}\right)^2 \sigma^2_a} \tag{3.20}
\]

This results in a best fit \(c/a = 1.683 \pm 0.011\) compared to the \(\chi^2\) result \(c/a = 1.682 \pm 0.009\).

3.2.4 Systematic correction to pinhole 2\(\theta\)

A correction to the 2\(\theta\) scattering angles calibrated with diffraction from the pinhole aperture was calculated to account for the spatial offset of the sample and the pinhole cylindrical aperture. A simple case of this correction is illustrated in Fig. 3.18.

The x-ray source, X, is at a position, \((r_x, \pi - \alpha, \phi_x)\), and the detector location is at a position, \((r_d, \beta, \phi_d)\). In this simple case, \(r_x = r_D = 27000\) \(\mu\)m, \(\alpha = \beta = 30^\circ\), the diameter of the aperture is 300 \(\mu\)m, and the XRS and detector are in plane (\(\phi_x = \phi_d = 0^\circ\).) The difference between 2\(\theta\)c and 2\(\theta\)nom, \(\Delta 2\theta\), is the desired quantity. 2\(\theta\)nom is equal to 2\(\alpha\) in this geometry. On the right in Fig. 3.18, the angle \(\theta_p\) can be written as

\[
\theta_p = \tan^{-1}\left[\frac{r_x \sin \theta_n}{r_x \cos \theta_n + d_a/2}\right] = \tan^{-1}\left[\frac{r_x \cos \alpha}{r_x \sin \alpha + d_a/2}\right].
\]

The angle 2\(\theta\)c = 180 – 2\(\theta\)_p = 180 – 2\(\tan^{-1}\left[\frac{r_x \cos \alpha}{r_x \sin \alpha + d_a/2}\right]\). This gives a value of \(\Delta 2\theta\) = 2\(\theta\)_c – 2\(\theta\)_nom = 0.55\(^\circ\), therefore this can be a substantial correction that must be accounted for in these data. Currently, a simple correction is applied that uses the \(\Delta 2\theta\) for the center pinhole element opposite the IP pixel.
A numerical ray tracing of the pinhole aperture was performed in order to understand the contribution to the $2\theta$ scattering angle from the inner pinhole cylindrical face and edges. The pinhole was finely gridded in cylindrical coordinates, $r, \phi,$ and $z$ for a thickness, $h_a$, a radial depth corresponding to two optical depths and over all azimuthal angles. Rays were launched from $X$ to each pinhole grid element, $C$, and then from $C$ to the detector element $D$. Along each ray path, the total path length, $s$, through the pinhole material was calculated. Then, the $2\theta_c$ from each pinhole grid point was weighted by $\exp[-\mu s]$, where $\mu$ is the linear absorption coefficient for the pinhole material, in order to calculate the expected $2\theta$ compared to the nominal, $2\theta_{nom}$.

The results of the simulations are shown in Fig. 3.19 for $\alpha = 30^\circ$, $r_x = 37$ mm, $r_d = 27$ mm, $h_a = 75$ $\mu$m, $d_a = 300$ $\mu$m, and $1/\mu = 3$ $\mu$m. The maximum correction to $2\theta$ was calculated to be about $0.45^\circ$ for the three cases shown: $\phi_x = \phi_d = 0^\circ$ (blue curve), $\phi_x = 0^\circ, \phi_d = 90^\circ$ (red curve), and $\phi_x = 0^\circ, \phi_d = 180^\circ$ (yellow curve.) The spike at $\beta = 30^\circ$ for the $\phi_x = 0^\circ, \phi_d = 180^\circ$ case corresponds to straight through x-rays, but the signal at this location will be overwhelmed by the direct x-ray source image. On
Figure 3.19: Difference in scattering angle, $\Delta \theta$, from the “nominal” center of the pinhole and the expected scattering angle calculated from a numerical ray trace of the pinhole aperture. On the right, a circle with a radius proportional to $\exp[-\mu s]$ is drawn for each pinhole grid point for the $\phi_x = \phi_d = 0^\circ$, $\beta = 30^\circ$ case.

the right in Fig. 3.19, an example coarse gridding of the pinhole is shown for the case $\phi_x = \phi_d = 0^\circ$ for $\beta = 30^\circ$. The radius of the circle drawn at each pinhole grid point is proportional to $\exp[-\mu s]$. For this configuration, the main contribution to the pinhole diffraction is the inner surface of the pinhole opposite the detector. This correction is significant because without it, a systematic error up to $0.45^\circ$ can occur.

### 3.3 Velocity Interferometer System for Any Reflector (VISAR)

A line-imaging Velocity Interferometer System for Any Reflector (VISAR) [57] detects Doppler shifts of a 532-nm probe beam reflecting off a moving surface in the target (e.g. sample interface through a transparent window, shock front, free-surface). The Doppler shifts are manifested as shifts in the fringe pattern recorded in a 2-D interferogram. The fringe shifts are proportional to the changes in the velocity of the
reflecting surface and these velocities are used to determine the pressure of the Al or Na samples. The intensity of the VISAR signal provides information about the target reflectance.

3.3.1 VISAR Instrumentation

An optical diagram showing the image relay from the target to the interferometer for the VISAR on OMEGA EP is shown in Fig. 3.20. The VISAR probe laser is a 50-ns high-power monochromatic injection-seeded frequency-doubled (532 nm, green) Q-switched Nd:YAG laser. The probe intensity can be adjusted to accommodate for the reflectivity of the target or the expected reflectivity of a shock (using a filter wheel comprising neutral density (ND) filters.) The probe laser is delivered to the input beamsplitter with a 1-mm optical fiber whose image is relayed to the target illuminating
a 1-mm area of the target with a spatially uniform intensity. The VISAR telescope is shown in the inset of Fig. 3.20. The f/3.3 input lens is a combination of L1 (meniscus) and L2 (achromat) to produce a relatively fast collection system. Lens L1, L2, and L3 are fixed in a tube that is mounted into the target chamber through a ten inch manipulator (TIM), allowing the focal point to be adjusted. The reflected beam is recollimated by L4 before being sent into a periscope, a dichroic mirror, and the optical table. The dichroic mirror reflects the 532-nm light towards two interferometers while transmitting other wavelengths produced by target self-emission used for streaked optical pyrometry (SOP) [60]. The self-emission is typically used to calculate a brightness temperature of high-temperature shock waves ($>10^7$ K), therefore SOP is used in these experiments to confirm that the temperature of the compressed target is less than 3000-4000 K.

The beam is relayed to a Mach-Zehnder interferometer shown in Fig. 3.21. M1 and M2 are silvered mirrors and B1 and B2 are 50-50 beam splitters for 532-nm. The beam first reaches a 532 nm 50-50 beamsplitter, B1, that splits it into two beams. An etalon is installed in one leg of the interferometer to impart a temporal delay on the wavefront and the optical path length (OPL) is adjusted to maintain image focus. Instead of using the Mach-Zehnder configuration to determine the relative phase shift between a sample and reference beam, the delay causes the beam to be interfered with itself at a time, $\tau$, later. A low-power green CW laser is used to align the interferometer which entails
adjusting the relative path differences between the two legs of the interferometer until
they are matched to within about 1.5 \( \mu m \) [58] and two overlapping images are produced
at B2. The delay etalon is then inserted in the delay leg and M2 is translated by a
distance, \( d = h (1 - 1/n_0) \), where \( h \) is the thickness of the delay etalon and \( n_0 \) is the
index of refraction of the etalon. This results in a total temporal delay,

\[
\tau = \frac{2h}{c} \left(n_0 - \frac{1}{n_0}\right).
\]  

(3.21)

This can be derived by calculating the time difference between the delayed, \( t_L \), and
undelayed leg, \( t_S \). The length of the delayed or long leg is \( x_L = x_S + 2d \), where \( x_S \) is the
length of the undelayed or short leg. Therefore, \( t_S = x_s/c \) and \( t_L = (x_L - 2h + 2hn_0)/c \)
gives \( \tau = t_L - t_S \), where \( c \) is the speed of light. Etalon delays between 10 ps and 310 ps
(\( h = 2 - 60 \) mm) can be used depending on the desired velocity sensitivity and temporal
resolution. (Due to the time delay, the optical phase at the output beamsplitter is a
combination of the light from the short and long paths.) Lastly, the output beamsplitter
is tilted in order to impose an interference pattern across the image to use as a phase
reference.

The target image is then focused onto the slit of an optical streak camera. The
streak camera platform was invented at the LLE and the platform is called the Rochester
Optical Streak System (ROSS) [61]. The primary components of a the VISAR streak
camera include a photocathode, a Photonis P820 streak tube, a phosphor screen, and
a SI 800 charged-coupled device (CCD). The streak camera produces an image with
intensity information as a function of both space and time. One-dimensional spatial
information of the target is acquired by imaging the target onto a slit. The light is
then incident on a photocathode and via the photoelectric effect produces a cascade of
electrons that are accelerated towards the back of a P820 streak tube. Within the streak
tube, there are a number of electron optics with the main component being the sweep
electrodes. These electrodes have a time dependent voltage that deflects the incoming
electrons at different angles depending on their arrival time. The electrons are then incident on a micro-channel plate (MCP), a phosphor screen, and a CCD in order to convert the electrons back into photons. Due to the sweeping electrodes, the light on the top of the phosphor screen corresponds to the electrons that arrived first and the light on the bottom of the phosphor screen corresponds to the last electrons to pass through the electrodes. In this way, temporal information about the light passing through the slit is contained in one dimensional of the image while 1-D spatial information is contained in the other dimension.

When in static mode (no streak), green light upon the photocathode focuses to 70 \( \mu \text{m} \) (FWHM) (line spread function). This corresponds to 395 timing resolution elements across the SI 800 CCD (2048 pixels*13.5 \( \mu \text{m} \)). This width is due to the transverse electron energy distribution off the photocathode which creates a finite width of a virtual focal point for the electron optics in the streak tube. This virtual image is focused, analogous to regular optics, down to the phosphor at the end of the streak tube. This produces a threshold on the timing resolution of the P820 streak tube. Assuming that two time resolution elements must be separated by two FWHM, the timing resolution of the P820 streak camera is 0.51\% of the sweep speed. The cathode sensitivity can be used to control the transverse electron energy distribution if used near the cutoff. This is because the electrons will have barely enough energy to overcome the work function of the photocathode. The timing resolution quoted here is sensitive to the cathode sensitivity curve and is only valid for green light [62].

3.3.2 VISAR Analysis

An example VISAR image from a PXRDIP experiment is shown in Fig. 3.22. The VISAR system is sensitive to changes in the phase, \( \Delta \phi(t) = \phi_S(t) - \phi_L(t) \). Therefore, when the target is not moving or moving at a constant velocity, no Doppler shifts are detected and the fringe pattern remains constant as a function of time, as seen in Fig.
Figure 3.22: (a) The PXRDIP target design for this VISAR data. (b) Sample PXRDIP VISAR image, s22477. (c) The extracted interface velocity from each interferometer (red and blue curves).

3.22 (b) at times before 4.5 ns. The lasers are fired at time corresponding to 0 ns, but time zero is not captured in the timing window of this VISAR image. The LiF window in this target is transparent to the VISAR probe, therefore the doppler shifts correspond to changes in the velocity of the Al-LiF interface. The first ramp compression wave reaches the Al-LiF interface at 4.5 ns and sets the interface into motion. This can be seen in the VISAR image as the interference pattern begins to shift. As the interface is accelerated to higher velocities, the interference continues to shift until it begins to plateau at 9.5 ns. A continuous interface velocity measurement is made over the duration of the experiment by tracking the phase shift of the interference pattern.

**Velocity per Fringe**

The proportionality between the number of fringe shifts in the interference pattern and velocity of the interface, or velocity per fringe (VPF), is derived here. First consider the number of wavelengths in the short leg, \( N_s \),

\[
N_s(t) = \frac{x_s}{\lambda(t)},
\]  
(3.22)
and in the delayed or long leg, $N_L$,

$$N_L(t) = \frac{x_L + 2hn(t) - 2h}{\lambda(t)}. \quad (3.23)$$

Constructive or destructive interference at the output beamsplitter is related to the difference in the number of wavelengths, $\Delta N = N_L - N_S - N_0$,

$$\Delta N = \frac{2h}{\lambda(t)} \left( n(t) - \frac{1}{n_0} \right) - N_0, \quad (3.24)$$

where the initial phase difference is $N_0 = \frac{2h}{\lambda_0} \left( n_0 - \frac{1}{n_0} \right)$. The wavelength of the probe beam, $\lambda_0$, will be Doppler shifted, $\lambda(t)$, as the target moves with a velocity, $v(t)$, given by

$$\lambda(t) = \frac{\lambda_0}{1 - \frac{2v(t)}{c}}, \quad (3.25)$$

where we use the approximation that $v(t) << c$ for shock and interface velocities.

The changes in the refractive index is expanded with respect to the change in wavelength due to the Doppler shift which is assumed to be small and equal to

$$n(t) \approx n_0 + \left( \frac{dn}{d\lambda} \right) \bigg|_{\lambda_0} (\lambda - \lambda_0) \approx n_0 - \lambda_0 \left( \frac{dn}{d\lambda} \right) \bigg|_{\lambda_0} \left( \frac{2v(t)}{c} \right). \quad (3.26)$$

The Doppler shift, Eq. 3.25, can be substituted into Eq. 3.24 to give the phase shift,

$$\Delta N = \frac{2h}{\lambda_0 \left( 1 - \frac{2v(t)}{c} \right)} \left( n_0 - \left( \frac{2v(t)}{c} \right) \lambda_0 \left( \frac{dn}{d\lambda} \right) \bigg|_{\lambda_0} - \frac{1}{n_0} \right) - \frac{2h}{\lambda_0} \left( n_0 - \frac{1}{n_0} \right). \quad (3.27)$$

This equation can be expanded into orders of $v(t)/c$ and keeping only terms up to
\( \Delta N = \frac{2\pi}{\lambda_0} (1 + \delta)v(t) \), \hspace{1cm} (3.28)

where \( \delta \) is due to dispersion in the etalon and is equal to \( \lambda_0 \frac{n_0}{n_0^2 - 1} \frac{dn}{d\lambda} \). For the OMEGA EP VISAR at 532 nm with fused silica etalons, \( \delta = 0.0318 \). The proportionality factor between the phase shift of the interference pattern and the velocity of the moving surface is called the velocity sensitivity or the velocity per fringe (VPF), and as seen in Eq. 3.28 is

\[
VPF = \frac{\lambda_0}{2\pi(1 + \delta)} = \frac{\lambda_0}{4n_0 h c} \left( n_0 - \frac{1}{n_0} \right) \left( 1 - \lambda_0 \frac{n_0}{n_0^2 - 1} \frac{dn}{d\lambda} \right).
\] \hspace{1cm} (3.29)

From this expression for the VPF, the velocity of a moving surface can be calculated from the phase with knowledge of the etalon thickness, the etalon refractive index, the initial probe laser wavelength, speed of light in vacuum, and the dispersion factor.

Fourier Transform Method

The Fourier transform method (FTM) is used for phase extraction from the VISAR images [63], and the steps are illustrated in Fig. 3.23. The VISAR image (Fig. 3.23a) can be described by this expression,

\[
g(x, y) = a(x, y) + b(x, y) \cos[2\pi f_0 x + \phi(x, y)] = a(x, y) + c(x, y) \exp[2\pi i f_0 x] + c^*(x, y) \exp[-2\pi i f_0 x],
\] \hspace{1cm} (3.30)

where \( \phi(x,y) \) is the phase that is related to the velocity, \( a(x,y) \) and \( b(x,y) \) are variations in the fringe pattern due to non-uniform illumination or transmission of the sam-
ple, \( c(x,y) = \frac{1}{2}b(x,y)\exp[i\phi(x,y)] \), and \( f_0 \) is the spatial carrier frequency due to the tilt of the output beamsplitter. The phase is extracted using the FTM method by simply taking a one-dimensional fast-Fourier-transform (FFT) of the image (Fig. 3.23 (a)). The result can be derived by taking the one-dimensional Fourier transform of Eq. (3.31) with respect to \( x \) giving,

\[
G(f,y) = A(f,y) + C(f - f_0,y) + C^*(f + f_0,y),
\]

(3.32)

where \( A(f_x,y) = F\{a(x,y)\} = \int_{-\infty}^{\infty} a(x,y) \exp[-2\pi if_x x] dx \) and equivalently for \( C \). This is evident considering the transform pair for a function \( \exp[\pi(ax + by)] \) is \( \delta(f_x - a/2, f_y - b/2) \) where \( \delta \) is the Dirac delta function. A frequency filter is then applied around one of the peaks in the power spectrum, in this case \( C(f - f_0) \), and all other frequencies are set to zero (Fig. 3.23 (b)). Thereby, separating the background signal, \( A(f,y) \), from the phase information. Once the filter is applied, the inverse Fourier transform is performed on \( G(f,y) \) with respect to \( f \) to obtain,

\[
D(x,y) = C(x,y) \exp[2\pi if_0 x] = C(x,y)[\cos(2f_0\pi x) + i \sin(2f_0\pi x)].
\]

(3.33)

The wrapped phase can be extracted by taking the inverse tangent of the real over the imaginary components of Eq. 3.33, shown in Fig. 3.23(c),

\[
W[\phi(x,y) + 2\pi f_0 x] = \arctan \left[ \frac{Re(D)}{Im(D)} \right].
\]

(3.34)

The final phase is obtained by removing the \( 2\pi \) jumps and subtracting the linear phase ramp (Fig. 3.23d). There are two interferometers with two different VPFs (different etalons) in order to resolve the \( 2\pi \) fringe jumps by comparing the possible velocity solutions. Then applying the VPF to the phase gives the velocity solution (Fig. 3.23 (e)).
Figure 3.23: Steps using the FTM for phase extraction from VISAR images. Reproduced from [Celliers et al., Rev. Sci. Instrum., Volume 75, Number 11 (2004) DOI: 10.1063/1.1807008], with the permission of AIP Publishing.
In these experiments, the sample-window interface velocity measurement is made through a ramp-compressed transparent window. The VISAR system measures the rate of change of the optical path length, \( \text{OPL} = \int_0^L n(x) \, dx \), where \( L \) is the thickness of the transparent window and \( n(x) \) is the refractive index of the window. Therefore, the VISAR measures an “apparent” velocity that must be corrected for \( n(x) \) in order to determine the “true” velocity.

A typical measurement setup is shown in Fig. 3.24. The optical path length in the window, \( Z_w \), is given by

\[
Z_w(t) = \int_{x_{fs}(t)}^{x(t)} n(x,t) \, dx, \tag{3.35}
\]

where \( n(x,t) \) is the refractive index of the window, \( x_{fs}(t) \) is the position of the free-
surface, and \( x(t) \) is the position of the reflecting interface. Meanwhile, the total OPL from a VISAR reference surface at \( x_V \) to the reflecting surface is,

\[
Z_V(t) = \int_{x_{fs}(t)}^{x(t)} n(x, t) \, dx + \int_{x_V}^{x_{fs}(t)} dx. \tag{3.36}
\]

The apparent velocity, \( u_{app} \), is given by the time derivative of total OPL,

\[
u_{app}(t) = \frac{dZ_V(t)}{dt},
\]

\[
= \frac{d}{dt} \left[ \int_{x_{fs}(t)}^{x(t)} n(x, t) \, dx \right] + \frac{d}{dt} [x_{fs}(t) - x_V], \quad \text{and}
\]

\[
= \frac{d}{dt} \left[ \int_{x_{fs}(t)}^{x(t)} n(x, t) \, dx \right] + u_{fs}(t), \tag{3.37}
\]

where \( u_{fs}(t) \) is the free surface velocity. From Eq. 3.37, it can be seen that in order to measure the true velocity, \( dx(t)/dt \), the refractive index of the window, \( n(x, t) \), must be known.

Eq. 3.37 can be simplified for the case of a reflecting shock traversing the window. For strong shocks, the original interface at \( x(t) \) is no longer tracked, but the shock front itself is tracked as it becomes highly conductive and reflective. For a shock front traveling at a shock velocity, \( U_S \), Eq. 3.37 simplifies to

\[
u_{S_{app}} = -\frac{d}{dt} \left[ n_0(x_{fs} - x_s(t)) \right] = n_0 U_S, \tag{3.38}
\]

where \( n_0 \) is the refractive index ahead of the shock front and \( x_s(t) \) is the position of the shock front. Therefore, the true velocity for a shock wave in a transparent dielectric is simply corrected by the refractive index of the window ahead of the shock front.

In these experiments, a ramp compression wave is traversing the window throughout the duration of the VISAR measurement. The ramp stress wave modifies the density and refractive index profiles in the window which result in Doppler shifts of the VISAR.
probe, hence apparent velocity changes. Hayes et al. [64] investigated this effect and found that the apparent and true velocities were related to the refractive index and density of the window material by,

$$\frac{dU_{app}}{dU_{true}} = n(x,t) - \rho(x,t) \frac{dn(x,t)}{d\rho(x,t)}.$$  \hspace{1cm} (3.39)

This equation is derived for unsteady waves in the window and under the assumption that there are no shocks in the window. For the special case where the refractive index of the window varies linearly with density, $n = a + b\rho$, Eq. 3.39 simplifies to

$$\frac{dU_{app}}{dU_{true}} = a + b\rho - \rho \frac{d(a + b\rho)}{d\rho} = a.$$  \hspace{1cm} (3.40)

For a simple ramp compression wave in a window with a refractive index that varies linearly with density and nothing else (e.g. temperature), the true velocity is related to the apparent velocity by a constant value that is the zero density refractive index, $U_{true}(t) = U_{app}(t)/a$. Eq. 3.40 is used to correct the VISAR measured velocities in these experiments with LiF windows because the LiF refractive index varies nearly linearly with density.

A summary of LiF refractive index measurements under both shock and ramp is shown in Fig. 3.25 [43, 45, 46, 65]. The fits to the data were forced through $n_0 = 1.3935$ and $\rho_0 = 2.6380$ g/cc. The experiments performed by Fratanduono et al. [43] (black curve) were performed on the OMEGA laser facility under ramp compression and with diamond ablators, therefore these measurements were made under similar conditions to these diffraction experiments. Fratanduono et al. found that the refractive index of LiF varied linearly with density and have a best-fit $n = 1.275(\pm 0.008) + 0.045(\pm 0.003)\rho$ (black dashed curve). These data are in good agreement with an extrapolation of shock compression data by LeLone et al. up to 20 GPa [Fig. 3.25 (gray line)]. Measurements by Davis et al. [46] are shown as the red curves in Fig. 3.25 and were performed under ramp compression on Sandia’s Z machine. Davis et al. find a non-linear refractive
index behavior that is better described by a power-law form. A linear fit to this data (red dashed curve) results in a zero-density refractive index of $a = 1.30$ compared to the Fratanduono et al., $a = 1.275$. This data is in good agreement with data from Rigg et al. [45] which were performed under shock-compression on a 2-stage gas gun. Rigg et al. proposes a power-law refractive index correction $U_{true} = b_1 U_{app}^{b_2}$ with $b_1 = 0.7827$ and $b_2 = 0.9902$.

Based on these extensive studies of the LiF refractive index, the VISAR analyses here used the refractive index corrections proposed by Fratanduono et al. and Rigg et al. The first uses an experimental setup similar to the one used here, and the second captures the non-linear refractive index behavior observed by Davis et al. The effect of these corrections on the velocity measurements is shown in Fig. 3.26. Four different refractive index corrections are shown in Fig. 3.26: the Fratanduono et al. linear correction (black), a linear correction to the data by Davis et al. (red), the proposed
Figure 3.26: Apparent to true velocity corrections proposed by Refs. [43, 45, 46].

iterative method by Davis et al. using hydrodynamic simulations (blue), and the Rigg et al. power law correction (gray). The power-law correction (gray) duplicates the most complete correction (blue) and therefore we have confidence using this correction for our analyses. This refractive index correction contributes to the systematic error in the velocity and hence pressure determination in these experiments. Therefore, it is important that the optical properties of the interferometric window are well characterized.

### 3.4 Pressure Determination

The goal of these experiments is to measure the crystalline phase of high-pressure materials. In order to determine the pressure state of the sample, the VISAR measured velocity histories are used as a boundary condition in a hydrodynamics method of characteristics calculation to determine the pressure history. In this work and neglecting strength, pressure and longitudinal stress are used interchangeably and $P = \sigma_{xx}$ due
to the inertial confinement of the target where $\sigma_{xx}$ is the longitudinal stress parallel to the stress wave propagation direction. The theory of the method of characteristics is discussed in Sec. 2.4. For these experiments, there are two classes of pressure determinations: transparent and opaque windows. In the first, the interface velocity, $u_p(t)$, between a transparent window and the sample is measured and in the latter, the free-surface velocity, $u_{fs}(t)$, is measured. A diagram of the two targets designs are shown in Fig. 3.27. Comparing the two velocity histories, the free-surface begins moving at about 19 ns while the interface begins moving much earlier in time, around 3 ns. Also due to the low tensile strength of diamond (opaque window), spall results in a measurement of constant velocity late in time (after 25 ns) as the VISAR tracks the “flyer” spall diamond layer. These two velocity measurements can be used to determine the pressure in the sample (red layer) using knowledge of the EOS of the window material.
Infinitely Thin Sample

First, we will discuss the simple case of an infinitely thin sample in a target with a transparent window. For an infinitely thin sample, the pressure in the sample is equal to the pressure in the window at the sample location. This is evident from the impedance matching boundary conditions,

\[ P_{\text{sample}}(\sigma_{\text{sample}}) = P_{\text{window}}(\sigma_{\text{window}}), \quad \text{and} \]
\[ u_{p,\text{sample}} = u_{p,\text{window}}. \quad (3.41) \]

From Eqs. 2.76 and 2.77 and assuming that the backward characteristics are zero at the interface \((S = 0)\),

\[ u_p = \frac{R + S}{2}, \]
\[ \sigma = \frac{R - S}{2}, \]
\[ S_{\text{window}} = 0, \]
\[ u_{p,\text{window}} = \sigma_{\text{window}}, \quad \text{and} \]
\[ P_{\text{sample}}(\sigma_{\text{sample}} = R_{\text{sample}} - u_p) = P_{\text{window}}(\sigma_{\text{window}} = u_{p,\text{window}}). \quad (3.42) \]

This gives the simple result that the pressure in the sample is equal to the pressure along the window principal isentrope at the measured particle velocity. An example of this simplifying analysis is shown in Fig. 3.28.

In Fig. 3.28, on the left are the measured interface velocities from the two interferometers in VISAR. The vertical dashed black lines show the timing of the x-ray probe for diffraction. The average particle velocity over the 1-ns probe duration is 7.06 \(\mu\text{m/\text{s}}\). On the right, the LiF principal isentrope from \textit{SESAME} 7271 is plotted. From
Figure 3.28: An example pressure determination for a target with an infinitely thin sample.

Eq. 3.42, the pressure in the sample is the pressure in the window at the measured $u_p$. The dashed black lines on the principal isentrope show that the pressure at the average measured particle velocity is 340 GPa. Therefore, the pressure in the sample is 340 GPa. But, in these experiments, we used samples with a thickness on the order of the optical depth of the sample at the x-ray wavelength in order to maximize the diffraction signal. Therefore, this simple calculation is not adequate to determine the pressure in the sample with considerable thickness.

**Transparent Window**

For transparent windows, the pressure at the sample-window interface is determined using impedance matching boundary condition [Eq. 3.42] and the measured interface velocity. The method of characteristics is then used to back-propagate the interface pressure into the thickness of the sample to determine the pressure in the sample in space and time. The characteristics calculation is run iteratively in order to perform a Monte Carlo (MC) error analysis for the pressure determination.
The first step of the pressure analysis is to apply the impedance matching boundary condition Eq. 3.42 to determine the pressure at the sample-window interface as discussed in the infinitely thin case. This step requires a model EOS for the window material. In this case, a numerical EOS table is used as discussed in Sec. 2.3.3. There are multiple EOS models to choose from, therefore the model which best matches measured ramp compression isentropes and shock Hugoniot data is chosen. In this case, we chose SESAME 7271v3 [46] because it reproduces the latest shockless compression data on LiF. The model is required in order to determine the pressure in the sample from $P_{\text{window}}(u_{p_{\text{window}}})$, in Eq. 3.42. Another EOS model for the sample is used to determine the value of $\sigma_{\text{sample}}$ which satisfies $P_{\text{sample}}(\sigma_{\text{sample}}) = P_{\text{window}}(u_{p_{\text{window}}})$. Once $\sigma_{\text{sample}}$ is known, $R$ and $S$ can be defined and launched at the Lagrangian sound speed, $C_L(\sigma)$. The characteristics are launched backwards into the Al sample and the values of $R$ and $S$ are adjusted as the characteristics intersect. The sample EOS model is used to recalculate $P(\sigma)$ and $C_L(\sigma)$ at each intersection. The characteristics are launched until they reach the front surface of the sample. The result is a map of characteristics intersections where the value of the pressure, temperature, $C_L$, etc. are known from the

Figure 3.29: A pressure map in a 20-µm Al sample (left) calculated using the method of characteristics and the measured interface velocity (right).
Figure 3.30: The pressure history in the Al sample calculated using the method of characteristics and a histogram of pressures in the sample (inset) during the 1-ns x-ray probe timing (vertical dashed black lines).

EOS model. An example pressure map, interpolated onto a uniform grid, is shown in Fig. 3.29.

On the right of Fig. 3.29, the measured interface velocity between an Al sample and LiF window is shown. The color of the velocity curve corresponds to a pressure (colorbar) at the Al-LiF interface using Eq. 3.42. On the left, the pressure map within a 20 µm Al sample is shown in an x-t diagram. The plateau in the velocity trace corresponds to a pressure plateau within the sample, however the plateau occurs slightly earlier in time at the front of the Al sample. The vertical dashed black lines show a 1-ns range where x-rays probed for XRD. The x-ray timing is such that the pressure in the Al is uniform and maximum. More importantly, the velocity measurement allows for the pressure during the x-ray exposure to be diagnosed. The average pressure as a function of time and a histogram of pressures during the x-ray exposure is shown in
Figure 3.31: (s22477) Pressure histograms from the Monte Carlo iterations of the characteristics algorithm. (a) The histogram of pressures in a sample during the 1-ns x-ray probe and throughout the thickness of the sample. The standard deviation, \( \Delta P \), gives an indication of the pressure gradients in the sample. (b) A histogram of the 2000 pressures calculated in the MC analysis. The standard deviation, \( \sigma_P \), is quoted as the error in the pressure measurement. (c) The histogram of 2000 standard deviations, \( \Delta P \), that has a standard deviation, \( \Sigma_P \).

In Fig. 3.30, the average pressure as a function of time throughout the Al sample is calculated by averaging over the spatial dimension of Fig. 3.29. The dashed blue lines show \( \pm \) one standard deviation. Early in time, the standard deviation in the pressure is large, but as the velocity profile plateaus, the spread in pressures is minimum. The x-rays are timed to probe at this instance, and the histogram of pressures during this 1-ns duration are shown in the inset of Fig. 3.29. The average pressure is 327 GPa and the standard deviation due to pressure gradients, \( \Delta P \), is 1.5 GPa.

The method of characteristics algorithm is performed 2000 times for each VISAR measurement in order to do a MC error analysis for the pressure determination. The experimental parameters are varied within their uncertainties: absolute timing error \([\pm 58 \text{ ps}]\), x-ray probe duration \([\pm 30 \text{ ps}]\), Al foil thickness \([\pm 2.5 \mu\text{m}]\), sample density \([\pm 0.01\%]\), and VISAR sensitivity \([\pm 5\% \text{ VPF}]\).

The output of the MC analysis is a table of average pressures in the Al sample, \( \langle P \rangle \), during the x-ray probe and a table of standard deviations in pressure, \( \Delta P \), of the Al sample during the x-ray probe due to spatial gradients [Fig. 3.31(a)]. A histogram
Figure 3.32: A pressure map in a Na sample and diamond window (left) calculated using the method of characteristics and a measured free-surface velocity (right).

of the 2000 average pressures is shown in Fig. 3.31(b). The standard deviation in the mean pressures, $\sigma_P$, is the quoted error in the pressure. This is distinct from the ensemble of the standard deviations, $\Delta P$, shown in Fig. 3.31(c) which has its own standard deviation, $\Sigma P$. The laser pulse shape is well designed for keeping the pressure gradients at a minimum. However, there are unavoidable systematic errors in the pressure determination including the window EOS optical and mechanical properties (including their temperature dependence).

**Opaque Windows**

Determining the pressure in a target with an opaque window is very similar to a transparent window, except there is the extra step of back-propagating the free-surface velocity throughout the window. As discussed earlier, the transparent window is preferable because the velocity measurement is made closer to the sample. The boundary condition used in this case is a measurement of the free-surface velocity. Instead of the
impedance matching boundary condition, the free surface boundary condition is that the pressure is zero. Therefore, at the free surface

\[
\sigma = P = 0, \quad \text{and} \quad R = S = u_{fs}(t)
\]

(3.43)

From Eq. 3.43, the measurement of the free-surface velocity allows for \( R \) and \( S \) to be defined. Again, the EOS of the window material must be known in order to calculate \( P(\sigma) \) and \( C_L(\sigma) \). The characteristics are back propagated into the window until the window-sample interface is reached. Then, the impedance matching boundary conditions are applied (Eqs. 3.42) and the steps outlined in the transparent window section are followed.

Figure 3.32 shows an example result from the method of characteristics algorithm with an opaque window. In Fig. 3.32, an h-t plot of the pressure within a Na sample and a diamond window is shown (the boundary is labeled with a vertical dashed white line). The horizontal white dashed lines show the timing of the x-ray probe for this sample. On the right, the free-surface velocity used as the boundary condition is shown. The color of the velocity trace corresponds to the pressure (colorbar) at the free-surface, which is always zero pressure. In this case, the timing was premature; it probed the sample while it was still compressing to maximum pressure and while it had substantial pressure gradients. This highlights another disadvantage of opaque windows which is that the free-surface velocity [Fig. 3.32 (right)] is not necessarily maximum when the pressure in the sample is maximum, therefore this analysis is required in order to determine if the timing was acceptable. This analysis assumes that there are no shocks in the window or equivalently that the shock forms at the instant it breaks out of the free-surface. The oscillations in the x-t diagram are a result of numerical gridding error because of the non-monotonic velocity profile causing crossing of the characteristics.
A pressure histogram for the Na sample during the x-ray timing is shown in Fig. 3.33. The Na sample was 41 µm thick and the x-ray timing was too early resulting in a standard deviation due to pressure gradients, $\Delta P = 41$ GPa. The characteristics algorithm is again used in a MC analysis to determine the errors in the same procedure as for transparent windows.
4 Aluminum


At standard conditions, aluminum is an $sp$-bonded metal with no $d$-band electrons, and the atoms are arranged in a face-centered cubic (fcc) crystal structure. Because of this simplicity, Al is a prototype metal for testing theoretical methods[66–69]. While structural predictions for Al exist up to many terapascals [11], there are no experimental data at pressures beyond 333 GPa.

We report on a series of experiments that use high-power lasers to ramp-compress aluminum (Al) up to 547 GPa. Under this quasi-isentropic compression, Al remains in the solid state and two solid–solid phase transformations are observed. In-situ x-ray diffraction is performed to detect the crystal structure. A velocimetry diagnostic measures particle velocities in order to infer the pressure in the Al sample. We show that a solid–solid phase transition, consistent with a transformation to a hexagonal close-packed (hcp) structure, occurs at $216 \pm 9$ GPa. At higher pressures, a transformation to a structure consistent with the body-centered cubic (bcc) structure occurs at $321 \pm 12$
GPa. An experiment at the National Ignition Facility probed both the hcp and bcc high-pressure phases in a single laser drive at 311±10 GPa and 547±19 GPa, respectively, using a two-backlighter configuration. These phase transitions are also observed in 6061-O (annealed) Al alloy at 175±9 GPa and 333±11 GPa, respectively. Correlations in the high-pressure crystallographic texture suggests the close-packed face-centered cubic (111), hcp (002), and bcc (110) planes remain parallel through the solid–solid fcc–hcp and hcp–bcc transformations.

4.1 Historical Context

Aluminum is predicted to undergo various solid–solid phase transformations to 10 TPa [11]. At ambient conditions, Al is a face-centered cubic (fcc) crystal. At 217 GPa and room temperature, fcc Al was observed to transform into a hexagonal close-packed (hcp) structure in diamond anvil cell (DAC) experiments [14]. The hcp phase was measured to be stable up to 333 GPa; beyond that, *ab initio* calculations were relied upon to predict the crystal structures of Al at extreme pressures and temperatures. Density-functional theory (DFT) predicts a transformation to body-centered cubic (bcc) Al at pressures between 316 GPa [16] and 363 GPa [70], along the principal isentrope. A bcc Al polymorph was synthesized in a microexplosion and recovered [71], but the transformation pressure was not measured. Here, the bcc phase was confirmed experimentally at 321±12 GPa under dynamic compression [1], additional details of which are discussed here.

The high-pressure phase diagram of Al is illustrated in Fig. 4.1. Shock compression melts Al in the fcc phase at 125 GPa [72, 73] due to the increase in entropy and temperature created by a shock. Here, ramp compression is used to follow a nearly isentropic compression path to investigate the hcp and bcc phases of Al. At even higher pressures (> 1 TPa), Al is predicted to no longer arrange in simple, close-packed structures, but transforms to open, incommensurate structures. The sequence of pressure-induced
Figure 4.1: Theoretical and experimental Al phase diagram. The phase boundaries (blue curves) and principal isentrope (black curve) are calculated by Ref. [16]. The principal Hugoniot (red curve) is calculated by Ref. [28]. The diamond-anvil-cell (DAC) data [14] for the fcc and hcp phases are shown as the black and red crosses along the 298-K isotherm. The solid black, red, and blue circles are data from this work in the fcc, hcp, and bcc phases, respectively. The black diamonds with red outlines and red diamonds with blue outlines are data that have diffraction from multiple phases. Temperature is represented here assuming the data lie on the principal isentrope, while taking into account additional entropy added by observed shocks (for shots above 405 GPa and the NIF data).
transitions is fcc–hcp (at 217 GPa, 298 K [14]), hcp–bcc (at 321 GPa, ~920 K [1]), with the next phase transformation predicted at 3.2 TPa and 0 K to a Al16–I4/mcm host-guest structure [11].

The equation of state (EOS) of Al is important in high-energy-density (HED) experiments because it is used as a impedance-matching standard [74–77]. Al has been studied using DAC [14], gas-gun [78, 79], nuclear explosion [80], pulsed-power [81–83], and laser [84–87] drivers under static, shock, and quasi-isentropic compression. On the Z machine at Sandia National Laboratory, the off-Hugoniot behavior of Al is critical in understanding their magnetically driven cylindrical liner implosions [10]. The measured pressure vs. density data were found to have a softer behavior than expected due to the error in the solid Al model for pressures above 200 GPa. Better knowledge of the Al EOS is required to avoid the introduction of systematic errors in HED measurements.

Quasi-isentropic, or ramp compression is used to compress materials to high pressures and lower temperatures than those accessible by shock compression [41]. The technique can use high-power lasers, pulsed-power, graded-density-impactors, etc., to compress samples from nanosecond (ns) to microsecond time scales. At these time scales, the pressure loading profiles and targets can be designed so that acoustic waves do not steepen to form a shock and Al may remain in the solid state at high-pressure where interesting phenomena are predicted, including solid–solid phase transformations. X-ray diffraction (XRD) measurements [36, 51] were developed at the OMEGA EP Laser Facility [35] and the National Ignition Facility (NIF) [5] that allow direct determination of lattice structure [49, 50], crystallographic texture [88, 89], and effects of material strength [90].

This work probed the high-pressure crystal structure of Al up to 547 GPa using laser-driven ramp compression and in-situ XRD. We observe a transformation from a fcc to an hcp structure at 216±9 GPa. This measurement duplicates the fcc–hcp transition observed in static DAC experiments but at nanosecond time scales and slightly
higher temperatures. At higher pressures, a transition to a bcc structure is observed at 321±12 GPa [1]. The bcc structure is measured to be stable to at least 547 GPa.

Pure Al and Al-6061 alloy have been shown to have profound differences in stiffness and dynamic strength [83, 87], and have distinct strain rate dependencies [91]. The existence of and pressure onset for solid-solid phase transformations in 6061-Al alloy is essential for interpretation and analyses of previous and future ramp compression experiments [10]. We present the first observation of the fcc–hcp and hcp–bcc transformations in 6061-O (annealed) Al alloy at 175±9 GPa and 333±11 GPa, respectively.

The initial crystallographic texture of the rolled Al foils was characterized and studied through the observed phase transitions. The high-pressure texture suggests that close-packed and nearly closed-packed planes remain parallel during the fcc–hcp and hcp–bcc transformations.

### 4.2 Experimental Details

Experiments were performed on the OMEGA EP laser [4] at the University of Rochester’s Laboratory for Laser Energetics and the National Ignition Facility (NIF) [5] at Lawrence Livermore National Laboratory. Figures 4.2 and 4.3 provides details about the experimental geometry. Ultraviolet 351-nm laser pulses were shaped to produce an irradiance profile that smoothly increases the applied pressure over 10 ns. The “ramped” pulse is designed for the specific target dimensions to avoid shock formation. An example of a delivered pulse shape is shown in Fig. 4.2 (c). The peak drive laser intensities ranged from $1.5 \times 10^{12}$ to $3.4 \times 10^{13}$ W/cm$^2$. A single drive beam irradiated the Al sandwich target at an angle of 23° with respect to the target normal. Distributed phase plates [92] were used to produce a focal spot with a super-Gaussian intensity distribution \( I = I_0 \times \exp \left[ -2 \left( \frac{r}{550 \mu m} \right)^{8.0} \right] \). Three different types of Al samples were used: 15- to 20-µm-thick Al (99.999% purity) rolled foils from Goodfellow, 18-µm-thick 6061-O (annealed) Al foils from ESPI Metals (rolled from 76-µm-thick stock),
and electron-beam–deposited 15-μm coatings on lithium fluoride (LiF). The rolling process resulted in a significant deviation from an “ideal” powder sample and produced strong preferred orientation (texture) of the crystal grains. The Al samples were sandwiched between plates of ⟨110⟩-oriented 20-μm-thick single-crystal diamond and ⟨100⟩-oriented 100-μm- or 150-μm-thick LiF. The target stack was mounted on a high-Z (tungsten, tantalum, or platinum) plate (75 to 150 μm thick) with a 300-μm-diameter pinhole aperture to provide x-ray collimation near the sample plane (Fig. 4.2(b)). The 1100-μm-diameter drive-laser spot size is large relative to the 300-μm-diameter collimating aperture in order to limit the XRD and velocimetry diagnostics’ field of view to only the center of the compressed region of the sample and ensures minimal lateral gradients.

An additional laser beam irradiated a backlighter foil with an irradiance of $2.5 \times 10^{15}$ or $4.0 \times 10^{15}$ W/cm$^2$ to optimize laser energy to x-ray conversion efficiency for Ge or Cu backlighter foils, respectively. The 8.37-keV (Cu) and 10.25-keV (Ge) He-α x rays are generated over the duration of the laser pulse and emit as a quasi-monoenergetic source positioned at an angle 23° with respect to the Al sandwich target normal. The drive and backlighter laser pulses are shown in Fig. 4.2(c).

X-rays scattered from interatomic lattice planes with spacings, $d$, constructively interfere when the Bragg condition, $\lambda = 2d \sin(\theta)$, is satisfied for an x-ray wavelength, $\lambda$, and x-ray incidence angle, $\theta$. A “powdered” material (i.e. one with randomly orientated crystal grains) will produce uniform cones of diffracted x rays for each allowed lattice plane for the material crystal structure. Powder diffraction is used in these experiments to measure the scattering angle, $2\theta$, between the incident and diffracted beams to determine the crystal structure. Under compression, the $2\theta$ for each lattice plane increases with decreasing interatomic spacing until a phase transformation occurs. When a new crystal structure is formed, an abrupt change in the scattering angles is observed as the symmetry, and therefore the structure factor, changes for the new atomic arrangement.

The in situ XRD diagnostic on OMEGA EP is called powder x-ray diffraction im-
Figure 4.2: The experimental geometry for ramp compression and simultaneous x-ray diffraction (XRD). (a) XRD patterns are detected in an image plate (IP)–lined box. An aperture on the back of the box allows the VISAR beam to probe the target. IP data from shot 22477 are shown for compressed hcp Al at 299 GPa together with ambient density W pinhole diffraction rings. (b) The main Al sandwich target is mounted on the front face of the box. The VISAR probe beam reflects off the Al/LiF interface. (c) The delivered laser ramp drive pulse shape (blue) and the 1-ns square x-ray source (XRS) laser pulse shape (red) are shown. The relative timing between the two pulses is chosen in order to probe the Al sample when the pressure is uniform.
age plates (PXRDIP) [36] and is shown in Fig. 4.2. The Debye–Scherrer diffraction cones from both the compressed sample and ambient density high-Z pinhole trace out conic sections on the image plates (IP’s) [52] lining the inside of a stainless steel box [shown in Fig. 4.2(a)]. Filters comprised of Cu or Al, for the Cu or Ge backlighters, respectively, are inserted in front of the IP’s to attenuate background from the x-ray backlighter and from the ablation plasma. Diffraction from the pinhole material is used as a reference to precisely determine the diffraction geometry. The diffraction lines from the compressed sample are identified and their 2θ values are measured with respect to these reference lines.

An experiment at the NIF probed both of the two high-pressure polymorphs of Al using a dual x-ray source (XRS) configuration shown in Fig. 4.3. The target comprised a beryllium ablator (26.3 µm), a germanium pusher/heat shield (22.0 µm), an Al foil (47.7 µm), and a LiF window (155.7 µm) (Fig. 4.3 (a)). The target assembly was mounted on a 94-µm-thick tantalum substrate with a 395-µm-diam pinhole. The drive comprised sixteen 351-nm beams with a 30-ns ramp pulse (Fig. 4.3 (c) black curve) that held the pressure in the Al constant for over 2 ns at two different pressures where the hcp and bcc phases were observed in the OMEGA experiments [1]. The NIF beams had phase plates to create a 1200-µm × 900 µm elliptical focal spot, and additional “tiled” beam pointing provided 2.2% transverse pressure uniformity over a 1.2-mm region [51]. Two sets of twenty-four 351-nm beams irradiated two separate Ge backlighter foils for 2 ns (Fig. 4.3 (c) red and blue curves). The backlighters were mounted at +29.1° and –29.3° with respect to the Al target normal, and the relative timing of the XRS emission was chosen to probe the two pressure plateaus in the Al pressure profile. The different backlighter positions produced overlapping but spatially offset XRD data on the image plates. The in situ XRD platform at NIF (see Fig. 4.3) is referred to as TARDIS (TARget diffraction in situ) [51]. To prevent overlapping calibration and compressed Al diffraction lines, no pinhole was used, instead fiducial wires and the direct XRS image are used to fit the diffraction geometry. Diffraction rings are assumed
Figure 4.3: The NIF experimental geometry for ramp compression and simultaneous x-ray diffraction [51]. (b) X-ray diffraction patterns are detected in an IP-lined cylindrical slice. The target in (a) is mounted in the center of the cylinder. An aperture allows the VISAR beam to probe the target. (c) The delivered laser ramp drive pulse (black) and the two 2-ns square XRS pulses (red and blue). The ramp pulse is designed to hold a uniform pressure in the Al at two different high pressures. The relative timing of the XRS1 and XRS2 pulses are chosen to probe the Al at the two pressure plateaus.
to lie along a constant \(2\theta\).

The pressure of the Al sample is determined using the measured Al–LiF particle velocities. A line-imaging VISAR (velocity interferometer system for any reflector) [58] detects Doppler shifts of a 532-nm probe beam reflecting off the accelerating Al–LiF interface through the transparent LiF window. The Doppler shifts are manifested as shifts in the fringe pattern recorded in a 2-D interferogram. The fringe shifts are proportional to the changes in the velocity of the reflecting surface, allowing one to measure the Al-LiF interface velocity as a function of time. LiF was chosen as the window material because it is transparent under ramp compression up to 800 GPa [43] and is transparent under shock compression to 215 GPa [44–46]. In addition, the optical and mechanical responses of LiF under ramp compression are well known [46, 47]. Shown in Figs. 4.2 (a) and 4.3 (b), a hole in the back of the PXRDIP box and TARDIS allows the VISAR probe to reflect off of the rear surface of the target mounted on the front of the box. The pressure determination from the measured particle velocities is discussed in Sec. 4.3.2.

### 4.3 Analysis

#### 4.3.1 X-ray diffraction data

XRD data were used to measure the density of the compressed Al, detect phase transformations, identify the crystal structure, and measure high-pressure crystallographic texture. The direct XRS image and reference diffraction calibration lines are identified and assigned their known \(2\theta\) values. A least-squares minimization routine determines best-fit values for the experimental geometry including image plate, XRS, and pinhole locations. The IP’s are projected into \(2\theta-\phi\) space, where \(\phi\) is the azimuthal angle around the Debye–Scherrer ring. Background subtracted \(2\theta-\phi\) projections of Al in the fcc (c), hcp (b), and bcc (a) phases are shown in Fig 4.4. The x-rays originating
Figure 4.4: Background subtracted $2\theta$-$\phi$ projections of XRD patterns in the (c) fcc (0 GPa, shot 24294), (b) hcp (291 GPa, shot 24289), and (a) bcc (466 GPa, shot 24292) phases of Al. The black, red, and blue arrows point to reference diffraction lines from the pinhole. The green ellipses mark single-crystal diffraction Laue spots from the diamond and LiF ablator/window plates. The lines from compressed Al are labeled with their $(hkl)$ plane and show significant texturing. White spaces are gaps between image plates.
from the ablation plasma create a smoothly varying background across the image plates and the background levels are higher at higher pressures, as seen in Fig. 4.4(a). The background subtraction is performed in the 2θ-φ space with a nonlinear peak clipping algorithm [93]. The IP’s show four diffraction lines from Al in the fcc phase at 0 GPa [Fig. 4.4(c)], three lines in the hcp phase at 291 GPa [Fig. 4.4(b)], and one line in the bcc phase at 466 GPa [Fig. 4.4(a)]. Additional features are visible on the IP’s due to single-crystal Laue diffraction from the diamond and LiF windows, edges of the IP’s, and filter edges. Azimuthally averaged lineouts of the 2θ-φ projections are plotted versus $Q [Q = (4\pi/\lambda)\sin(\theta)]$, for x-ray wavelength, $\lambda$, in Fig. 4.5.

Two distinct changes in crystal symmetry are observed in the XRD data with increasing pressure, indicative of two structural phase transformations. The XRD pat-
tern for undriven pure Al foil is shown in Figs. 4.4(c) and 4.5(c). This pattern shows strong initial texture; for example, the fcc (111) line is present only at azimuthal angles, $\pm 150^\circ$. The texture is also apparent in the fcc (200), (220), and (311) lines. When pressure is increased to 291 GPa [Figs. 4.4(b) and Figs. 4.5(b)], the fcc (200) peak disappears and the hcp (100) peak and hcp (101) peak form the characteristic hcp triplet along with the hcp (002) peak. At the highest pressures, the hcp peaks disappear and a single intense peak is observed. The single peak, labeled in Figs. 4.4(a) and Figs. 4.5(a), is consistent with the bcc (110) diffraction line and shows significantly less texture than the initial rolled foil. A summary of these data was presented previously in Ref. [1].

In a single laser experiment, two high-pressure phases of Al were observed at the NIF. One 2-ns x-ray exposure (XRS 1) was timed coincident with the first pressure plateau at 311$\pm$10 GPa, and the diffraction pattern showed three hcp Al lines [(100), (002), and (101); upper-left portion of Fig. 4.6]. The second x-ray exposure (XRS 2) was timed with the pressure plateau at 547$\pm$19 GPa, and the diffraction pattern showed three lines [(110), (200), (211)] from bcc Al [centered on the right-hand side of Fig. 4.6]. The observed $2\theta$ for these lines in the bcc phase corresponds to a density of 6.9$\pm$0.1 g/cc and a lattice parameter $a = 2.35\pm0.01$ Å. This is the highest pressure structural data for solid Al ever reported. The observation of three reflections from the bcc phase confirms the single reflection in the OMEGA data as bcc, indicating that Al is a bcc metal above 321$\pm$12 GPa. The NIF XRD platform has a greater x-ray brightness than the OMEGA XRD platform and was able to record the two additional higher-angle peaks.

### 4.3.2 Pressure determination

Accurate pressure measurements are facilitated with the use of transparent LiF windows that allows one to directly measure of the Al–LiF interface velocity using VISAR.
Figure 4.6: Stereographic projection of XRD data taken at NIF at 311 ± 10 GPa in the hcp phase (left) and 547 ± 19 GPa in the bcc phase (right). A textured hcp triplet is visible on the upper left, and a change in symmetry to the bcc phase is visible on the right.
With knowledge of the optical and mechanical response of LiF under ramp compression [43, 46, 47], the pressure at the Al–LiF interface can be deduced. To determine the mean pressure within the finite-thickness Al sample, a correction is applied to Al–LiF pressure using the method of characteristics. Previous studies used single-crystal diamond windows which become opaque under ramp-compression above \( \sim 100 \) GPa [49, 50]. The use of a transparent LiF window eliminates the need to back-propagate a free-surface velocity and the systematic errors associated with the diamond EOS, strength effects, and assumptions of wave interactions within the window. The use of a LiF window additionally improves accuracy of the pressure determination because it has a wave-impedance much closer to that of Al compared to diamond, thus only a small correction to the interface pressure is needed to obtain the pressure inside the sample. This method could also provide additional information about the reflectivity under ramp compression.

The pressure determination for shot 22477 is outlined in Fig. 4.7. The Al–LiF interface velocity as a function of time is measured with an accuracy of \( \sim 5\% \) of the velocity per fringe (VPF). The VPF’s used in the two interferometers were 1.64 and 2.74 \( \mu m/\text{ns/fringe} \); the two recorded velocities are shown in Fig. 4.7(b) overlaid on the VISAR interferogram.

A characteristics algorithm is used to map the pressure in the Al sample in space and time, shown in Fig. 4.7(c) [32, 33]. The characteristics solver assumes that the thermodynamic quantities under isentropic compression propagate at the local sound speed along hydrodynamic characteristics [25]. Therefore, the fluid flow can be solved as a grid of forward- and backward-propagating characteristics.

The boundary condition at the Al–LiF interface is the continuity of particle velocity and normal stress. An EOS model for the Al sample and window material is used. The inputs into the characteristics-propagation algorithm used here include the measured apparent Al–LiF particle velocity, EOS SESAME 7271 and 7271v3 [46, 47] for LiF, Kerley 3700 EOS for Al [28], refractive index models for LiF [43, 45], Al sample
Figure 4.7: An example of the pressure determination for OMEGA shot 22477. (a) The sample assembly is directly driven by a 10-ns ramp pulse (blue), and the Cu x-ray backlighter is driven by a 1-ns square pulse (red). (b) The VISAR streak image along with the corresponding Al–LiF interface velocities (green, blue) from each interferometer. (c) Position in the 20-μm-thick Al sample versus time pressure map (color bar) calculated from the Al–LiF interface velocity shown in (b). The velocity is used as a boundary condition in a characteristics calculation that back-propagates the equations of motion into the Al sample to determine the pressure in space and time throughout the sample. The vertical dashed white lines show the 1-ns duration of the XRS. (d) The average pressure (solid blue) throughout the thickness of the Al as a function of time. The dashed blue lines show the standard deviation in the pressure state. The vertical black dashed lines show the timing of the XRS. Over the 1-ns XRS emission, the Al is at a maximum, uniform-pressure state of $327 \pm 2$ GPa. The pressure histogram shows the ensemble of pressures throughout the thickness of the Al, with standard deviation $\Delta P$, during the x-ray exposure.
thickness, and the XRS probe time and duration.

From the characteristics code, the average pressure throughout the thickness of the Al over the duration of the x-ray probe can be determined (Fig. 4.7 (d)). To assess the errors, the characteristics calculation was performed 2000 times for each shot, varying the individual experimental parameters within their uncertainties. The Monte Carlo (MC) routine randomly calls either the SESAME 7271 or the more-compressible 7271v3 to include error in the LiF EOS. The MC routine also randomly uses either a power law or linear refractive-index correction proposed by Refs. [45] and [43], respectively, to include error in the refractive-index correction. The power law method proposed by Rigg et al. captures the non-linear refractive index behavior of LiF measured by Davis et al. The linear refractive-index correction gives a systematically higher velocity than the non-linear refractive index correction which results in up to a 3% higher pressure.

The mean and standard deviation, $\sigma_P$, from the MC error analysis are given as the value and error for the measured pressure during the x-ray exposure. The standard deviation, $\sigma_P$, of the mean pressure state in the sample ranged from 3.2% to 6.5% of the mean pressure. In addition to the histogram of mean pressure values from the MC ensemble, there is a range of pressure values during the x-ray exposure due to pressure gradients in the sample, as shown in the inset of Fig. 4.7(d). The average standard deviation, $\Delta_P$, from the MC analysis of the pressure state in the sample due to pressure gradients ranged from 0.6% to 15.3% of the mean pressure.

The 660-nm VISAR data from NIF shot 161027 shown in Fig. 4.8 exhibits two plateaus in velocity at $\sim$7 and $\sim$9 $\mu$m/ns during which XRD data were acquired. (The two VPFs used in the two interferometers were 5.46 and 3.13 $\mu$m/ns/fringe.) The deduced pressure for the first 2-ns XRD exposure was 311$\pm$10 GPa, and the second exposure was timed with the pressure plateau at 547$\pm$19 GPa. As shown in Fig. 4.8 (b), the VISAR data showed a 3.54-km/s jump in the particle velocity at the time of breakout into the Al–LiF interface. Assuming the jump is a signature of shock formation, a shock
Figure 4.8: (a) Inset: NIF target with a half coating on the rear surface. Raw VISAR data for NIF shot 161027. The top half of the streak image shows fringe motion produced from reflection off the reflective coating on the free surface of the target. Breakout from the free surface is seen at 29.5 ns. The fringe motion on the bottom half of the streak image is produced from reflection off the uncoated portion of the target and therefore tracks the Al–LiF interface velocity. (b) The true particle velocity as a function of time using a zero-density refractive index, $a = 1.275$ [43] for the refractive-index correction. The vertical dashed black lines show the timing and duration of the XRS probe times.
pressure of $\sim95$ GPa and a shock temperature of $\sim3120$ K at the Al–LiF interface is calculated from impedance matching using the Al SESAME 3722 and LiF 7271 Hugoniots. (In the OMEGA data, shocks were observed only in experiments above 415 GPa with a jump of 1.6 km/s in the particle velocity ($\sim33$ GPa, $\sim790$ K) being the strongest shock due to the diamond Hugoniot elastic limit (HEL) wave [94].) Therefore, the Al in the NIF data is at an elevated temperature state compared to the Al in the OMEGA data; its implications are discussed in Sec. 4.4. Data that do not lie on the principal isentrope in Fig. 4.1 are at an elevated temperature due to these small shocks and are plotted on their shock-ramp path.

4.4 Results

4.4.1 Pure Al

A pressure scan was performed with 26 shots for pure Al to measure the pressure onset for the fcc–hcp and hcp–bcc phase transitions. A plot of these data is shown in Fig. 4.9 as the lattice $d$ spacing and density versus pressure, and the data from NIF are labeled. The data are plotted as black (fcc), red (hcp), and blue (bcc) points. The data are compared to the Kerley 3700 principle isentrope (black, red, and blue lines) using the ideal $c/a$ ratio for the hcp phase in Fig. 4.9 (a) [28]. The vertical dashed black lines are plotted at the measured onset pressure for the fcc–hcp and hcp–bcc phase transitions. Compression in the fcc phase is consistent with the Al isentrope (black curves) to 216±9 GPa, where an additional peak from hcp (101) is first observed. A region of coexistence is observed to 238±9 GPa, and the hcp (100) and (002) diffraction peaks are also detected. The diffraction data are consistent with the hcp phase until 321±12 GPa, where the bcc (110) peak is observed. A second coexistence region is observed up to 363±14 GPa. At higher pressures, a single diffraction peak from bcc (110) is observed to 547±16 GPa. The highest-pressure data point at 547±19 GPa is
Figure 4.9: (a) Lattice interatomic spacing, $d$-spacing, calculated from Bragg’s law using the measured scattering angles versus pressure calculated from VISAR Al–LiF interface velocities shown as the solid black, red, and blue markers [1]. The black, red, and blue curves are calculated from the Kerley 3700 principal isentrope [28]. (b) The best-fit density for the observed (hkl) diffraction peaks versus pressure are shown as the solid black, red, and blue markers. The data are compared to various models including the Al principal isentrope (solid black) calculated from Kerley 3700 [28], multiphase Al principal isentrope from SESAME 3722 [70] (dashed black), DAC data (black and red crosses), and fits to that data (dashed gray) from Ref. [14]. Reproduced with permission from Phys. Rev. Letters 119, 175702 (2017). Copyright 2017 American Physical Society.
from the NIF shot and shows diffraction peaks from bcc (110), (200), and (211). The observation of additional bcc diffraction peaks further constrains the crystal structure. Figure 4.9(b) plots the best-fit density for the assigned crystal structure as a function of pressure. These data are summarized in Appendix A.

The data are compared to various models in Fig. 4.9(b) including the chemical model-based Kerley 3700 principal isentrope [28], the 3-active-electron DFT-based SESAME 3722 multiphase principal isentrope [70], and the room-temperature DAC data[14]. The multiphase description is required in the EOS model for agreement with the density jump observed in our data for the bcc phase. Sjostrom et al. predicted the fcc-to-hcp transition to occur at 195 GPa (780 K) and the hcp-to-bcc transition at 363 GPa (920 K) along the principle isentrope [70]. Kudasov et al. calculated the same transitions at 198 and 320 GPa, respectively [16]. The onset pressures calculated by Kudasov et al. using an all-electron DFT model are in agreement with the measured onset pressures. Their calculated transition pressures are 8% lower and 0.3% lower than the measured onset pressures for the fcc–hcp and hcp–bcc transitions, respectively. A plot of the best-fit $c/a$ ratios for the hcp phase is shown in Fig. 4.10. The weighted mean, $1.65 \pm 0.01$, is larger than the ideal ratio, 1.633. This is also larger than the $c/a$ ratio used by Kudasov et al., 1.615, however, that $c/a$ ratio was optimized independent of temperature.

We observe a coexistence of fcc–hcp and hcp–bcc phases near the transition pressures. The measured spatial and temporal gradients within the Al sample are not large enough to explain the coexistence observed over 22-GPa and 43-GPa ranges. For the two shots with fcc–hcp coexistence, the maximum standard deviation in pressure due to spatial gradients, $\Delta P$, is 12 GPa compared to 22 GPa. And for the three shots with hcp–bcc coexistence, the maximum standard deviation in pressure due to spatial gradients, $\Delta P$, is 12 GPa compared to 43 GPa. The fcc–hcp coexistence has been observed in other materials, including Xe [95], due to the development of stacking disorder in the fcc lattice to form hcp. Coexistence and hysteresis are observed in the $\alpha$(bcc)$-$\varepsilon$(hcp)
Figure 4.10: The best-fit $c/a$ ratios for the hcp phase. The black dashed line shows the ideal $c/a$ ratio, 1.633. The solid and dashed red lines are drawn at the weighted mean and the standard deviation in the weighted mean for this data, 1.65±0.01, respectively. We do not observe a trend in $c/a$ with pressure.

transition for iron, and it is attributed to a large elastic strain energy [96].

The NIF data show considerably less compressible behavior compared to the OMEGA data due to the initial shock heating of the sample (Fig. 4.9). The analysis of the observed shock was discussed in Sec. 4.3.2. The pressure and temperature at the Al–LiF interface due to the shock were $\sim$95 GPa and $\sim$3120 K, respectively. The observation of the hcp phase with the initial shock heating was not expected from DFT calculations, as shown in Fig. 4.1; the DFT-calculated fcc–hcp–bcc triple point is at 255 GPa and 2900 K [70]. An estimate for the lower bound of fcc–hcp–bcc triple point can be determined from the NIF shot by calculating an isentrope from the observed Hugoniot state. The “shock–ramp” path was calculated using SESAME 3722, and the estimated temperature along the shock–ramp path at 311 GPa was $\sim$4200 K and $\sim$4960 K at 547 GPa. The pressure–temperature state for the lower pressure is well into the bcc phase in DFT-calculated phase diagrams by Refs. [16] and [70]. However, the shocks generated with ramp compression are typically growing in strength with time due to the
ramped irradiance. Therefore, 1-D radiation-hydrodynamic simulations give a better estimate of the temperature gradients within the sample. The NIF data in Fig. 4.1 are plotted at the average temperature in Al from pre-shot hydrodynamic simulations. The lower bound on the temperature is the temperature at the front surface of the Al from the simulation and the upper bound on the temperature is from the shock-ramp isentrope calculated from the observed Hugoniot state. The NIF hcp data point lies in the bcc region of the theoretical phase diagram; however, substantial temperature gradients exist. Data from OMEGA that do not lie on the principal isentrope in Fig. 4.1 are at an elevated temperature due to small shocks and are plotted on their shock-ramp path.

4.4.2 Al 6061-O alloy

Previous authors have observed significant differences in stiffness and stress dependent strength in pure Al and Al 6061 alloy under ramp compression [83, 87]. Additional experiments reported that the difference in the dynamic strength was most likely due to the difference in impurity levels and strain rate effects [91]. Due to the distinct properties of pure and alloy Al, we performed an independent study of the fcc–hcp and hcp–bcc phase transformations in Al 6061-O (annealed temper).

Al 6061 was chosen because it has been widely studied under ramp and shock compression [10, 77, 83] including studies of strength [97] and the onset of plastic flow [91]. Pulsed-power experiments by Lemke et al. [10], used magnetically driven Al 6061 cylindrical liner implosions to infer pressure-density data in various samples. Systematic differences in their measured and simulated velocities were conjectured to be caused by solid-solid phase transitions occurring in the Al-6061 liners, but there were no reported measurements of these transitions before this work.

In these experiments, the alloy stock was composed of 97.39% Al, 0.92% magnesium, 0.61% silicon, and 0.53% iron by weight, plus other less-abundant elements. A summary of the Al-6061-O data (black, red, and blue points) is shown in Fig. 4.11
Figure 4.11: The interatomic lattice d-spacing versus pressure for the Al 6061-O (annealed) alloy (black, red, and blue points). The pure Al data are shown for comparison as the white points. All three phases are observed in the compressed alloy. The vertical dashed black lines are the pressure onsets for the fcc–hcp and hcp–bcc transformations in the pure Al. The fcc–hcp transition is observed at 40-GPa lower pressure than the pure Al. Additional data are required to make a similar comparison for the hcp–bcc transition.
along with the pure Al data (white points). The fcc–hcp and hcp–bcc phase transformations are shown for the Al alloy. The hcp (101) peak is first observed at 175±9 GPa and the bcc (110) peak at 333±11 GPa. Similar to pure Al, regions of coexistence are observed over a 52-GPa range for fcc and hcp and a 42-GPa range for hcp and bcc. For the two shots with fcc–hcp coexistence, the maximum standard deviation in pressure due to spatial gradients, $\Delta P$, is 11 GPa and for the two shots with hcp–bcc coexistence, the maximum standard deviation in pressure due to spatial gradients, $\Delta P$, is 9 GPa. Therefore, the coexistence is not due to the spatial gradients in the sample.

The pressure onset for the hcp phase in the alloy is 40 GPa lower than in the pure Al. Additional data are needed to make the same comparison for the hcp–bcc transformation. This pressure onset difference is unexpected based on the results by Smith et al. [91] who found that the Al 6061-T6 peak elastic precursor stress was insensitive to strain rate at the onset of plastic flow compared to pure Al. This difference in the rate dependence of peak elastic precursor stress suggests that the onset stress for the fcc–hcp and hcp–bcc phase transformations would be lower in pure Al than Al 6061 for strain rates in the thermal activation regime. Otherwise, the phase-transformation onset stress would be the same for pure and alloy Al if the strain rate is in the phonon-drag–dominated regime. Based on the sample thicknesses and loading rates used in this study, pure and alloy Al have the same onset stress for plasticity, therefore, one would not expect the phase boundaries to shift for the pure and alloy Al. This is because the Peierls stress would be the same for both materials [98]. Unexpectedly, the measured pressure onset for the hcp phase in the alloy is lower than in the pure Al. However, the alloy investigated here was a different temper than used by Smith et al., which can cause differences in the distribution of precipitates in the Al matrix and can affect its mechanical properties. In diffusional phase transformations, the precipitates can act as heterogeneous nucleation sites for the hcp phase, but more data are required before conclusions on the kinetics of plastic flow and phase transformations can be drawn.
4.4.3 High-pressure texture

We observe significant correlations in the high-pressure texture between the fcc, hcp, and bcc phases of Al [1]. In Fig. 4.12(a), pole figures [(111) and (200)] for the rolled foils used in these experiments show strong initial texture; the initial preferred orientation is nearly fiber textured which is ideal for studying mechanisms of atomic rearrangement [99]. The pole figures were collected using a Philips X’Pert High Resolution Materials Research Diffractometer. The pole figures show the (200)$_{fcc}$ plane normals are nearly parallel ($0^\circ$ to $15^\circ$) to the pressure-loading axis. The initial texture of the (200) fcc planes can be seen in Fig. 4.12(b) in a diffraction pattern from an undriven shot where the (200) diffraction ring has limited azimuthal extent on the IP’s. Also shown in Fig. 4.12(a), the (111)$_{fcc}$ plane normals have a preferred orientation of $40^\circ$ to $60^\circ$ with respect to the pressure-loading direction. The (111) diffraction ring in Fig. 4.12(b) is only visible on a single IP (left).

The crystallographic texture was tracked through the fcc–hcp and hcp–bcc phase transformations. Lineouts along the azimuthal angle of the close-packed Debye–Scherrer rings are shown in Fig.4.12(c) in the fcc, hcp, and bcc phases. The yellow-shaded regions of Fig. 4.12(c) highlight the peaks in the texture that persist in the three phases for the fcc (111), hcp (002), and bcc (110) planes. The persistence of the initial texture in the close-packed planes suggests that those planes remain parallel through the transformations. These data are consistent with the Shoji–Nishiyama orientation relation (OR) [100] for the fcc–hcp transition and the Burgers OR [101] for the hcp–bcc transition. These OR’s provide the relationship between specific planes and directions in parent and child crystals. The texture can also be seen in Fig. 4.4 in the $2\theta$–$\phi$ projections. In Fig. 4.4(a), the bcc (110) shows less texture than the original sample due to the atomic rearrangement from multiple phase transformations; however, the peaks at $\pm150^\circ$ persist to 466 GPa.
Figure 4.12: (a) Pole figures for the (200) and (111) planes for the 99.999% pure Al foil used in these experiments. (b) Stereographic projection of IP data from shot 24294. Diffraction lines from both undriven Al [same foil as pole figures in (a)] and the W pinhole are present in the data. This diffraction pattern gives an indication of the initial texture of the Al foil and this texture was tracked up to high-pressure. (c) Lineouts along the azimuthal angle, $\phi$, of the Debye-Scherrer ring for the closest packed planes in the fcc (black), hcp (red), and bcc (blue) phases. The yellow-shaded regions highlight peaks in the texture that persist through both phase transformations.
5 Dynamic XRD Studies of Sodium

The work in this Chapter is being prepared for publication in a peer-reviewed journal.

Extreme compression can alter the free-electron behavior of simple metals such as elemental sodium. At pressures greater than 200 GPa, Na is predicted to transform to a transparent electride structure where valence electrons are localized in interstitial regions [12, 19]. Laser driven ramp-compression is used to compress Na into this unexplored pressure regime to investigate the crystal structure, optical properties, and melting behavior of Na. X-ray diffraction is used to constrain the crystal structure and detect melting. Optical reflectivity measurements are used to detect metal-insulator transitions and simultaneous velocimetry is used to infer the Na pressure. We show the highest pressure solid x-ray diffraction and reflectivity data on Na to date.

5.1 Historical Context

Due to their relative simplicity, group I – alkali metals have been the model for ‘simple’ systems under high-pressure because of the single $s$ electron in the valence band. In 1933, Wigner and Seitz published the free electron model for the properties of Sodium [102]. The model treats metals as a gas of free electrons that obey the Pauli exclusion
principal arranged on a periodic lattice. The wavefunction of the single valence electron, $\psi(x)$, is a plane wave that satisfies the Schrödinger equation, $\hat{H}\psi_n(x) = E_n \psi_n(x)$, for a negligible periodic potential where $E_n = -\frac{\hbar^2}{2m_e} \left(\frac{\pi}{L}\right)^2$. Here, $L$ is the length of the box that the electron is confined in, $m_e$ is the mass of the electron, and $n$ is the principal quantum number. The Na bulk modulus, heat capacity, electrical conductivity etc. are well described by this model at ambient conditions. The assumptions of this model break down as high pressure produces high densities where the core electrons occupy a larger fraction of the volume of the metal. Thus, Na does not behave like a simple free-electron metal under high pressure, as core–valence overlap modifies the equation of state. In addition, orthogonality and Pauli exclusion can force the valence electrons to occupy interstitial regions creating an insulating electride phase [15, 19].

5.1.1 Structure

Na transforms from simple cubic structures to complex low-symmetry phases at high-pressure and low-temperature as shown in Fig. 5.1. Na is a body-centered-cubic (bcc) metal at ambient conditions, transforms to face-centered-cubic at 65 GPa, and then adopts a series of low-symmetry phases near the minimum of the melting curve at 118 GPa and 300 K [13]. Synchrotron diamond-anvil cell (DAC) single crystal XRD experimental work [13] investigated the low-symmetry phases near the melting minimum, measuring seven different crystal phases. The structures vary from the relatively simple oP8 phase to a structure containing 512 atoms per unit cell (mP512). At low temperatures, face-centered cubic Na transforms to a cubic cI16 phase at 105 GPa then to a primitive orthorhombic oP8 structure at 117 GPa. The oP8 phase is stable only between 117–125 GPa, and interestingly it is predicted by first-principles structure searching algorithms to become stable again between 1.75–15.5 TPa [103]. Depending on the temperature and directionality of heating (upon recrystallization or melting), a series of complex
Figure 5.1: Phase diagram of Na taken directly from [17] based on Refs. [13] and [18]. The highest pressure data for Na are at 200 GPa from high resolution Raman spectroscopy [17] and DAC XRD [12] experiments. The melting curve above 140 GPa is extrapolated (black dashed curve), and in the pink-blue striped region, the existence of solid or liquid Na is unknown. Reprinted figure with permission from M. Marqués et al., Physical Review B, Volume 83, 184106 (2011). Copyright 2018 by the American Physical Society.
structures were observed including: a primitive monoclinic mP512 phase, an incom- 
munsurate host-guest tI19 phase (also observed in Potassium), a body-centered tetrag-
onal tI50 phase, a c-centered orthorhombic oC120 phase, and a triclinic aP90 phase. 
The relatively small pressure and temperature ranges for some of these structures sug-
gests a rich free-energy landscape that is sensitive to slight changes in both pressure 
and temperature. It is expected that the liquid state has a similar structural complexity 
at the melting temperature minimum, and experimental data in the liquid may provide 
insight into the mechanisms for this complex behavior [13].

A transformation from a reflective metal to an optically transparent solid hP4 phase 
was observed near 200 GPa [12, 17] in room-temperature DAC experiments along with 
a dramatic change in the Raman spectra [12]. The insulating behavior is attributed to 
the localization of charges in interstitial positions. Guided by first-principles structure-
searching results, Ma et al. claim their results are consistent with an hP4 electride 
structure shown in Fig. 5.2. The hP4 phase is a 6-fold coordinated highly distorted 
double hexagonal close-packed (dhcp) structure and is the elemental analog to the NiAs 
structure. The space group is P6$_3$/mmc with 4 atoms per unit cell and there are two Na 
positions: (0, 0, 0) and (2/3, 1/3, 1/4). Similar to the Ni$_2$In structure, the Na$^+$ ions are 
located at the positions of the Ni atoms and the interstitial electrons are located at the

Figure 5.2: The hP4 electride structure where the purple spheres represent the Na$^+$ 
atoms and the blue spheres/clouds represent the localized electrons [104].
In atom positions: (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4).

Simulated diffraction patterns from the tI19 (147 GPa), hP4 (320 GPa), and oP8 (117 GPa) crystal phases were generated using the 3D crystal visualization software, VESTA [104], and are shown in Fig. 5.3 (a). The tI19 phase is an incommensurate host-guest structure meaning there is a framework of host atoms (yellow atoms) and the guest structure forms chains of atoms (red atoms) along the channels of the host structure. The ratio of the $c$ lattice parameter for the host, $c_H$, and the guest, $c_G$, structure is irrational meaning the number of atoms per unit cell is a non-integer number. The tI19 structure belongs to the tetragonal $I4/mcm$ space group. From single-crystal DAC XRD diffraction data [105], the lattice parameters were found to be, $a_{host} = b_{host} = 6.9962 \, \text{Å}$ and $c_{host} = 3.3992 \, \text{Å}$ at 147 GPa. The host Na atoms are located on the $16k$ Wykoff site, $(x, y, 0.5)$, where $x = 0.7899$ and $y = 0.0882$. The guest atoms were found to have a lattice parameter $c_{guest} = 2.05 \, \text{Å}$ and are located at $(0.5, 0, 0)$. For the diffraction pattern shown in Fig. 5.3, the guest atoms were given an occupancy of 0.825 to give the correct amount of guest atoms per host unit cell, $(3.3,)$ resulting in a total of 19.3 atoms per host unit cell. The atomic displacement anisotropic thermal parameters were set to, $U_{11} = U_{22} = 0.012$ and $U_{33} = 0.7$, for the guest atoms. The guest atoms significantly modify the intensity of the reflections from the host atoms [106].

The oP8 structure belongs to the orthorhombic $Pmna$ space group and at 117 GPa has lattice parameters $a = 4.76505 \, \text{Å}$, $b = 3.02030 \, \text{Å}$ and $c = 5.2512 \, \text{Å}$ as discovered in DAC XRD experiments by Gregoryanz et al. [13]. The Na atoms are located at $(0.0151, 0.25, 0.1801)$ and $(0.1641, 0.25, 0.5861)$. The diffraction patterns from the tI19 and oP8 phases are compared to the hP4 phase at 320 GPa with lattice parameters $a = 2.784 \, \text{Å}$, $c = 3.873 \, \text{Å}$ and no interstitial electrons. The diffraction patterns shown in Fig. 5.3 will later be compared to our experimental data and these structures are the candidates considered for the crystalline phase above 200 GPa.

The experimental phase diagram for Na (Fig. 5.1) has been investigated only up to 200 GPa, and more exotic behavior is predicted above these pressures [103, 107].
Figure 5.3: (a) Simulated diffraction patterns of the oP8 (117 GPa, yellow), tI19 (147 GPa, blue), and hP4 (320 GPa, red) crystal phases of Na for Cu He\textsubscript{x} x-rays (8.37-keV). (b) 3D structural models for the tI19, hP4, and oP8 phases generated using the crystal structure visualization software, VESTA [104].
Our experiments utilized high-pressure \textit{in situ} x-ray diffraction to measure the complex structures of Na as a function of pressure in the unexplored pressure regime greater than 200 GPa.

### 5.1.2 Optical Reflectivity and Melting Temperature

The electronic properties of Na are altered dramatically at high-pressure: Na has been observed to transform from a highly reflective metal to an optically transparent phase at 200 GPa. This large bandgap, insulating behavior may be due to $p$-$d$ hybridization as the $3d$ bands drop in energy relative to the $3p$ and $3s$ bands, where the valence electron is located in low-density. The hybridization enables electron localization in interstitial regions. From the optical absorption spectrum edge, Ma \textit{et al.} measured a large bandgap (at least $\sim 1.3$ eV) for the insulating phase \cite{12}. Assuming an hP4 structure in their GW calculations (the name is from the use of a single-particle Green’s function [$G$] and a screened Coulomb interaction [$W$]) \cite{108}, the bandgap is predicted to increase to 6.5 eV upon compression at 600 GPa shown in Fig. 5.4. This is counterintuitive because pressure typically leads to gap closure and metallization due to a broadening of the conduction bands (as observed in hydrogen \cite{109}), however electron localization causes the bandgap to widen upon compression. The VISAR probe beam at 2.33 eV (green dashed line) is equal to the band gap at $\sim 240$–$375$ GPa and is used in these experiments to detect changes in reflectivity.

At higher pressures, first principles methods calculate that Na becomes an ‘unconventional’ electride, with a strongly anisotropic absorption spectrum \cite{107}. Ab initio calculations solve the Bethe-Salpeter equation (BSE) for the dielectric function as a function of pressure with an electron-hole interaction perturbing Hamiltonian. Na is optically transparent for light polarized in the $ab$ plane but reflective for light polarized along the $c$-axis. At 420 GPa, the optical depths at the VISAR probe wavelength are calculated to be 1200 $\mu$m and 5 $\mu$m for the in-plane and $c$-axis polarizations, respec-
Figure 5.4: Bandgap energy calculated for a range of volumes at 0 K using DFT with PAW potentials (red) in VASP, pseudopotential methods (black) in ABINIT, and GW approximation (blue) from Ma et al. [12]. The 532-nm, 2.3 eV, VISAR probe energy is shown in green and is used to detect transparency.

In addition to complex structural and electronic properties, the melting curve of Na decreases with increasing pressure for a relatively wide range of pressures (over 100 GPa) and drops below room temperature at 118 GPa [Fig. 5.1]. X-ray diffraction measurements on compressed Na reveal a maximum in the melting temperature in the bcc phase followed by a sharp decrease in the fcc phase [18]. The same study also measured an increase in the melting temperature above 125 GPa and up to 130 GPa. This second change in concavity of the melting curve was confirmed by Marques et al. in a series of XRD and Raman spectroscopy measurements [17]. Above 130 GPa in the tI19 phase, heating to 550 K did not melt the Na sample and therefore the melting curve increases dramatically above 140 GPa. The complex melting curve of Na is due to the interplay of complex liquid and solid structures at these temperatures and pressures. The pressure dependence of the electron localization alters the bulk and shear moduli,
Figure 5.5: Absorption spectrum calculations for hP4-Na at 420 GPa by Gatti et al. [107]. The real (red) and imaginary (blue) components of the refractive index for light polarized in the \textit{ab} plane (a) and along the \textit{c}-axis (b). (c) The optical depths are 1200 \textmu m and 5 \textmu m for the in plane and \textit{c}-axis polarizations, respectively, at the VISAR probe beam energy.

which could explain the anomalous melting behavior in Na [17]. Based on calculations of the electronic localization function, it is predicted that temperatures in excess of 2500 K are required to melt Na at 200 GPa [17]. Our experiments measure the absence of XRD reflections to detect melting at pressures greater than 125 GPa where there are no experimental data and large theoretical uncertainty.

5.2 Experimental Method

X-ray diffraction and optical reflectivity experiments were performed on ramp-compressed Na using the OMEGA EP laser [4]. The experiment built on the successes of Al diffraction experiments [1] discussed in Chapter 4. The x-ray diffraction signal from Na is similar to Al due to the proximity of their atomic numbers. The intensity of scattered radiation depends on the scattering from each electron in the atom and is proportional to \(Z^2\).

The targets comprise Na samples (10 – 50 \textmu m thick) sandwiched between \(⟨110⟩\)-
Figure 5.6: (a) The target design for Na reflectivity measurements. The diamond pusher is coated with Ti stripes and the LiF or MgO rear window is half-coated with Ti. (b) A simulated VISAR image for Na that undergoes a sequence of transitions from metallic to absorbing to transparent. (c) The time history of the absorption (in optical depths [blue]) and reflectivity [orange] used to make the simulated VISAR image in (b). The Na is reflective when both the absorption and reflectivity are high, then becomes absorbing when the absorption is high but the reflectivity is low. Finally, Na is transparent when the absorption drops and the reflectivity is low.

oriented 20-μm single-crystal diamond ablators/pushers and ⟨100⟩-oriented 70–150 μm thick single-crystal LiF, MgO, or ⟨110⟩-oriented diamond windows. Targets with transparent LiF and MgO are used for simultaneous diffraction and reflectivity measurements while the opaque diamond window targets are used for diffraction-only experiments. The targets were assembled in a ultra high purity glove box with either an Ar or N₂ environment due to Na’s high reactivity with water. The Na metal was thinly sliced and then compressed between the diamond pusher and window to the desired thickness using a piston cylinder cell. No epoxy is applied between the Na and window to eliminate the need to convolve the epoxy transmission in the reflectivity determination. Prior to removal from the glove box, the target is sealed with a continuous layer of epoxy around the perimeter of the target to prevent reaction with the atmosphere during transportation from the glove box to the target chamber.

Coatings on the target ablator and rear window allow for a measure of the change in reflectivity in Na as it is compressed. A Ti coating (1000 Å) on the bottom-half of the transparent window and Ti stripes (1000 Å) on the diamond ablator are in contact
with the Na as shown in Fig. 5.6 (a). Simulated VISAR data for this target design is shown in Fig. 5.6 (b). Ti is chosen to maintain high dynamic range in the reflectivity sensitivity because of its relatively low reflectivity at 532 nm (57.5 %). The VISAR probe beam reflects off the Ti coating through the transparent window providing unambiguous tracking of the Na-window interface velocity throughout the compression of the Na (as seen on the bottom-half of the simulated VISAR image in Fig. 5.6(b)). The reflectivity of the Ti coating also allows for the transmission of the window to be decoupled from the variation in the reflectivity of the Na. In order to detect transparency in compressed Na, a reflectance pattern of Ti stripes is placed between the diamond and Na that can be detected on the top-half of the VISAR field of view if Na becomes transparent (shown late in time on the top half of the VISAR data in Fig. 5.6 (b)).

The intensity of the return VISAR signal is sensitive to the real and imaginary components of the Na refractive index. The sequence of transitions from metallic to absorbing to transparent can be captured in the VISAR intensity and a striped reflectance pattern would be visible if Na became transparent. In addition, the increasing band gap energy with increasing pressure and density (Fig. 5.4) can be detected with absorption of the VISAR probe beam. This target design provides information about the electronic properties of Na at high pressures and elevated temperatures where Na is predicted to be in an insulating electride phase.

The OMEGA EP laser ramp compressed or shock-ramp compressed Na to pressures in excess of 300 GPa where the melting curve is predicted to sharply increase. The high compressibility of Na made the design of the laser pulse shape for ramp compression challenging. The bulk modulus of Na is 6.3 GPa, 12 times smaller than Al. To prevent the ramp wave from steepening into a shock in the Na sample, two 10-ns pulses were stitched together to create a 20-ns ramped laser pulse shape with a low-energy “foot” to allow the first pulse to pre-compress the sample before the main drive compressed the sample to the final maximum pressure. The composite pulse shape is shown in Fig. 5.7 (a) (blue). Results from 1D LILAC radiation hydrodynamics simulations using this
Figure 5.7: (a) A 20-ns stitched ramp laser pulse shape (blue) and the x-ray backlighter 1-ns pulse shape (red) delivered on shot 27967. (b) Results from LILAC simulations for this 610 J pulse shape and a C[25 µm]Na[18.5 µm]LiF[101 µm] target assembly. A peak pressure of 305 GPa is reached in the Na sample, and the x-ray probe time is shown by the vertical dashed white lines.

Pulse shape and a C[25 µm]Na[18.5 µm]LiF[101 µm] target assembly are shown in Fig. 5.7 (b). For this 610 J ramp pulse, the Na sample is predicted to reach a uniform peak pressure of 305 GPa at 17.9 ns. These simulations were used to determine the optimal x-ray probe time for XRD.

Two beams irradiated the Na sandwich target at an angle of 23° with respect to the target normal with a peak irradiance ranging from $3.0 \times 10^{15}$ to $4.7 \times 10^{15}$ W/cm$^2$. For the main drive beams, 1100-µm diameter distributed phase plates produced a focal spot with a super-Gaussian intensity distribution $\{ I = I_0 \times \exp[-2(r/550 \mu m)^{8.0}] \}$ to ensure transverse spatial uniformity in the sample. Two additional 1250-J beams irradiated a Cu backlighter foil with a 1-ns square pulse [Fig. 5.7 (a) (red)] at an intensity of $2.5 \times 10^{15}$ W/cm$^2$ to create 8.37 keV He-α x-rays for XRD. The x-rays are generated over the duration of the pulse length (1-ns) and those emitted at an angle 23° with respect to the Na target normal are selected by a pinhole aperture.

The experimental geometry is shown in Fig. 5.8. The Debye-Scherrer rings from
Figure 5.8: (a) X-ray diffraction patterns are collected on image plates (IP) lining a stainless steel box [36] in a diagnostic referred to as PXRDIP [Sec. 3.2]. The target is held on the front of the box and on the opposite side, the VISAR probe beam enters through a 25-mm-diam circular aperture. (b) The x-ray diffraction target assembly is mounted on a 300-µm or 800-µm diameter collimating W or Ta pinhole.
the compressed Na sample are collected in an IP lined box (PXRDIP) [Sec. 3.2] [36] with Kapton (25 µm) and Cu filtering (12.5 – 25 µm) to attenuate background x rays other than Cu He-α. In addition to diffraction from Na, calibration diffraction patterns from the edges of a 300-µm or 800-µm diameter W or Ta pinhole are used to determine the IP, XRS, and pinhole locations relative to the diffraction lines. An 800-µm-diam pinhole is used for the reflectivity measurements to increase the VISAR field-of-view for the spatial features (stripes). The high-Z pinhole limits the field-of-view of the IPs to only the center of the 1100-µm driven region of the target and provides additional shielding of the IPs from the large x-ray background from the XRS and Na target ablation plasmas.

The lattice plane \( d \) spacings are calculated using the Bragg condition, \( \lambda = 2d \sin(\theta) \), for an x-ray wavelength, \( \lambda \), and x-ray incidence angle, \( \theta \). Diffraction patterns from uncompressed Na indicate large grain sizes. The scattering angle, 2\( \theta \), resolution is 1° and precision is 0.2° [51]. The pressure is calculated using a characteristics algorithm and either the Na-window interface velocity or diamond free-surface velocity assuming an EOS and refractive index model for the window [32, 33] [Sec. 3.4]. The velocities are measured using a line-imaging velocity interferometer system for any reflector (VISAR) that detects Doppler shifts of a 532-nm probe beam reflecting off a moving surface in the target [Sec. 3.3] [58]. The Doppler shifts are manifested as shifts in a fringe pattern recorded in a 2-D interferogram using an optical streak camera. To see the striped reflectance pattern more clearly, the etalon leg of one of the interferometers is sometimes blocked to collect a non-fringing image. Simultaneous velocimetry and XRD allows for measurements that constrain the high-pressure phase diagram of Na.
5.3 Results

5.3.1 X-ray Diffraction

Solid Na was observed at 301 – 418 GPa, well above the 140 GPa data maximum shown in Fig. 5.1. For thick samples and low pressures (< 200 GPa), no diffraction lines were observed indicating that the Na melted. The presence of diffraction peaks above 300 GPa suggests that the Na melts and also resolidifies on nanosecond time scales, and the melting temperature increases dramatically above 140 GPa. These are the highest pressure observations of solid Na to date.

A diffraction pattern from Na compressed to 418±45 GPa is shown in Fig. 5.9 (a). The diffraction pattern has 6 peaks from compressed Na (green tics). We observe two additional higher angle peaks than observed by Ma et al. The diffraction pattern collected by Ma et al. is highly textured whereas we observe a more powder-like distribution of the Na grains. At 190 GPa, Ma et al. indexed four diffraction peaks from the hP4 phase as (010), (011), (012), and (110) with lattice parameters \(a = b = 2.92 \, \text{Å}\) and \(c/a = 1.46\). The same four peaks are observed in these data. The peaks are indexed for the hP4 phase in Fig. 5.9, however with the two higher angle peaks, the fit to the hP4 phase is not perfect.

To correctly index the diffraction peaks, a comparison of the observed \(d\) spacing to both the \(c/a\) ratio and the density is shown in Fig. 5.10 (a). The bands represent the change in the \(d\) spacing for each lattice plane of the hP4 phase as a function of the \(c/a\) ratio for a range of densities, 5.8 – 7.3 g/cm\(^3\). The DFT predicted \(c/a\) ratio at 420 GPa \(c/a = 1.356\) is plotted on Fig. 5.10 (a) (vertical solid gray line) for comparison with the data at 418 GPa (horiztonal gray dashed lines). Using the DFT prediction as a guide, the first four largest spaced planes [(010), (011), (012), and (110)] agree well with the data, but the two smallest spaced planes do not agree well with the possible options [(200), (021), (013)]. The (200) peak is ruled out because the intensity is expected to be much lower than the (021) and (013) planes, as shown in Fig. 5.10 (b). These two
Figure 5.9: (a) Background subtracted 2θ-φ projections of a Na XRD pattern at 418±45 GPa. The green and red lines label Na and pinhole calibration diffraction lines, respectively. The lines from compressed Na are labeled with their hP4 (hkl) plane. White spaces are gaps between image plates. (b) A time versus Lagrangian position plot of the pressure in the Na sample and C rear window. The measured free-surface velocity is back propagated from the diamond free-surface to the C pusher-Na interface. The white dashed lines shown the boundary between the Na and diamond and the 1-ns timing of the x-ray probe. (c) The pressure histogram during the x-ray exposure for the 34-μm thick Na sample has a mean pressure of 418 GPa and a standard deviation of 45 GPa.
Figure 5.10: (a) The \( d \) spacing for the lattice planes of the hP4 phase as a function of the \( c/a \) ratio. The seven colored bands are the \( d \) spacings for densities between 5.8–7.3 \( \text{g/cm}^3 \). The gray horizontal lines are drawn at the \( d \) spacings observed in shot 26479 (Fig. 5.9). The vertical gray line is the value for the \( c/a \) predicted by DFT in Ma et al. at 420 GPa. (b) A simulated diffraction pattern for the hP4 phase with lattice parameters \( a = b = 2.784 \text{ Å} \) and \( c/a = 1.39 \) and for a Cu He\( \alpha \) x-ray source (8.37-keV).

Additional peaks are important for correctly identifying this high pressure phase.

The XRD probe time was slightly delayed from the ideal timing resulting in a standard deviation due to pressure gradients, ±45 GPa, as shown in Fig. 5.9 (b) and (c). The target used in this experiment was a diamond sandwich assembly, C[26]Na[34]C[67], where the target dimension notation is Material [Thickness (\( \mu \text{m} \))]. A time versus Lagrangian position plot of the pressure in the Na sample and C rear window is shown in Fig. 5.9 (b). The measured free-surface velocity is back propagated from the diamond free-surface (at 127 \( \mu \text{m} \)) to the C pusher-Na interface (at 26 \( \mu \text{m} \)). The white dashed lines shown the boundaries between the Na and diamond window and the 1-ns timing of the x-ray probe. The oscillations are a result of numerical gridding error because of the non-monotonic velocity profile causing crossing of the characteristics. The histogram of pressures in the Na during the x-ray exposure is shown in Fig. 5.9 (c) and the mean pressure in the Na is calculated to be 418 GPa with a standard deviation of 45 GPa.
Figure 5.11: Background subtracted $2\theta$-$\phi$ projections of a Na XRD pattern at $323\pm30$ GPa. The green and red lines label Na and pinhole calibration diffraction lines, respectively. The lines from compressed Na are labeled with their hP4 ($hkl$) plane.
Figure 5.12: The observed $d$ spacing for the lattice planes as a function of the pressure determined from velocimetry (black points). The red curves are the extrapolations of the pressure-volume ($H_0^2$) relation measured by Hanfland et al. up to 100 GPa [110] for the hP4 phase [using a $c/a = 1.3895$ (DFT at 320 GPa [12])].

Thicker Na samples were used in favor of thinner samples for the diffraction targets to increase the scattered x-ray signal. The use of diamond sandwich targets also resulted in the observation of the highest angle diffraction peaks in these experiments because they reached high pressure but at a lower temperature than the LiF/MgO windows. This is caused by the strong re-shock of the ramp wave off the large impedance mismatch Na-C (window) interface creating a high-pressure but low temperature in the sample.

The observed Na diffraction peaks lattice spacings are plotted as a function of the measured pressures in Fig. 5.12 confirming a single, reproducible high-pressure solid phase of Na is accessible by ramp-compression. This phase was observed between 301–418 GPa, and data from only diamond sandwich targets are shown. Although the number of peaks observed varies between experiments, the (011), (110), and (012) peaks appear on all the shots. In some cases, the (010) peak was obscured by a pin-
Figure 5.13: A temperature-pressure phase diagram of Na with the solid diffraction data (black diamonds) plotted assuming isentropic compression in order to put a lower bound Clapeyron slope. The SESAME principal Hugoniot (red), LEOS 110 principal isentrope (black), and the melting temperature measurements by Gregoryanz et al. [18] (blue) are plotted for comparison to this data.

hole diffraction peak. An XRD pattern at 323±30 GPa for a diamond sandwich target with a thicker sample, C[40]Na[58]C[77], is shown in Fig. 5.11 where the (010) peak is not observed because it is coincident with the pinhole diffraction line. The thicker sample results in better signal to noise for the Na diffraction peaks, however the higher angle peaks are not observed in this experiment. Due to the variability of the Na sample thicknesses and ill-defined pressure-density-temperature state accessed by ramp-compression, each experiment reaches a different final temperature state, but the same crystalline phase is observed on all shots. There is no evidence of multiple temperature-sensitive phases like those observed near the minimum of the melting temperature at 118 GPa [13].

A lower bound on the slope of the melting curve of Na can be deduced from these data assuming isentropic compression and the measurement of the melting temperature by Gregoryanz et al. at 130 GPa [18], shown in Fig. 5.13. Assuming that the melting curve phase boundary is a straight line between the highest pressure data by
Gregoryanz et al. at 130 GPa and 354 K and our data at 301 GPa and 1270 K [assuming the smallest possible temperature from isentropic compression (LEOS 110)], an estimate of the lower bound of the Clapeyron slope is calculated to be $\frac{\partial T}{\partial P} = 5.4$ K/GPa (blue dashed line). The isentrope calculated from LEOS 110 most likely differs from the actual Na isentrope because the table does not include the observed complex phase behavior. In addition, we confirm that Na melts and resolidifies on nanosecond timescales. A separate experiment was performed to verify that Na melts upon compression. The Na was compressed by only a 50-J 10-ns foot of the laser pulse [first 10-ns of Fig. 5.7(a)], and no Na diffraction peaks were observed. Therefore, the measurement of solid Na confirms that Na melts and resolidifies on nanosecond time scales and the melting temperature increases dramatically above 130 GPa.

5.3.2 Optical Reflectivity

Optical reflectivity data suggest Na at high pressures does not become transparent at temperatures accessed here. Example VISAR data using the reflectivity target design [Fig. 5.6 (a)] is shown in Fig. 5.14. The peak pressure reached in this shot was 360 GPa using a 621 J laser pulse shape (48 J in the 10-ns foot and 573 J in the 10-ns ramp), and the Na sample is relatively thin (C[35]Na[28]LiF[102]) to prevent shock formation in the Na sample. At an x-ray exposure corresponding to 306 GPa, two diffraction peaks were observed in the XRD data confirming the Na was in a solid phase. Reflectivity signal from the Na-LiF interface is located on the top-half of the image while signal from the Ti-LiF interface is on the bottom-half of the image. There is a dramatic modification of the optical reflectivity due to reflectance from the Na-half of the image compared to the Ti-half. On the Ti-half of the target, the Ti-LiF interface is tracked throughout compression and release. On the other hand, the Na-LiF interface velocity is measured up to and during peak compression then at 20.5-ns the VISAR probe is absorbed and only a series of ghost reflections are collected. The event at 23.7-ns is break-out of the ramp wave from the free-surface of the LiF window. No evidence
of the imposed reflectance pattern behind the Na layer is observed. The absorption of the VISAR probe is not due to the window transmission because the absorption feature does not appear across the entire image. These data suggests that Na becomes absorbing, however the pressure onset of the absorption is unexpected because it does not occur during increase in compression but after peak compression.

In other experiments, the absorbing phase of Na was not reproducible with similar sample thicknesses and laser drive; either continuous absorption (blanking) or no absorption was observed across the VISAR images. The underlying reflectance pattern in the target was never observed, indicating Na did not become transparent. A VISAR image for a C[28]Na[42]MgO[83] target driven by a 690 J (35 J in the 10-ns foot and 655 J in the 10-ns ramp) pulse is shown in Fig. 5.15. Three diffraction peaks from Na were observed in this shot. In red, the time-resolved optical pyrometry data is plotted on the VISAR data showing the correlation of the VISAR probe blanking with increase in the self-emission of the shock front in the window. In this case, the decrease in the VISAR return signal is due to the window becoming opaque due to shock formation. For the experiment shown in Fig. 5.14, similar self-emission signal is observed meaning that a shock is likely forming in the LiF window, but it is unclear why only Na-LiF half of the target blanks.

In thinner samples, changes in reflectivity but no blanking or reflectance pattern is observed. Fig. 5.16 (a) shows VISAR data from a C[25]Na[19]LiF[101] target driven by a 50 J and 559 J foot and ramp laser pulse shape, respectively. Optical pyrometry data show no indication of shock formation, and therefore no blanking is observed. The XRD data reveal at least four solid diffraction lines from the Na sample at 270 GPa.

To study the variation of the reflectivity as a function of pressure, the amplitude of the fringes or the total number of CCD counts are used to quantify the reflectance. In Fig. 5.16 (b), the total number of CCD counts in the VISAR image corresponding to the Na-LiF interface (blue) and the Ti-LiF interface (orange) are normalized to the Ti-LiF side and plotted as a function of pressure. The green, yellow, and red points
Figure 5.14: Raw VISAR data for Na compressed to 360 GPa using a transparent window and containing Ti coatings to detect changes in reflectivity (C[35]Na[28]LiF[102]) (inset). Return signal corresponding to the Na-LiF interface is on the top-half of the image while the signal from the Ti-LiF interface is on the bottom-half. The laser drive had 48 J and 573 J in the 10-ns foot and 10-ns ramp, respectively. [s27790]
Figure 5.15: A VISAR image for a Na target using a transparent MgO window and containing Ti coatings to detect changes in reflectivity (C[28]Na[42]MgO[83]). Return signal corresponding to the Na-LiF interface is on the top-half of the image while the signal from the Ti-LiF interface is on the bottom-half. The laser drive had 35 J and 655 J in the 10-ns foot and 10-ns ramp, respectively. Blanking of the probe beam at 18.5-ns is attributed to shock formation in the MgO window indicated by the time-resolved optical pyrometry signal (red). A microscope image through the high-Z pinhole shows the half-Ti coating and Na interface (top-right). [s27971]
Figure 5.16: (a) Reflectivity data at 532-nm for a reflectivity target (C[25]Na[19]LiF[101]) driven by a 50 J foot and 559 J ramp pulse shape compressed to 285 GPa. Reflection off the Na-LiF interface is on the top-half of the image while the bottom-half contains information about the reflectivity of the Ti-LiF interface. A microscope image through the high-Z pinhole shows the half-Ti coating and Na interface (top-right). (b) The integrated CCD counts from the VISAR image shown in Fig. 5.16 for the Na-LiF interface (blue) and Ti-LiF interface (orange) normalized to the Ti side are shown as a function of pressure. Time markers indicate 15 (green), 20 (yellow), and 23 (red) nanoseconds. Upon compression and release, there is no difference between the two interfaces implying that the variation in the reflectivity is due to the window. [s27967]
are time markers at 15, 20, and 23 nanoseconds. The reflectivity of both interfaces as a function of pressure follows identical trends for both compression and release, meaning the observed decrease in reflectivity is due only to the window transmission.

The density of free electrons in the conduction band is estimated using the band gaps shown in Fig. 5.4 \( [E_g] \), the isentropic temperature assumed in Fig. 5.13 \([T]\), the mass density shown in Fig. 5.10 \([\rho]\), and assuming the Boltzmann factor for the probability of free electrons, \( N_e \sim \exp(-E_g/kT) \). The critical density of the VISAR (532-nm) probe beam is \( 3.9 \times 10^{21} \text{ cm}^{-3} \), and the total electron density of the compressed Na solid is \( 1.9 \times 10^{24} \text{ cm}^{-3} \) \([\rho = 6.57 \text{ g/cm}^3]\). For the GW band gap estimation \( [E_g = 3.0 \text{ eV}] \), a temperature of 5640 K or 0.48 eV is required to thermally populate the conduction band so that the VISAR probe reflects at the critical surface as observed in our experiments \([\text{Fig. 5.16}]\), and an even lower temperature, 2820 K or 0.24 eV, is required considering the band gap estimated by DFT \( [E_g = 1.5 \text{ eV}] \). Using the lower bound isentropic temperature \([T = 1270 \text{ K}]\), the free electron density is \( 2.4 \times 10^{12} \text{ cm}^{-3} \), and the density is not enough to absorb or reflect the probe beam. However, temperatures of a few thousand kelvin are reasonable in these experiments because hydrodynamic simulations show that shocks are forming in the highly compressible thick (\( \sim >10 \mu\text{m} \)) Na samples.

This experiment confirms that at conditions accessible by ramp-compression and on nanoseconds timescales that Na remains reflective to at least 290 GPa. Although the reflectivity data vary depending on the Na thickness and laser drive, the underlying striped reflectance pattern is never observed. Null experiments were performed (i.e. without a Na sample) with both LiF and MgO windows to verify that the stripe pattern could be detected through these windows under ramp compression and with glue layers; the striped pattern was prominent in the VISAR intensity throughout ramp compression. These results indicate that elevated temperatures modify the properties of compressed Na due to thermal population of the conduction band and temperature delocalization of electrons from the interstitial regions.
6 Conclusion

Pressure induces significant changes in a materials’ structural and optical properties. At extreme conditions (> 100 GPa), the valence and core electrons contribute to bonding and ‘simple’ metals no longer exhibit free-electron-like behavior. At standard conditions, aluminum is a simple face-centered cubic metal with no \( d \)-band electrons. Previous room-temperature static-compression measurements discovered a fcc–hcp phase transformation, but no data existed beyond 333 GPa before this work, although DFT predicts exotic phases to tens of terapascals. Al is one of the most extensively studied materials at high pressure, as it is frequently used as a material standard in HED experiments where it is assumed the behavior of the standard material is well characterized.

This produced the first observation of body-centered cubic Al at 321±12 GPa. We observe three diffraction lines from the solid bcc phase in Al compressed to 547±19 GPa. X-ray diffraction measurements were performed on solid pure and 6061-O Al compressed to 547 GPa [1] and 479 GPa, respectively. The fcc–hcp transition onset is observed at 216±9 GPa in pure Al [1] and at 175±9 GPa in 6061 Al. This duplicates the observation (for pure Al), in static compression, of the fcc–hcp transition under dynamic compression conditions, nanosecond time scales, and high strain rates. We observed the fcc–hcp phase transition at a 40-GPa lower pressure in the 6061 Al than in pure Al. This is unexpected from the previously observed discrepancy in the rate dependence of the peak elastic precursor between pure and 6061 Al [91]. The impurities
do not cause the phase boundaries to shift to higher pressures. The hcp–bcc transition onset is observed at $321 \pm 12$ GPa in pure Al [1], and $333 \pm 11$ GPa in the alloy. The stress–density data are in better agreement with the all-electron DFT isentrope by Kudasov et al. [16] than the conductive-electron DFT SESAME 3722 isentrope [70] and the chemical model-based Kerley 3700 isentrope [28]. The initial texture of the rolled foils is maintained in the high-pressure texture of the close-packed planes, suggesting that the close-packed planes remain parallel through the fcc–hcp and hcp–bcc transitions. These data resolved the discrepancy between simulated and measured velocities in magnetically driven Al liner implosions at Sandia’s Z machine [10] and will serve as the high-pressure model for solid, ramp compressed Al in future HED experiments.

At ambient conditions, the properties of Sodium are well described by the nearly-free-electron model that treats the valence electrons as a gas of free-electrons. The ‘simplicity’ of this metal makes it ideal for testing \textit{ab initio} models for the structural and electronic properties of metals at extreme compressions. Previous measurements have revealed that Na behaves far from free-electron-like and that quantum mechanical treatment of both the valence and core electrons is required to reproduce experimental observations. Under static-compression, Na was observed to become transparent to visible light at 200 GPa and that the electrons occupy the spaces between atoms. However, no structural data existed beyond 200 GPa and no melting temperature data existed beyond 140 GPa, before this work.

Na was compressed into an unexplored pressure regime ($>200$ GPa) to determine the highest pressure structure, reflectivity, and melting behavior in Na using simultaneous x-ray diffraction and optical reflectivity measurements. These data are the highest pressure structural and electronic properties dataset for an alkali metal, a prototypical system to guide theory for ultradense matter beyond the Thomas Fermi model. We discovered that Na melts and resolidifies on nanosecond timescales into a phase consistent with the hP4 structure, however unexpectedly remains reflective to 290 GPa. We observed a dramatic increase in the melting temperature above 200 GPa, and constrained
the Clapeyron slope to be at least $\frac{\partial T}{\partial P} = 5.4$ K/GPa. These results emphasize the importance of temperature on structure and electron localization.
Bibliography


A  Pure Al data summary
The target dimension notation is Material [Thickness] and C is (110)-oriented single-crystal diamond. Al* indicates electron-beam-deposited samples. The velocity is the maximum true velocity over the entire streak record using the linear refractive-index correction [43] and the uncertainty is ±0.16 μm/ns, not including error associated with the refractive-index correction. The x-ray energies for the Cu and Ge backlighters are 8.37 keV and 10.25 keV, respectively. The probe times are the start of the 1-ns XRS pulse duration. The error associated with the timing is ±58 ps including considerations in beam timing, absolute VISAR timing, etc.

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